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Ground-Water Monitoring Plan, Water Quality, and Variability of Agricultural Chemicals in the Missouri River Alluvial Aquifer near the City of Independence, Missouri, Well Field, 1998–2000

Water-Resources Investigations Report 02–4096

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CONTENTS

FIGURES

TABLES

Ground-Water Monitoring Plan, Water Quality, and Variability of Agricultural Chemicals in the Missouri River Alluvial Aquifer near the City of Independence, Missouri, Well Field, 1998–2000

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Abstract

A detailed ground-water sampling plan was developed and executed for 64 monitoring wells in the city of Independence well field to characterize ground-water quality in the 10-year zone of contribution. Samples were collected from monitoring wells, combined Independence well field pumpage, and the Missouri River at St. Joseph, Missouri, from 1998 through 2000.

In 328 ground-water samples from the 64 monitoring wells and combined well field pumpage samples, specific conductance values ranged from 511 to 1,690 microsiemens per centimeter at 25 degrees Celsius, pH values ranged from 6.4 to 7.7, water temperature ranged from 11.3 to 23.6 degrees Celsius, and dissolved oxygen concentrations ranged from 0 to 3.3 milligrams per liter. In 12 samples from the combined well field pumpage samples, specific conductance values ranged from 558 to 856 microsiemens per centimeter at 25 degrees Celsius, pH values ranged from 6.9 to 7.7, water temperature ranged from 5.8 to 22.9 degrees Celsius, and dissolved oxygen concentrations ranged from 0 to 2.4 milligrams per liter. In 45 Missouri River samples, specific conductance values ranged from 531 to 830 microsiemens per centimeter at 25 degrees Celsius, pH ranged from 7.2 to 8.7, water temperature ranged from 0 to 30 degrees Celsius, and dissolved oxygen concentrations ranged from 5.0 to 17.6 milligrams per liter.

The secondary maximum contaminant level for sulfate in drinking water was exceeded once in samples from two monitoring wells, the maximum contaminant level (MCL) for antimony was exceeded once in a sample from one monitoring well, and the MCL for barium was exceeded once in a sample from one monitoring well. The MCL for iron was exceeded in samples from all monitoring wells except two. The MCL for manganese was exceeded in all samples from monitoring wells and combined well field pumpage.

Enzyme linked immunoassay methods indicate total benzene, toluene, ethyl benzene, and xylene (BTEX) was detected in samples from five wells. The highest total BTEX concentration was less than the MCL of toluene, ethyl benzene, or xylene but greater than the MCL for benzene. Total BTEX was not detected in samples from any well more than once. Atrazine was detected in samples from nine wells, and exceeded the MCL once in a sample from one well. Alachlor was detected in samples from 22 wells but the MCL was never exceeded in any sample.

Samples from five wells analyzed for a large number of organic compounds indicate concentrations of volatile organic compounds did not exceed the MCL for drinking water. No semi-volatile organic compounds were detected; dieldrin was detected in one well sample, and no other pesticides, herbicides, polychlorinated biphenyls, or polychlorinated napthalenes were detected.

Dissolved ammonia, dissolved nitrite plus nitrate, dissolved orthophosphorus, alachlor, and atrazine analyses were used to determine the spatial and temporal variability of agricultural chemicals in ground water. Detection frequencies for dissolved ammonia increased with well depth, decreased with depth for dissolved nitrite plus nitrate, and remained relatively constant with

depth for dissolved orthophosphorus. Maximum concentrations of dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus were largest in the shallowest wells and decreased with depth, which may indicate the land surface as the source. However, median concentrations increased with depth for dissolved ammonia, were less than the detection limit for dissolved nitrite plus nitrate, and decreased with depth for dissolved orthophosphorus. This pattern does not indicate a well-defined single source for these constituents. Dissolved orthophosphorus median concentrations were similar, but decreased slightly with depth, and may indicate the land surface as the source. Seasonal variability of dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus concentrations is not well-defined for samples grouped by month. Individual sample results from the Missouri River and the combined Independence well field pumpage show a seasonal trend that may indicate the effect of induced recharge from the Missouri River on the well field. Individual results and samples from seven wells indicate relatively constant dissolved ammonia concentrations, low dissolved nitrite plus nitrate concentrations in all but one well, and a more well-defined seasonal variation of dissolved orthophosphorus than either dissolved ammonia or dissolved nitrite plus nitrate.

Larger detection frequencies in the shallow depth intervals and the large maximum concentrations of alachlor and atrazine in the shallower wells indicate that the source of these chemicals to shallow ground water most likely is the land surface rather than induced river recharge. Seasonal variability of alachlor is not well-defined from samples grouped by month. Individual results from the combined Independence well field pumpage and samples from seven wells indicate variation in both alachlor and atrazine with time, but the degree and timing of the variation is not consistent. This inconsistency most likely is caused by varying rates of transport from the land surface to wells, different rates of degradation of both alachlor and atrazine in soil and ground water, the timing and area of application, and multiple source areas in and around the Independence well field. Alachlor and atrazine concentrations in the Missouri River at Hermann, Missouri, increased in spring, greater concentrations continued until late summer or early fall, and lower concentrations occurred in late fall and winter. Alachlor and atrazine concentrations most likely followed a similar trend in the Missouri River near the Independence well field. The lack of a seasonal trend similar to that of the Missouri River in the combined Independence well field pumpage and the monitoring wells may indicate that the source of alachlor and atrazine to ground water is the land surface rather than the Missouri River.

INTRODUCTION

The city of Independence, Missouri, operates a well field within the city limits of Sugar Creek, Missouri, in the Missouri River alluvial aquifer. About 250,000 people in several communities are supplied water from the well field which has an average production of 27 million gallons per day. Planned development in the vicinity of the well field has heightened awareness of potential sources of ground-water contamination and made monitoring ground-water quality near the well field necessary. Development includes extension of an existing landfill 0.5 to 1.0 mile south of the alluvial plain and within the Mill Creek Basin that drains into the alluvial plain, commercial development near the existing well field, highway construction adjacent to the well field, and expansion of the well field to the west and north of the river. In addition, nearby highway and rail line traffic, the use of fly ash for mine stabilization south of the well field, a closed oil refinery south of the well field, land application of solid waste across the river to the west, and nearby agricultural activity have caused concerns about accidental and human activity that may adversely affect ground-water quality.

Seasonal changes in ground-water quality of the alluvial aquifer can be caused by changes in land-use activities, such as the seasonal use of agricultural chemicals, changes in aquifer recharge caused by seasonal changes in the rate of rainfall and evapotranspiration, river stage fluctuations that can cause river water to enter the aquifer or cause water from the aquifer to drain into the river, or the application of salt to roads during winter months. Agricultural chemicals commonly are applied in the spring before planting; however, recharge that can occur in late fall or winter when evapotranspiration is negligible can move previously applied agricultural chemicals into the aquifer. The most widespread sources of potential ground-water contamination to the Independence well field are nonpoint source areas related to agricultural use of fertilizers and pesticides. Numerous potential point sources also exist near the well field. Potential sources of ground-water contamination within the contributing recharge area of the Independence well field are agricultural, commercial, industrial, and residential properties; and highways, landfills, railroads, solid waste land application sites, mines, and water ways (Kelly, 1996). The long-term presence of these potential sources of ground-water contamination increases the probability that contamination of the aquifer may occur. However, the background quality of ground water in the zone of contribution (ZOC), the part of the aquifer from which the well field obtains its water, was largely unknown prior to 1998.

In response to the ground-water quality concerns, the U.S. Geological Survey (USGS) and the city of Independence, Missouri, completed a study of ground-water flow in the area of the well field (Kelly, 1996). Results of the study included types and locations of potential ground-water contamination source areas, analysis of changes in ground-water flow, changes in ground-water travel time and contributing recharge areas from planned well-field expansion, and the design of a ground-water monitoring network in the area of the Independence well field consisting of 75 wells in 35 clusters. Site conditions, land owner concerns, and changes in planned development near the well field resulted in the installation of a monitoring well network of 27 well clusters (fig. 1).

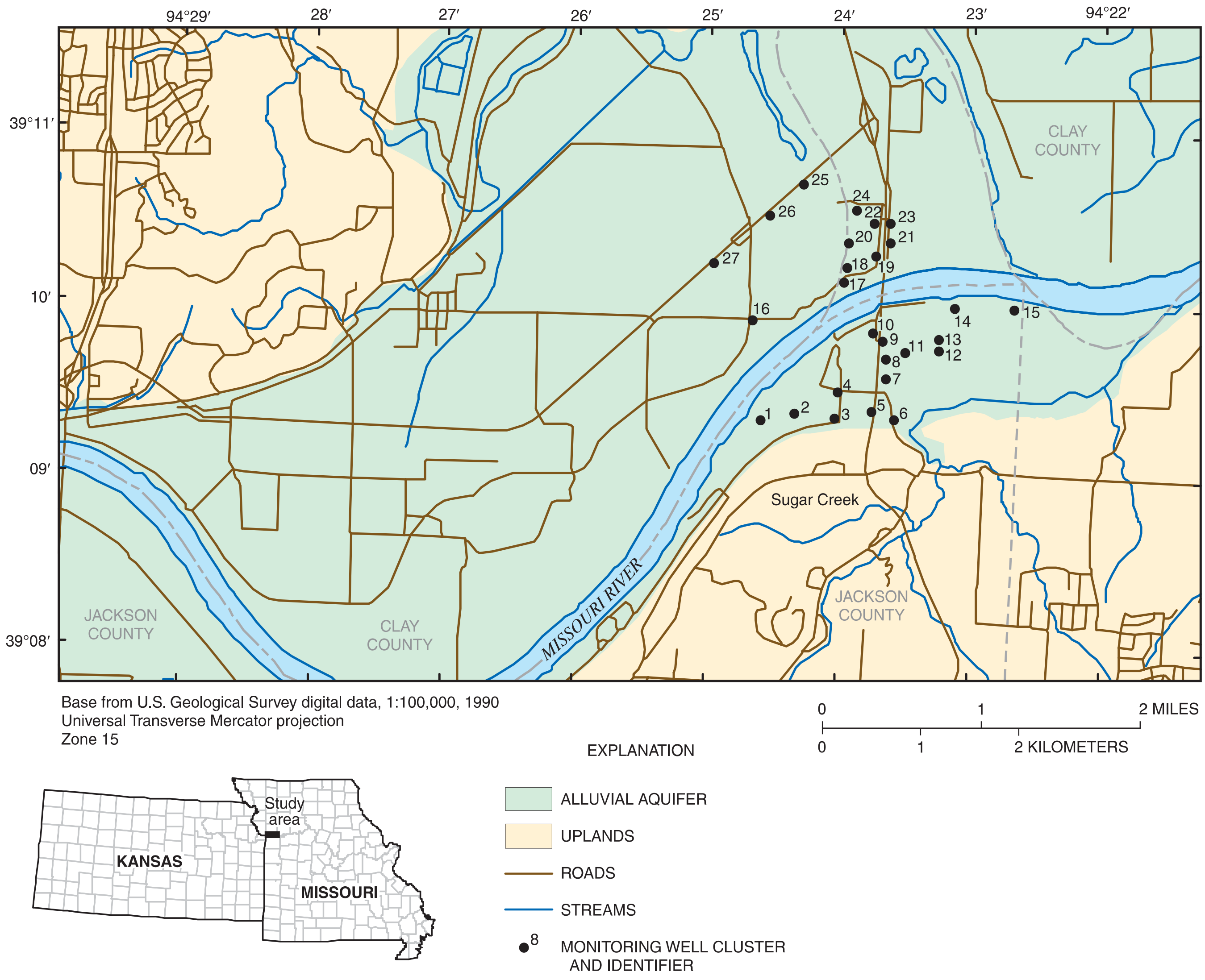
The scope of this study described in this report was to develop a ground-water monitoring plan, characterize overall ground-water quality of the Missouri River alluvial aquifer within the 10-yr (year) ZOC to the city of Independence well field, and determine the spatial and temporal variability of selected agricultural chemicals in ground water from 1998 through 2000. The purpose of this report is to present the ground-water monitoring plan and water-quality data obtained during the study, and to describe the overall ground-water quality and seasonal variation in agricultural chemicals within the 10-yr ZOC of the city of Independence well field. Characterization of ground-water quality of the Missouri River alluvial aquifer will provide information that can be used to infer ground-water quality in other areas of the Missouri River alluvial aquifer and in alluvial aquifers of other large rivers. Agricultural chemicals can impact ground-water quality in many landscapes. Results of this study will provide information about agricultural impacts on ground-water quality within the contributing recharge area of a large water-supply well field.

GROUND-WATER MONITORING PLAN

The ground-water monitoring network design was based on simulated ground-water travel time in the area of the well field and the location of potential sources of ground-water contamination (Kelly, 1996). Because ground-water travel time between the screened interval of each monitoring well and the nearest supply well of the well field has been calculated, the estimated time available to respond to ground-water contamination, if detected with the monitoring network, also is known based on the well in which it is detected. The ground-water monitoring plan is based on ground-water travel times between each monitoring well and the well field, the estimated time required for adequate response to detected ground-water contamination, the existing water quality of the aquifer, and the type and source of potential contamination each monitoring well is intended to intercept.

Ground-Water Monitoring Well Network

The city of Independence installed a ground-water monitoring well network in 1997 and 1998 consisting of 64 wells in 27 clusters as shown in figure 1. Some monitoring well locations were changed from the original design in response to site conditions, land owner concerns, and changes in planned development. Monitoring well nomenclature, as used in this report, is based on a well nest number and a designation of the simulated ground-water travel time from the screened interval of each monitoring well to the well field (Kelly, 1996). For example, well 1-5 yr belongs to well nest 1 and has a 5-yr simulated ground-water travel time from the monitoring well to the production well field. Well 24-3 yr belongs to well nest 24 and has a 3-yr simulated ground-water travel time from the well to the well field. The city of Independence has assigned another nomenclature to the monitoring well network. For example, well 1-5 yr is designated well 1-A. Combined untreated water from all wells that were in use in the well field



Base from U.S. Geological Survey digital data, 1:100,000, 1990
Universal Transverse Mercator projection
Zone 15

Figure 1. Ground-water monitoring well network for the Independence, Missouri, well field.

was sampled during the study, and these samples were designated INDEP. The Missouri River was sampled monthly at St. Joseph, Missouri, (about 95 miles upstream from the Independence well field) under the USGS Ambient Water-Quality Program. Sample results from this site are designated as MORIV. Each monitoring well was located to intercept potential source types of contamination that exist within the contributing recharge area of the Independence well field. Well or sample site names, the type of potential source each well is intended to intercept, location, and well construction information are listed in table 1, at the back of this report.

Well Sampling Schedule and Constituents of Analysis

All wells in the monitoring well network were sampled initially and analyzed for constituents as determined by potential contamination source type to characterize the alluvial water quality within the 10-yr ZOC. Laboratory analyses for each type of potential contamination source are listed in table 2, at the back of this report. Wells 2-2 yr, 4-1 yr, 6-5 yr, 11-1 yr, and 19-0.5 yr were selected from the initial sampling to have samples analyzed for a larger number of constituents, including those required by drinking water standards for the State of Missouri. These constituents for the expanded analyses included physical properties, bacteria, major ions, trace elements, nutrients, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), pesticides, polychlorinated biphenyls (PCBs), polychlorinated napthalenes (PCNs), and herbicides. From these data, a long-term sampling schedule for the monitoring well network was developed, and consists of annual sampling on a 3-yr rotation. A short-term sampling schedule also was developed to characterize seasonal changes in selected agricultural chemicals. The short-term sampling plan included quarterly sampling and analysis for selected constituents of at least 1 well in each of the 27 well clusters combined with more frequent sampling of a subset of these wells for agricultural chemicals only. Wells sampled from each type of sampling schedule are listed in table 3, at the back of this report. Occasionally, a well scheduled for sampling was changed because the well was dry or other site conditions prevented sampling. In these cases, the well in the nest with a screened interval closest to that well was sampled. Wells 2-5 yr, 4-3 yr, and 4-5 yr (combined results), 11-1 yr and 11-3 yr (combined results), 12-3 yr, 15-2 yr, 16-10 yr, 24-5 yr, and INDEP were sampled for all quarterly and agricultural chemical sampling events.

Methods of Sample Collection and Analysis

Ground-water samples were collected using a stainless steel pump with Teflon impeller and tubing. Water was pumped from the well and continuously monitored for specific conductance, pH, temperature, and dissolved oxygen in a flow-through chamber. Samples were collected after values for these properties had stabilized. Occasionally, shallow wells did not contain enough water for stabilization of these values before the well became dry. At these times, the well was pumped dry and samples were collected when water levels within the well recovered. When on-site conditions did not permit vehicular access to some well clusters, samples were collected after a minimum of three well volumes were removed from the well with a disposable bailer. Water samples were collected during this study according to the methods described in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, 1997–1999).

Measurements of specific conductance, pH, water temperature, and dissolved oxygen were recorded at the time of sampling in a flow through chamber after values for these properties stabilized. Specific conductance was measured using a portable conductivity meter with temperature compensation and calibrated with standard buffers that bracketed the expected values of specific conductance for the sample. Values for pH were measured using a temperature compensated portable pH meter calibrated with standard buffers that bracketed the expected sample pH values. Water temperature was measured using a thermistor thermometer. Dissolved oxygen was measured using a temperature compensated portable dissolved oxygen meter calibrated to a zero dissolved oxygen solution.

Fecal coliform and fecal streptococci bacteria densities were prepared for analysis within 1 hour of sample collection at the USGS laboratory in Independence, Missouri. Fecal coliform and fecal streptococci samples were analyzed using methods listed in table 4, at the back of this report.

Samples for analysis of most major ions and trace element were filtered through 0.45 μm (micron) filters, collected in 250-mL (milliliters) acid rinsed, polyethylene bottles, and preserved with nitric acid to a pH of 2. Samples for analysis of mercury were filtered through 0.45 μm filters, collected in 250-mL, acid-rinsed glass bottles, and preserved with a nitric acid-potassium dichromate solution. Samples for analysis of fluoride, sulfate, and chloride were filtered through 0.45 μm filters and collected in a 250 mL polyethylene bottles. Samples for analysis of all major ions and trace elements were chilled to 4 ^{o}C (degrees Celsius) and shipped to the laboratory the same day. Analytical methods, minimum reporting levels (MRLs), maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs) for major ions and trace elements are listed in table 4.

Samples for nutrient analysis were filtered through a 0.45-μm glass fiber filter and collected in 125-mL brown polyethylene bottles, chilled to 4 ^{o}C and shipped to the laboratory the same day. Analytical methods, MRLs, and MCLs for nutrient samples were analyzed using methods listed in table 4. All shipped samples described above were sent to the USGS National Water Quality Laboratory in Arvada, Colorado.

Samples for atrazine, alachlor, and total benzene, toluene, ethyl benzene, and xylene (total BTEX) were collected in 125-mL amber glass bottles and chilled to

$4\ ^{o}C$. Analyses for BTEX, atrazine, and alachlor were conducted using enzyme linked immunosorbent assay (ELISA) methods (Thurman and others, 1990) at the USGS laboratory in Independence, Missouri. ELISA methods are semi-quantitative and less precise than gas chromatograph-mass spectrometer (GC-MS) methods and were used in this study as a screening tool to indicate variations of tested constituents with time. The ELISA methods for BTEX, atrazine, and alachlor are sensitive to similar compounds, and results may indicate the presence of these additional compounds (Thurman and others, 1990). Minimum reporting levels, MCLs, reporting units and cross-reactive compounds for total BTEX, atrazine, and alachlor, determined using ELISA are listed in table 5, at the back of this report. Results of these analyses are presented as total BTEX, atrazine, or alachlor, but also may indicate the presence of other related compounds. Because of the semi-quantitative nature of these analyses, comparisons between analysis results for total BTEX, atrazine, or alachlor and their respective MCLs for drinking water are presented for descriptive purposes only.

Samples for volatile organic chemical analysis were collected in three-40-mL amber glass septum vials completely filled to exclude air bubbles. Samples were preserved with hydrochloric acid to a pH of 2, chilled to $4\ ^{o}C$, and shipped to the laboratory the same day. Volatile organic compounds were analyzed using methods listed in table 6, at the back of this report. Samples for SVOCs, pesticides, herbicides, PCNs, and PCBs were collected in a baked 1-L (liter) amber glass bottle, chilled to $4\ ^{o}C$, and shipped to the laboratory the same day. Samples for diquat were collected in 1-L high-density polyvinyl chloride bottles, preserved with sodium thiosulfate, chilled to $4\ ^{o}C$, and shipped to the laboratory the same day. Semi-volatile organic compounds were analyzed using methods listed in table 7, at the back of this report. Pesticides, PCNs, PCBs, herbicides and diquat were analyzed using methods listed in table 8, at the back of this report.

Quality assurance/quality control (QA/QC) methodology was used for all water sampling. This included replicate samples, equipment blanks, field spikes, and using ground-water sampling protocol as defined in the QA/QC plan for the USGS Water Resources Division, Missouri District (on file at the U.S. Geological Survey office, Rolla, Missouri). Replicate samples are used to assess the adequacy of the sampling process in obtaining a representative sample. Replicate samples are two complete samples collected at the same time. Both samples are prepared, packed for shipping, analyzed identically, and used to assess sample-collection technique and laboratory analysis. Equipment blanks are prepared with certified inorganic blank water, and used to assess the cleanliness of sampling equipment. Field spikes can be used to determine the extent of matrix bias or interferences on analyte recovery and degradation during shipping. Concentrations of major ions and trace elements in replicate and blank samples obtained during the study are listed in table 9, at the back of this report. Results indicate that the sample collection and processing equipment was not compromising sample quality. Concentrations of nutrients in replicate and blank samples obtained during the study are listed in table 10, at the back of this report. Results from the nutrient replicate sample from well 26-5 yr on September 24, 1998, were less than the sample and indicated a problem with sample collection. Results from the nutrient blank sample from well 23-5 yr on May 19, 1999, indicated insufficient equipment cleaning methods. Subsequent to each of these events, sample collection and preservation methods were reviewed and closely followed, and equipment cleaning methods were enhanced. Concentrations and percent recovery of pesticides in field spike samples obtained during the study are listed in table 11, at the back of this report. Results indicate that the sample matrix was not compromising analytical results.

WATER-QUALITY RESULTS

Physical Properties, Bacteria, Major Ions, Trace Elements, and Cyanide

The MCLs for major ions, trace elements, and cyanide are based on total recoverable concentrations, but water samples analyzed were filtered. Filtered samples typically have lower concentrations of a constituent than the same unfiltered sample. The difference in sample concentration between filtered and unfiltered samples typically is larger for surface water than for ground water because suspended particles usually are filtered as water moves through the aquifer. The comparisons of MCLs based on total recoverable concentrations to the analytical results obtained from filtered samples collected during this study are for illustrative purposes only.

Physical properties include, specific conductance, pH, water temperature, and dissolved oxygen (table 12, at the back of this report). In 328 ground-water samples, specific conductance values ranged from 511 to 1,690 µS/cm (microsiemens per centimeter at 25 degrees Celsius), pH values ranged from 6.4 to 7.7, water temperature ranged from 11.3 to 23.6 ^{o}C, and dissolved oxygen concentrations ranged from 0 to 3.3 mg/L (milligrams per liter) (table 12). In 12 combined well field pumpage samples, specific conductance values ranged from 558 to 856 µS/cm, pH values ranged from 6.9 to 7.7, water temperature ranged from 5.8 to 22.9 ^{o}C, and dissolved oxygen concentrations ranged from 0 to 2.4 mg/L (table 12). In 45 samples from the Missouri River, specific conductance values ranged from 531 to 830 µS/cm, pH values ranged from 7.2 to 8.7, water temperature ranged from 0 to 30 ^{o}C, and dissolved oxygen concentrations ranged from 5 to 17.6 mg/L (table 12). Both highest and lowest ground-water temperatures were measured in well 15-2 yr. This well is located between the Missouri River and a well of the Independence well field, and is affected by induced recharge from the Missouri River. The highest temperature was recorded on February 25, 2000, and the lowest temperature was recorded on August 23, 1999, indicating a seasonal offset caused by travel time from the river to the well.

Fecal coliform and fecal streptococci densities in ground water samples with detected colonies and samples from the Missouri River at St. Joseph are listed in table 13, at the back of this report. Fecal coliform bacteria were present in four wells (5 of 194 samples) and ranged from 1 to 500 col/100 mL (colonies per 100 milliliters) (table 13), with a median of 0.0 col/100 mL. The 500 col/100 mL occurred in well 25-10 yr on May 26, 1999, and was the only detection for this well in six samples. The high fecal coliform count and the single detection may indicate contamination of the sample during the analysis; however, sample blanks before and after analysis did not have any fecal coliform bacteria counts. Fecal coliform bacteria were present in the Missouri River in all 33 samples, from 43 to 35,000 col/100 mL, with a median of 440 col/100 mL. Fecal streptococci bacteria were present in 10 wells (11 of 194 samples) and ranged from 1 to 41 col/100 mL, with a median of 0.0 col/100 mL. Fecal streptococci bacteria was detected in the Missouri River in all samples and ranged from 7 to 20,000 col/100 mL, with a median of 205 col/100 mL. The detection of fecal coliform and fecal streptococci bacteria in water samples may indicate the presence of raw sewage in the water.

Dissolved major ions include calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, fluoride, and silica. Median concentrations of major ions and iron in ground water monitoring wells, combined well field pumpage, and the Missouri River are listed in table 14, at the back of this report. Although iron is considered a trace element, it is included with the discussion of major ions because it was found at high concentrations in almost all ground-water samples. Ground water was dominated by calcium and bicarbonate ions. Results of all analyses for major ions are listed in table 15, at the back of this report. The MCLs and SMCLs for drinking water for sulfate, chloride, fluoride, and iron, are listed in table 4. The MCL for iron [300 µg/L (micrograms per liter)] was exceeded in all monitoring wells except wells 3-10 yr and 24-5 yr. No samples analyzed for chloride or fluoride exceeded the MCL; however, the SMCL for sulfate (250 mg/L) was equalled or exceeded in wells 1-5 yr (260 mg/L) and 4-1 yr (250 mg/L).

Results of analyses for dissolved trace elements are listed in table 16, at the back of this report. MCLs for drinking water for total recoverable aluminum, antimony, arsenic, barium, cadmium, chromium, copper, cyanide, lead, manganese, mercury, selenium, silver, thallium, and zinc are listed in table 4. The MCL for antimony (6 µg/L) was exceeded in well 16-10 yr (6.7 µg/L). The MCL for barium (2,000 µg/L) was exceeded in well 16-5 yr (2,100 µg/L). The MCL for manganese (50 µg/L) was exceeded in all samples from monitoring wells and INDEP.

Nutrients

Results of analyses for nutrients are listed in table 17, at the back of this report. Dissolved ammonia was detected in samples from all wells (230 of 246 samples), and concentrations ranged from 0.02 to 5.1 mg/L as nitrogen (N). Dissolved ammonia was detected in the Missouri River in 29 of 45 samples, and concentrations ranged from 0.02 to 0.46 mg/L. Dissolved nitrite plus nitrate was detected in samples from 21 wells (46 of 296 samples), and concentrations ranged from 0.05 to 6.97 mg/L as N. All sample concentrations of dissolved nitrite plus nitrate were less than the 10 mg/L MCL for drinking water. Dissolved nitrite plus nitrate was detected in the Missouri River in

43 of 45 samples, and detections ranged from 0.03 to 3.7 mg/L as N. Dissolved nitrite was detected in 31 wells (60 of 246 samples), and concentrations ranged from 0.01 to 0.09 mg/L as N. Dissolved nitrite was detected in the Missouri River in 28 of 45 samples, and concentrations ranged from 0.01 to 0.07 mg/L as N. Dissolved orthophosphorus was detected in at least one sample from each well (185 of 246 samples) and concentrations ranged from 0.01 to 0.99 mg/L as phosphorus (P). Dissolved orthophosphorus was detected in the Missouri River in 44 of 45 samples, and concentrations ranged from 0.01 to 0.36 mg/L as P.

Enzyme Linked Immunosorbent Assay (ELISA)

Total BTEX was detected in four wells and INDEP (5 of 118 samples), and concentrations ranged from 0.03 to 0.33 mg/L (table 18, at the back of this report). No MCL for total BTEX exists (table 5). The largest total BTEX detection of 0.33 mg/L in INDEP on May 27, 1999, is less than the MCL of toluene (1,000 µg/L), ethyl benzene (700 µg/L), or xylene (10,000 µg/L), but greater than the MCL for benzene (5 µg/L). The smallest BTEX detection of 0.03 mg/L is greater than the MCL for benzene. Total BTEX was not detected in any well more than once.

Atrazine was detected in eight wells and INDEP (30 of 344 samples), and concentrations ranged from 0.05 to 7.51 µg/L (table 19, at the back of this report). The MCL for atrazine (3 µg/L) was exceeded in one sample from well 16-10 yr (7.51 µg/L) on May 5, 1999. Atrazine was detected in 2 samples from well 16-10 yr, in 8 samples from INDEP, and in 14 samples from well 15-2 yr.

Alachlor was detected in 22 wells (59 of 352 samples), and concentrations ranged from 0.05 to 0.43 µg/L (table 19). Concentrations were less than the MCL for alachlor (2 µg/L) in all samples. Alachlor was detected in 2 samples from wells 10-2 yr, 11-3 yr, and 12-3 yr, in 3 samples from well 15-1 yr, in 4 samples from wells 14-0.5 yr and 20-1 yr, in 7 samples in well 24-5 yr, in 8 samples from INDEP, and in 14 samples from well 15-2 yr.

Initial Sampling

Initial samples were collected from all wells. Wells 2-2 yr, 4-1 yr, 6-5 yr, 11-1 yr, and 19-0.5 yr were selected to have samples analyzed for the additional constituents listed in tables 6, 7, and 8. The VOCs (table 6) ethyl benzene (0.21 µg/L), toluene (1.1 µg/L), and xylene (0.45 µg/L) were detected in well 11-1 yr on July 22, 1998. All detected concentrations of VOCs were substantially less than their respective MCL for drinking water. No SVOCs (table 7) were detected during the initial sampling event. Dieldrin (0.001 µg/L) was the only pesticide (table 8) detected in well 11-1 yr on July 22, 1998. No other pesticides, PCBs, PCNs, or herbicides were detected during the initial sampling in wells 2-2 yr, 4-1 yr, 6-5 yr, 11-1 yr, and 19-0.5 yr.

SPATIAL AND TEMPORAL VARIABILITY OF SELECTED AGRICULTURAL CHEMICALS IN GROUND WATER

Agricultural chemicals can affect ground-water quality in areas where they are used, and the amount of agricultural chemicals in ground water may vary with the timing of their application. The most widespread sources of potential ground-water contamination to the Independence well field are non-point sources related to agricultural use of fertilizers and pesticides. The herbicides alachlor and atrazine are applied to cropland to control weeds; alachlor primarily is used on soybeans, atrazine on corn and milo. Leaching of pesticides and fertilizer-derived nitrogen and phosphorus below the crop root zone can cause these constituents to move into ground water. Analyses of dissolved ammonia, dissolved nitrite plus nitrate, dissolved orthophosphorus, alachlor, and atrazine were used to determine the spatial and temporal variability of agricultural chemical concentrations in ground water and characterize the most likely source of these constituents in ground water.

Dissolved ammonia had the greatest concentration, was most frequently detected, and was the most dominant nitrogen species detected in ground water. However, dissolved nitrite plus nitrate was predominant wherever dissolved oxygen was present. To determine the spatial variability of dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus with depth, wells were grouped into depth intervals of 0 to 12, 12 to 18, 18 to 24, and 24+ (greater than 24) m (meter). The detection frequencies and maximum, minimum, and median concentrations for dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus for samples from each depth interval were determined and are shown in figure 2. Detection frequencies for dissolved ammonia were largest (100 percent) for the 18 to 24 and 24+ m depth intervals, smallest (90 percent) for the 0 to 12 m depth interval, and increased with depth interval. The maximum dissolved ammonia concentration (5.1 mg/L) was largest for a sample in the 0 to 12 m depth interval. Minimum dissolved ammonia concentrations were less than the detection limit for the 0 to 12 m and 12 to 18 m depth intervals. Median dissolved ammonia concentrations were similar for all depth intervals, with the largest (0.65 mg/L) for the 24+ m depth interval and smallest (0.44 mg/L) for the 18 to 24 m depth interval.

Detection frequencies for dissolved nitrite plus nitrate were largest (24 percent) for the 0 to 12 m depth interval and smallest (5 percent) for the 24+ m depth interval, and decreased with depth interval. The maximum dissolved nitrite plus nitrate concentration (6.97 mg/L) was for a sample in the 12 to 18 m depth interval. Minimum and median concentrations were less than the detection limit for all depth intervals.

Detection frequencies for dissolved orthophosphorus were largest (75 percent) for the 18 to 24 m depth interval and smallest (67 percent) for the 24+ m depth interval. The maximum dissolved orthophosphorus concentration (0.99 mg/L) was for a sample in the 12 to 18 m depth interval. Minimum concentrations were less than the detection limit for all depth intervals. Median dissolved orthophosphorus concentrations were similar for all depth intervals, with the largest (0.021 mg/L) for the 0 to 12 m depth interval and smallest (0.014 mg/L) for the 24+ m depth interval.

Detection frequencies for dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus were fairly constant for all depth intervals (fig. 2). Detection frequencies increased with depth for dissolved ammonia, decreased with depth for dissolved nitrite plus nitrate, and remained relatively constant with depth for dissolved orthophosphorus. The increase in dissolved ammonia detections and decrease in dissolved nitrite plus nitrate detections may be caused by a decrease in dissolved oxygen in ground water with depth, rather than indicating the location of a potential source of nitrogen to ground water. Maximum concentrations of dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus were largest in the shallowest depth intervals and decreased with depth, which may indicate a land surface source. However, median concentrations slightly increased with depth for dissolved ammonia, were less than detection for dissolved nitrite plus nitrate, and slightly decreased with depth for dissolved orthophosphorus. This pattern does not indicate a well-defined single source for these constituents. Increased median dissolved ammonia concentrations at depth may have been caused by a build up of nitrogen at depth as dissolved ammonia in ground water moved downward and became unavailable for plant use or by another source of nitrogen such as the Missouri River. Median dissolved nitrite plus nitrate concentrations less than the detection limit indicate a lack of dissolved oxygen in ground water. Median dissolved orthophosphorus concentrations were similar, but decreased slightly with depth, and may indicate a land surface source.

To determine the seasonal variability of dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus, samples obtained during the study in 1998, 1999, and 2000 were grouped by month. Detection frequencies and maximum, minimum, and median concentrations for dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus by month are shown in figure 3. From these data, seasonal variability of dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus concentrations is not well defined. However, combining sample results from all wells may mask seasonal trends in water quality because variations in hydraulic properties cause different rates of water movement from the source of these constituents to each well.

Samples from wells 2-5 yr, 4-3 yr, and 4-5 yr (results combined), 11-1 yr and 11-3 yr (results combined), 12-3 yr, 15-2 yr, 16-10 yr, and 24-5 yr, the combined Independence well field pumpage, and the Missouri River at St. Joseph, Missouri, were analyzed for dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus to help determine the seasonal variability of agricultural chemicals. Results from these analyses are shown in figure 4. Analyses of samples from the Missouri River indicate relatively constant dissolved ammonia concentrations and a seasonal trend for dissolved nitrite plus nitrate and dissolved orthophosphorus with peak concentrations occurring in spring and summer and lower concentrations during the rest of the year. Results from the combined Independence well field pumpage indicate dissolved ammonia concentrations increased slightly in

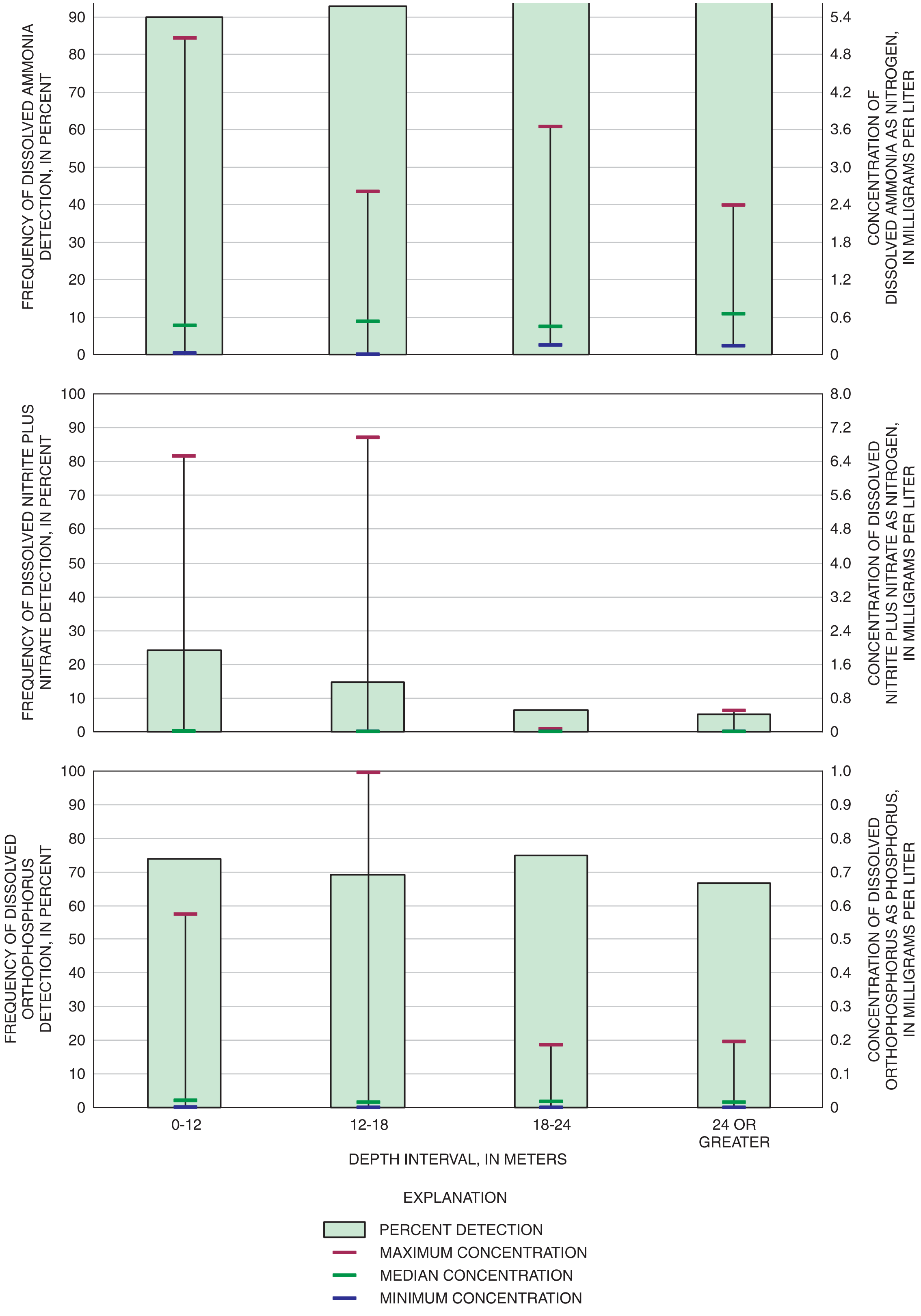


Figure 2. Frequency of detection and concentration of dissolved ammonia, nitrite plus nitrate, and orthophosphorus for samples grouped by well depth.

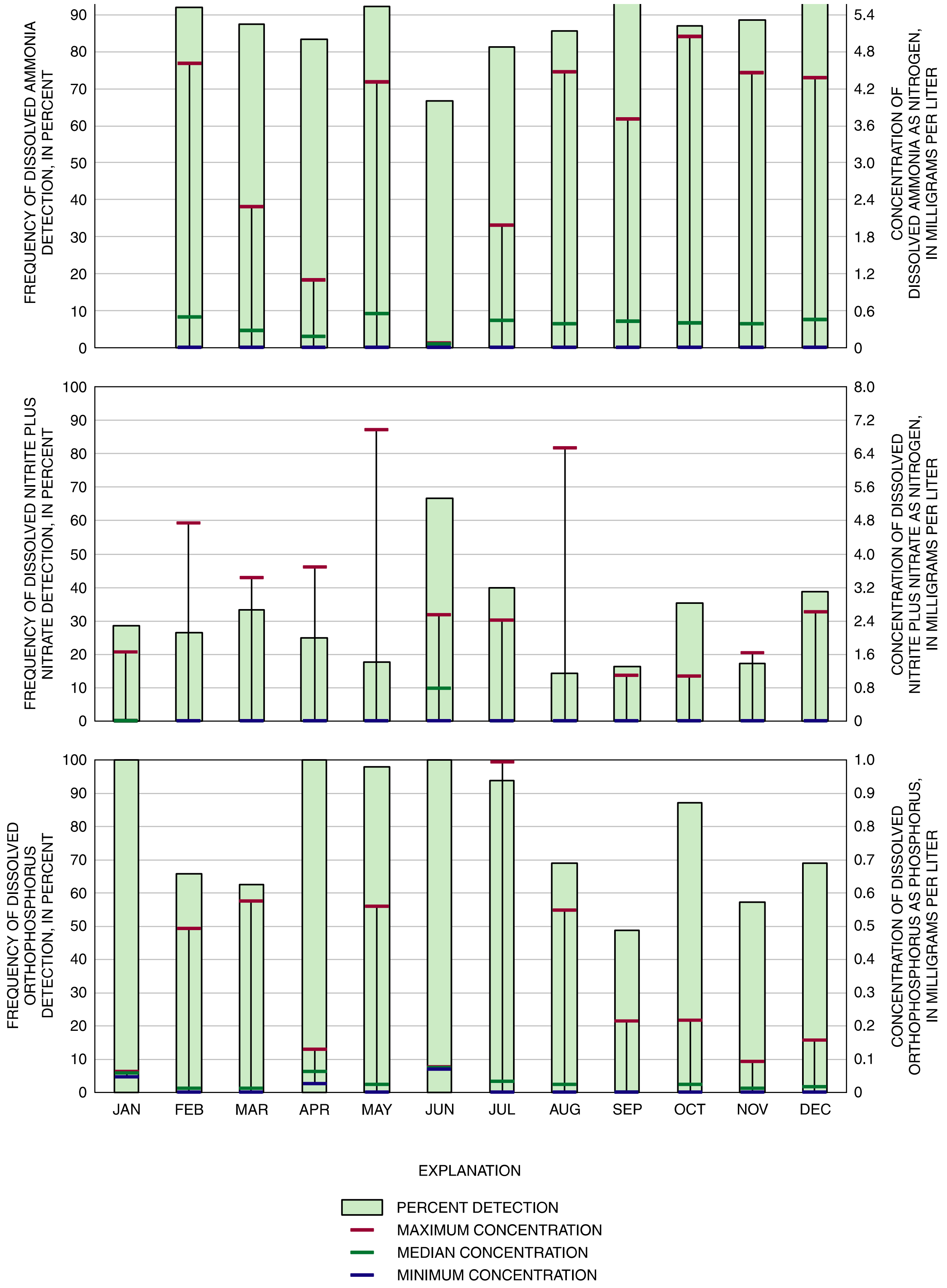


Figure 3. Frequency of detection and concentration of dissolved ammonia, nitrite plus nitrate, and orthophosphorus for samples grouped by month, 1998–2000.

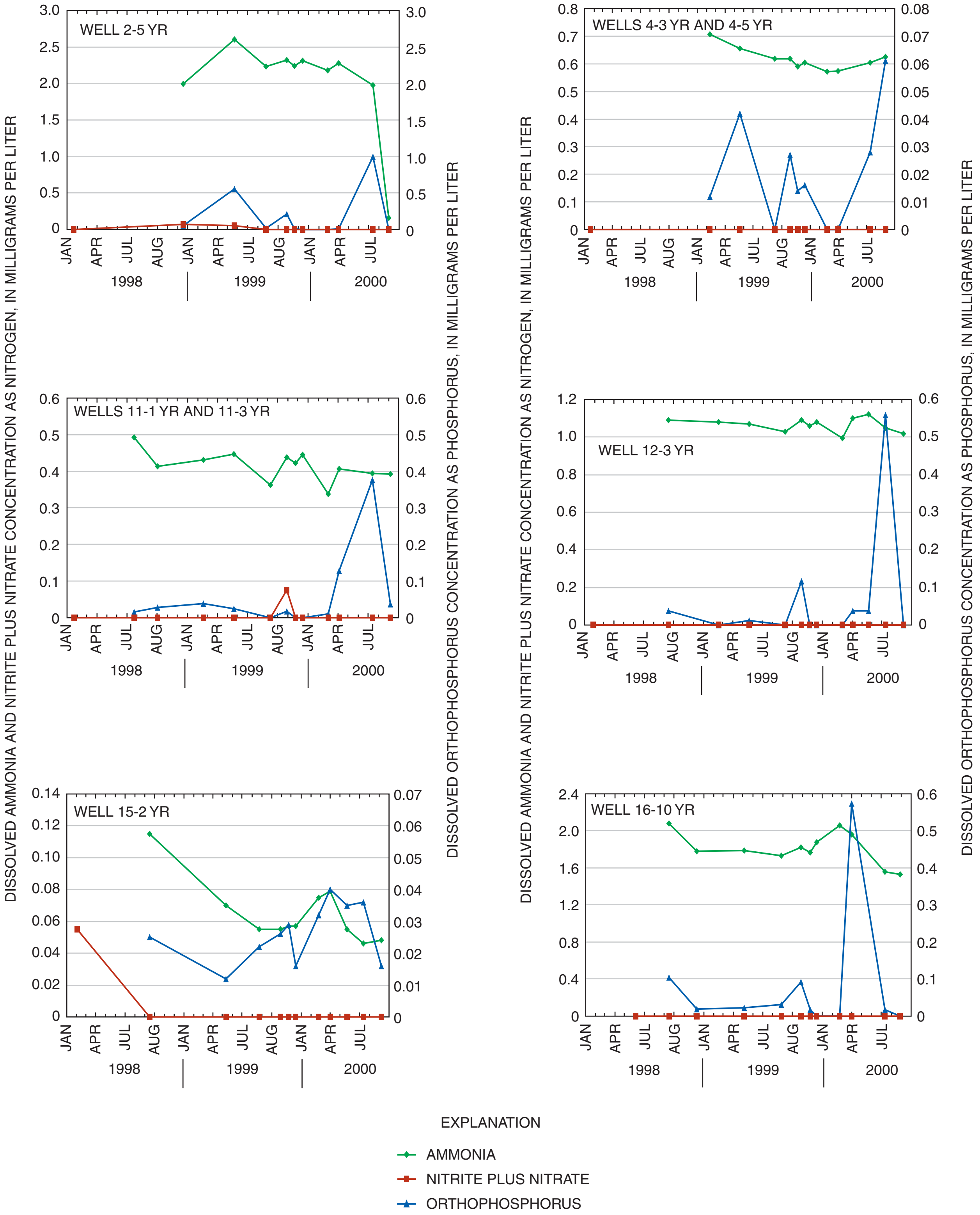


Figure 4. Dissolved ammonia, nitrite plus nitrate, and orthophosphorus in water samples from selected monitoring wells, the Independence well field, and the Missouri River at St. Joseph, Missouri.

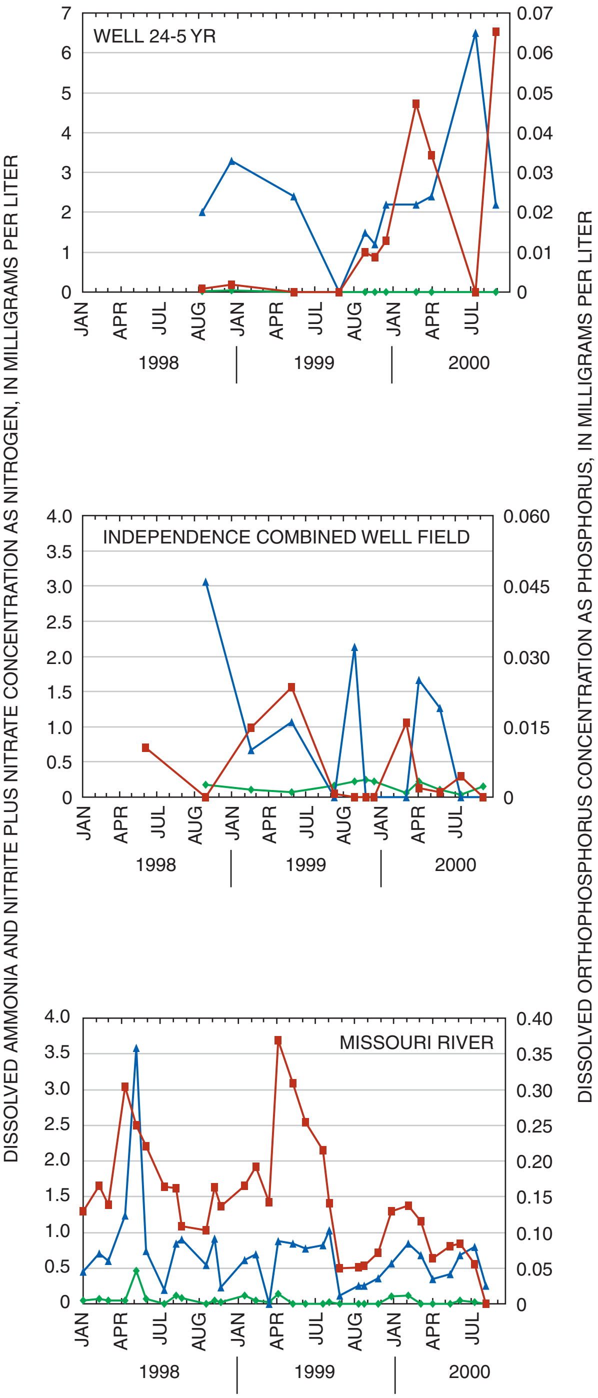


Figure 4. Dissolved ammonia, nitrite plus nitrate, and orthophosphorus in water samples from selected monitoring wells, the Independence well field, and the Missouri River at St. Joseph, Missouri—Continued.

the fall of 1999 and again in the spring and fall of 2000, but remained fairly constant with little variability. A likely seasonal trend for dissolved nitrite plus nitrate may exist, with the peak concentrations occurring in the spring or summer similar to the seasonal variation in the Missouri River. The similarity between the dissolved nitrite plus nitrate peaks in the Missouri River and the combined Independence well field pumpage results may indicate that the Missouri River is a source of agricultural chemicals to the Independence well field, and illustrates the effect of induced recharge from the river on well field pumpage.

The seasonal variability of dissolved ammonia for samples from individual wells is not as well defined as that for either the Missouri River or the combined Independence well field pumpage (fig. 4). Dissolved ammonia concentrations in these well samples remained relatively constant, with the exception of well 2-5 yr, where the dissolved ammonia concentration decreased in September 2000.

Dissolved nitrite plus nitrate concentrations were small in all samples from wells except 24-5 yr, where dissolved nitrite plus nitrate concentrations were greater than dissolved ammonia concentrations during the study. The small dissolved nitrite plus nitrate concentrations in samples from well 24-5 yr in late 1998 and most of 1999 were followed by a large increase beginning in the fall of 1999, and peaked in February and March 2000. Dissolved nitrite plus nitrate concentrations decreased in late spring and summer 2000, and then increased in September 2000. Small dissolved nitrite plus nitrate concentrations in samples from well 24-5 yr during 1998, followed by the large variations of dissolved nitrite plus nitrate concentrations greater than river concentrations and the absence of dissolved ammonia during 1999 and 2000, indicate surface application of fertilizer as the likely source. However, without a detailed history of fertilizer application times and rates for nearby cropland, the cause of the variation of dissolved nitrite plus nitrate in samples from this well cannot be verified.

The seasonal variability of dissolved orthophosphorus in ground water is more evident than that of either dissolved ammonia or dissolved nitrite plus nitrate (fig. 4). Dissolved orthophosphorus results for samples from individual wells generally show a small increase during the summer and fall of 1999. Dissolved orthophosphorus concentrations were lower in early spring 2000, and then sharply increased in all well samples in late spring and summer 2000.

To determine the spatial variability of alachlor and atrazine with depth, wells were grouped into depth intervals of 0 to12, 12 to 18, 18 to 24, and 24+ m. Detection frequencies and maximum, minimum, and median concentrations for alachlor and atrazine samples from each depth interval are shown in figure 5. Detection frequencies of alachlor (fig. 5) decrease with depth and are largest (24 percent) for the 0 to 12 m depth interval and smallest (7 percent) for the 24+ m depth interval. Maximum alachlor concentrations were largest (0.43 µg/L) for the 0 to 12 m depth interval and smallest (0.12 µg/L) for the 18 to 24 m depth interval. Median alachlor concentrations were less than the detection limit for all depth intervals.

Detection frequencies of atrazine were largest (10 percent) for the 12 to 18 m depth interval and smallest (0 percent) for the 18 to 24 m depth interval. Maximum atrazine concentrations were largest (7.51 µg/L) at the 0 to 12 m depth interval and smallest (below detection) for the 18 to 24 m depth interval. Median atrazine concentrations were less than the detection limit for all depth intervals. Larger detection frequencies in the shallow depth intervals and the large maximum concentrations of alachlor and atrazine in the shallower wells indicate that the source of these chemicals to shallow ground water most likely is the land surface rather than induced river recharge.

To determine the seasonal variability of alachlor and atrazine in ground water, results of sample analyses from 1998 through 2000 were grouped by month. Alachlor detection frequencies (fig. 6) were largest (28 percent) for November and smallest (10 percent) for January. Peaks in maximum alachlor concentration occurred for June (0.37 µg/L), September (0.37 µg/L), and November (0.43 µg/L). Minimum and median alachlor concentrations were less than the detection limit (0.05 µg/L) for all months. Detection frequencies of alachlor were slightly larger in spring and early summer, lower in late summer, increased slightly in the fall, and peaked in November. This slight seasonal variation of alachlor with peaks occurring in spring and fall likely is due to movement of surface-applied alachlor with aquifer recharge during spring (when rainfall is greater) and fall (when evapotranspiration is reduced). The maximum concentration of alachlor varies substantially, but a seasonal variability of alachlor in ground water is not well defined from these data.

Atrazine detection frequencies were largest (18 percent) for June and smallest (0 percent) for December and January. The maximum atrazine concentration occurred in May (7.51 µg/L). Minimum and median atrazine concentrations were less than the detection limit (0.05 µg/L) for all months. The detection frequencies and maximum atrazine concentrations indicate a slight seasonal variability of atrazine in ground water, with higher detection frequencies in spring and fall, lower detection frequencies in summer and winter, and the largest maximum concentration in spring. Combined sample results may mask seasonal trends in water quality because of different rates of water movement to each well.

Samples from the Missouri River at St. Joseph were not analyzed for alachlor or atrazine during the study. However, alachlor and atrazine were analyzed in samples collected from the Missouri River at Hermann, Missouri. The USGS operates a continuous streamflow gaging station at this site (Hauck and Nagel, 1999, 2000, 2001). These data are presented in figure 7 to illustrate how these constituents varied in the Missouri River during the study period.

A consistent seasonal variability of alachlor and atrazine concentrations for samples from the combined Independence well field pumpage and individual wells is not apparent (fig. 7). Variability in both alachlor and atrazine concentrations with time is indicated by the data, but the degree and timing of the variation is not consistent. This inconsistency is most likely caused by varying rates of transport from the land surface or the river to wells, different rates of degradation of both alachlor and atrazine in soil and ground water, the timing and area of application, and multiple source areas in and around the Independence well field. Alachlor and atrazine concentrations in the Missouri River at Hermann varied seasonally from 1998 through 2000 (Hauck and Nagel, 1999, 2000, 2001). Concentrations of both alachlor and atrazine increased in spring, and larger concentrations continued until late summer or early fall. Smaller concentrations occurred in late fall and winter. Alachlor and atrazine concentrations during the study probably followed a similar trend in the Missouri River near the Independence well field. The lack of a similar seasonal trend in the combined Independence well field pumpage and the monitoring wells may indicate that the source of alachlor and atrazine to ground water is the land surface rather than the Missouri River.

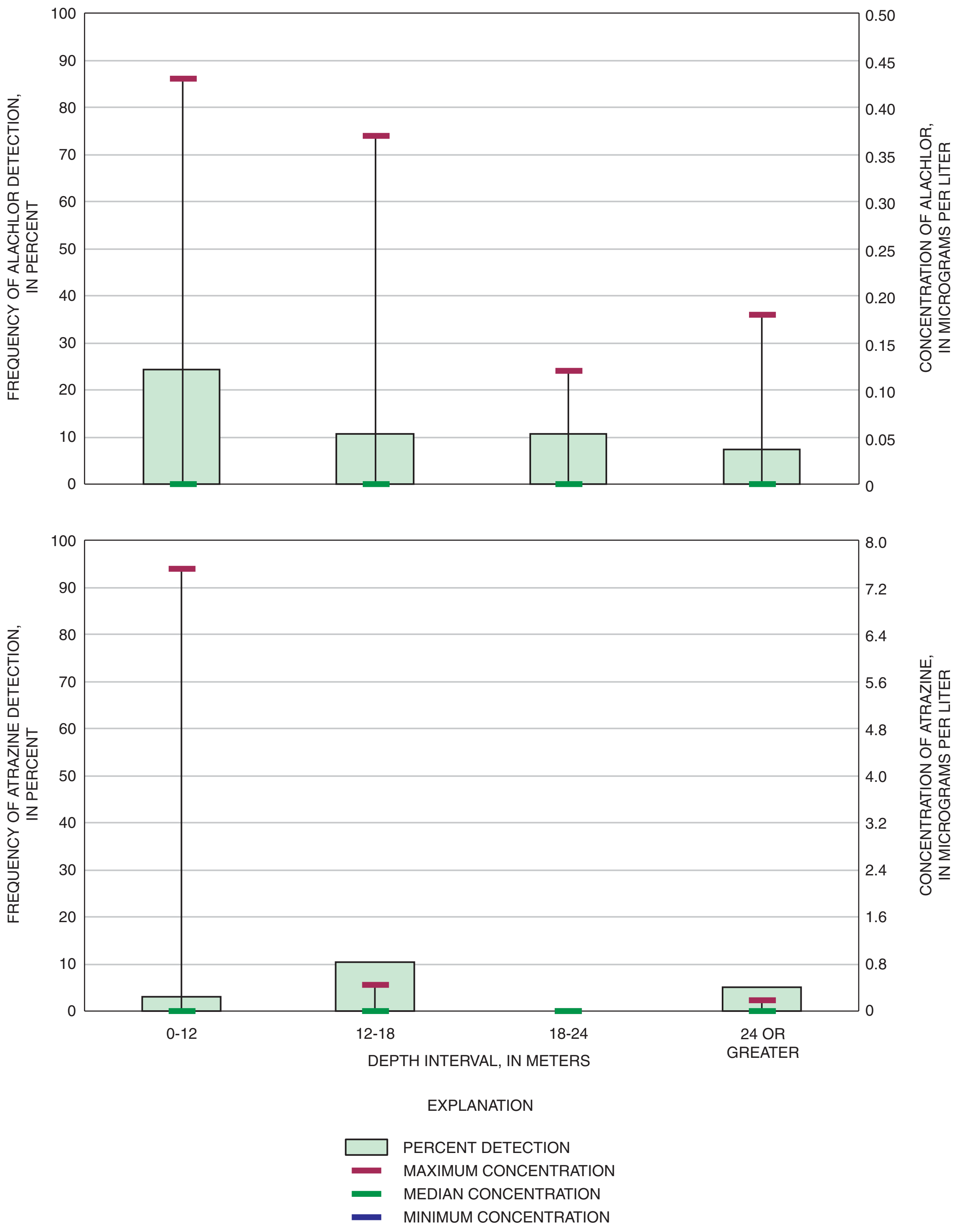


Figure 5. Frequency of detection and concentration of alachlor and atrazine for samples grouped by well depth.

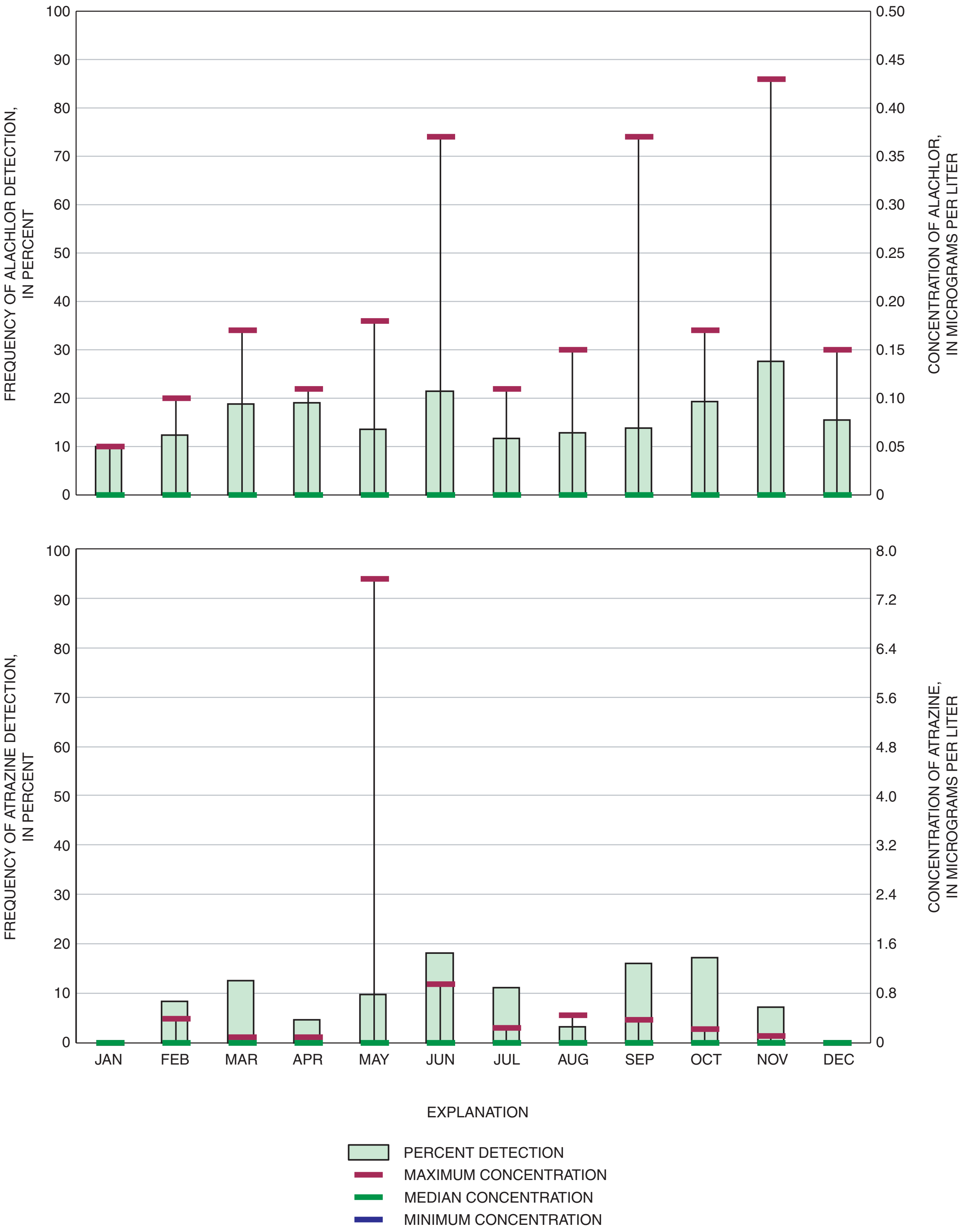


Figure 6. Frequency of detection and concentration of alachlor and atrazine for samples grouped by month, 1998–2000.

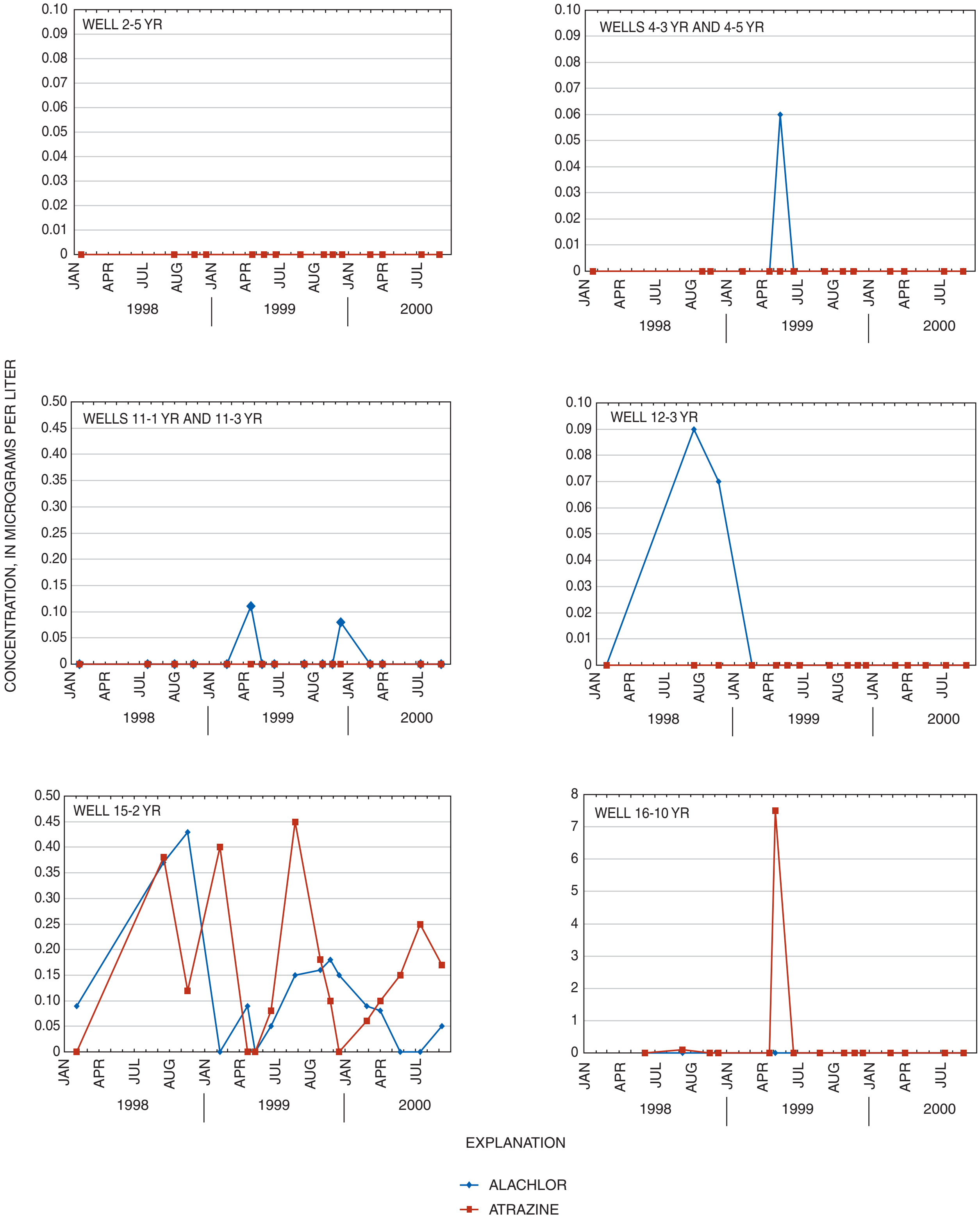


Figure 7. Alachlor and atrazine concentration in water samples from selected monitoring wells, the Independence well field, and the Missouri River at Hermann, Missouri.

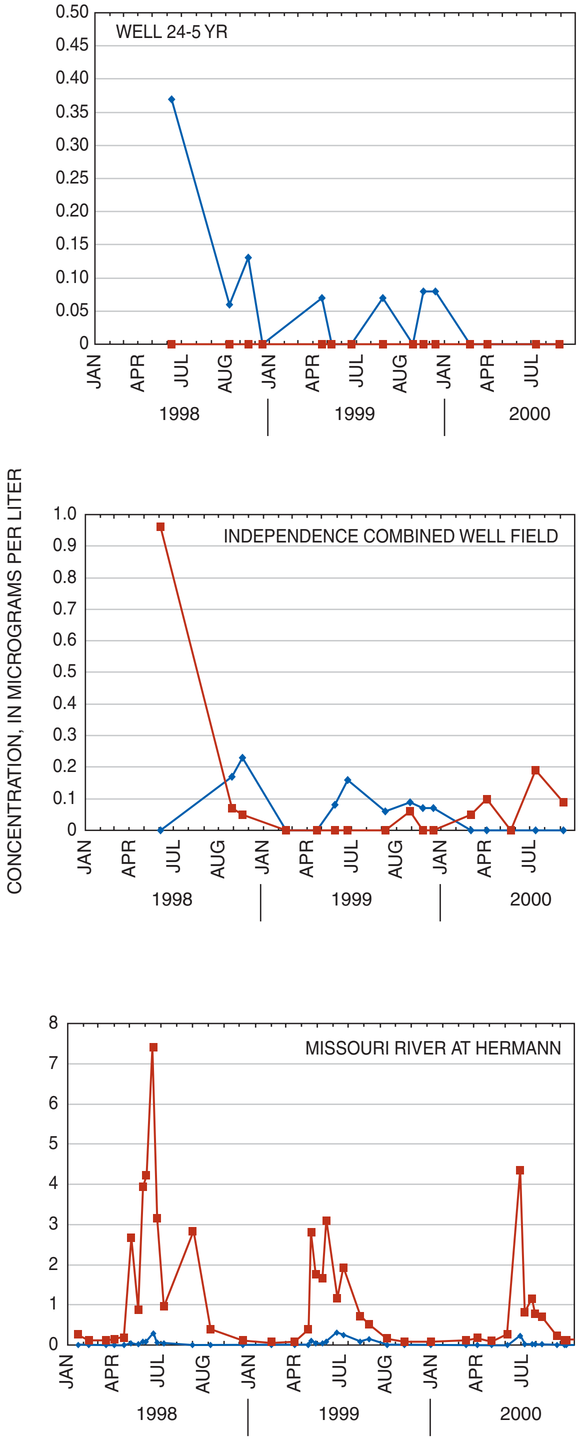


Figure 7. Alachlor and atrazine concentration in water samples from selected monitoring wells, the Independence well field, and the Missouri River at Hermann, Missouri—Continued.

SUMMARY

A ground-water monitoring plan was developed for the 64 monitoring wells in the city of Independence well field. Ground water was sampled from wells in the monitoring well network from 1998 through 2000. All wells in the monitoring well network were sampled initially to characterize the alluvial water quality within the 10-year zone of contribution. Five wells were selected from the initial sampling event to have samples analyzed for a large number of organic constituents. A long-term sampling schedule for the monitoring well network was developed and consists of annual well sampling on a 3-year rotation. A short-term sampling schedule was developed to characterize general water quality and seasonal changes in selected agricultural chemicals in the Missouri River alluvial aquifer in the area surrounding the Independence well field. The short-term sampling plan consisted of quarterly sampling of at least one well per well nest, combined with more frequent sampling of a subset of these wells for agricultural chemicals.

Samples collected from five of the wells during the initial sampling event were analyzed for a large number of constituents including physical properties, bacteria, major ions, trace elements, nutrients, volatile organic compounds, semi-volatile organic compounds, pesticides, polychlorinated biphenyls, polychlorinated napthalenes, and herbicides. Physical properties, bacteria, major ions, trace elements, nutrients, atrazine, and alachlor were analyzed in samples collected from initial, annual, and quarterly sampling events. Physical properties, bacteria, nutrients, atrazine, and alachlor were analyzed in samples collected from agricultural sampling events.

In 328 ground-water samples from the 64 monitoring wells and combined well field pumpage samples, specific conductance values ranged from 511 to 1,690 microsiemens per centimeter at 25 degrees Celsius, pH values ranged from 6.4 to 7.7, water temperature ranged from 11.3 to 23.6 degrees Celsius, and dissolved oxygen concentrations ranged from 0 to 3.3 milligrams per liter. In 12 samples from the combined well field pumpage samples, specific conductance values ranged from 558 to 856 microsiemens per centimeter at 25 degrees Celsius, pH values ranged from 6.9 to 7.7, water temperature ranged from 5.8 to 22.9 degrees Celsius, and dissolved oxygen concentrations ranged from 0 to 2.4 milligrams per liter. In 45 Missouri River samples, specific conductance values ranged from 531 to 830 microsiemens per centimeter at 25 degrees Celsius, pH ranged from 7.2 to 8.7, water temperature ranged from 0 to 30 degrees Celsius, and dissolved oxygen concentrations ranged from 5.0 to 17.6 milligrams per liter.

The secondary maximum contaminant level for drinking water for sulfate was exceeded once in samples from two monitoring wells, the maximum contaminant level for antimony was exceeded once in one well, and the maximum contaminant level for barium was exceeded once in one well. The maximum contaminant level for iron was exceeded in all monitoring wells except two wells. The maximum contaminant level for manganese was exceeded in all samples from monitoring wells and combined Independence well field pumpage.

Total benzene, toluene, ethyl benzene, and xylene (BTEX) was detected in samples from five wells, but was not detected more than once in any well. Alachlor was detected in 22 of 64 wells; the maximum contaminant level for alachlor was not exceeded in any sample results. Multiple detections of alachlor occurred in samples from eight wells and in combined well field pumpage (INDEP). Atrazine was detected in 9 of 64 wells; the maximum contaminant level for atrazine was exceeded once in one well. Atrazine was detected twice in one well, 8 times in INDEP, and 14 times in another well.

Three volatile organic compounds were detected in samples from the initial sampling of the five wells, but none exceeded the maximum contaminant level for drinking water. No semi-volatile organic compounds were detected during the initial sampling event. The pesticide dieldrin was detected in one well. No other pesticides, herbicides, polychlorinated biphenyls, or polychlorinated napthalenes were detected during the initial sampling event.

Analyses of dissolved ammonia, dissolved nitrite plus nitrate, dissolved orthophosphorus, alachlor, and atrazine were used to determine the spatial and temporal variability of agricultural chemicals in ground water for this study. Detection frequencies increased with well depth for dissolved ammonia, decreased with depth for dissolved nitrite plus nitrate, and remained relatively constant with depth for dissolved orthophosphorus. Maximum concentrations of dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus were largest in the shallowest wells and decreased with depth, which may indicate the land surface as the source. However, median concentrations increased with depth for dissolved ammonia, were less than detection for dissolved nitrite plus nitrate, and decreased with depth for dissolved orthophosphorus. This pattern does not indicate a well-defined single source for these constituents. Dissolved orthophosphorus median concentrations were similar but decreased slightly with depth and may indicate the land surface as the source. Seasonal variability of dissolved ammonia, dissolved nitrite plus nitrate, and dissolved orthophosphorus concentrations is not well defined for samples grouped by month. Individual sample results from the Missouri River and INDEP show a seasonal trend that may indicate the effect of induced recharge from the Missouri River on the well field. Individual results of samples from seven wells indicate relatively constant dissolved ammonia concentrations, low dissolved nitrite plus nitrate concentrations in all but one well, and a more well-defined seasonal variation of dissolved orthophosphorus than that of either dissolved ammonia or dissolved nitrite plus nitrate.

Larger detection frequencies in the shallow depth intervals and the large maximum concentrations of alachlor and atrazine in the shallower wells indicate that the source of these chemicals to shallow ground water most likely is the land surface rather than induced river recharge. Seasonal variability of alachlor is not well defined from results grouped by month. Individual results from the combined Independence well field pumpage and seven wells indicate variation in alachlor and atrazine with time, but the degree and timing of the variation is not consistent. This inconsistency is most likely caused by varying rates of transport from the land surface to wells, different rates of degradation of alachlor and atrazine in soil and ground water, the timing and area of application, and multiple source areas in and around the Independence well field. Alachlor and atrazine concentrations in the Missouri River at Hermann varied seasonally; concentrations of both increased in spring, greater concentrations continued until late summer or early fall, and lower concentrations occurred in late fall and winter. Alachlor and atrazine concentrations most likely followed a similar trend in the Missouri River near the Independence well field. The lack of a similar seasonal trend similar to that of the Missouri River in the INDEP and the monitoring wells may indicate that the source of alachlor and atrazine to ground water is the land surface rather than the Missouri River.

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