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Effects of Farming Systems on Ground-Water Quality at the Management Systems Evaluation Area Near Princeton, Minnesota, 1991-95

Water-Resources Investigations Report 98-4128

U.S. Department of the Interior
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By M.K. Landon, G.N. Delin, J.A. Lamb[1], J.L. Anderson[1], and R.H. Dowdy[2]

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Water-Resources Investigations Report 98-4128

Contents

Figures

Figures--continued

Tables

Conversion Factors and Abbreviations

Multiply	By	To obtain
centimeters (cm)	0.3937	inches
centimeter per second (cm/s)	.03281	foot per second
centimeter per day (cm/d)	.03281	foot per day
centimeter per year (cm/yr)	.03281	foot per year
meter (m)	3.281	foot
kilometer (km)	.6215	mile
hectare (ha)	2.471	acres
square kilometer (km^2)	.3861	square mile
liter (L)	.2642	gallon
cubic meter (m^3)	35.31	cubic foot
kilograms per cubic meter (kg/m^3)	.06243	pounds per cubic foot
kilograms per hectare (kg/ha)	.8924	pounds per acre
degrees Celsius (°C)	1.8(°C)+32	degrees Fahrenheit

Chemical concentrations are given in metric units. Chemical concentrations of substances in water are given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as mass (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

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.

Abbreviations used in this report:

Atrazine plus metabolites—Sum of atrazine plus atrazine-metabolites DEA and DIA

D^2R—The ratio of DIA to DEA

DAR—The ratio of DEA to atrazine

DEA—De-ethylatrazine

DIA—De-isopropylatrazine

DO—Dissolved oxygen

MCL—Maximum contaminant level

MPORT—Multiport well

Nitrate-N—Nitrate nitrogen

TOC—Total organic carbon

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By M.K. Landon, G.N. Delin, J.A. Lamb[1], J.L. Anderson[1], and R.H. Dowdy[2]

Abstract

Ground-water quality in an unconfined sand and gravel aquifer was monitored during 1991-95 at the Minnesota Management Systems Evaluation Area (MSEA) near Princeton, Minnesota. The objectives of the study were to:

(1) describe the effects of three farming systems on ground-water quality, and

(2) evaluate the factors affecting ground-water quality and transport of agricultural chemicals at the site.

Concentrations of nitrate nitrogen (nitrate-N) in the upper 1 meter (m) of the saturated zone were greatest beneath the two cropped areas having a potato-sweet corn annual rotation (median concentrations of 23 and 22 mg/L). Concentrations of nitrate-N were least beneath a cropped area having a field corn-soybean annual rotation (median of 14 mg/L); another cropped area having the field corn-soybean rotation had similar nitrate-N concentrations to those beneath a cropped area having field corn in consecutive years (continuous corn)(medians of 17 mg/L).

Concentrations of atrazine plus metabolites de-ethylatrazine (DEA) and de-isopropylatrazine (DIA), atrazine plus metabolites, were significantly greater during 1994-95 than during 1992-93 beneath all cropped areas in the upper 1 m of the saturated zone. Concentrations of atrazine plus metabolites during 1994-95 were greatest beneath the continuous corn (median of 1.07 µg/L), intermediate beneath one cropped area with the potato-sweet corn rotation (median of 0.37 µg/L), and least beneath the other cropped area with the potato-sweet corn rotation, the field corn-soybean rotation, and background areas (medians ranging from 0.11 to 0.21 µg/L), for which concentrations were not significantly different. Concentrations of atrazine plus metabolites during 1992-93 were mostly similar beneath the different cropped areas and background areas. DEA was the predominant atrazine-metabolite detected in ground water; the average DEA to atrazine ratio was 8.0. The herbicides metribuzin, alachlor, and metolachlor were rarely detected in ground water at trace levels and could not be linked to the MSEA farming systems, with the exception of metribuzin detections during 1993-94 at concentrations of 0.14-1.24 µg/L beneath one cropped area where metribuzin was applied to potatoes.

Peak concentrations of chloride and bromide tracers were usually detected in the upper 2 m of the saturated zone 11 to 19 months after application. Peak concentrations of nitrate-N and atrazine plus metabolites were usually detected about 13 to 27 months and 2 years after application, respectively.

The estimated proportion of applied nitrogen that reached ground water ranged from about 13 to 50 percent with an average of 30 percent. Differences in the concentrations of nitrate-N in ground water between different cropped areas were related to varying nitrogen application rates, timing of nitrogen application, timing of recharge in relation to crop rotation, and differences in nitrogen uptake by crops. In order of importance, plant uptake and leaching to ground water likely account for most of the nitrogen applied. Denitrification likely is an important mechanism affecting nitrate-N concentrations at depths greater than 2 m below the water table.

The proportion of applied atrazine in ground water, detected as atrazine or its metabolites, ranged from 0 to about 1 percent with an average of 0.37 percent. The small proportion of applied atrazine detected in ground water indicates that atrazine was predominantly affected by processes occurring in the soil such as adsorption and degradation. Concentrations of atrazine plus metabolites were related to application rates.

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Introduction

The Management Systems Evaluation Area (MSEA) Program was part of a multi-scale, interagency initiative to evaluate the effects of agricultural systems on water quality in the Midwest corn belt. Five primary MSEAs were selected to represent a variety of hydrogeologic settings and the geographic diversity of prevailing farming practices in the region (Delin and others, 1992).

The Minnesota MSEA was near Princeton, Minnesota, in the Anoka Sand Plain, an area of glacial outwash covering about 4,400 km^2 (Delin and others, 1992). The primary interagency research objective was to evaluate the effects of selected farming systems on ground-water quality in a sand-plain area. Research at the Minnesota MSEA was cooperatively conducted primarily by the University of Minnesota Department of Soil, Water, and Climate; the U.S. Department of Agriculture-Agricultural Research Service (USDA-ARS); and the U.S. Geological Survey (USGS). The Minnesota Pollution Control Agency (MPCA) provided assistance for water-quality monitoring. The Department of Geology and Geophysics at the University of Minnesota also assisted in the evaluation of ground-water quality.

Purpose, Scope, and Objectives

This report describes the results of ground-water-quality sampling at the Minnesota, MSEA during 1991-95. The purpose of this report is to (1) describe the effects of three farming systems on ground-water quality, and (2) evaluate the factors affecting the ground-water quality and transport of agricultural chemicals at the site.

The report emphasizes constituents in ground water, such as chloride, nitrate nitrogen, sulfate, and selected herbicides and herbicide metabolites, that were directly related to chemical application on cropped areas. Concentrations of other chemical constituents in ground water are only discussed in the context of being tracers or indicators of the effects of agriculture on ground-water quality or geochemical conditions.

Location and Description of Study Area

The 65 hectare (ha) research area is located about 5 km southwest of Princeton, Minnesota, (fig. 1) and about 80 km northwest of Minneapolis and St. Paul. Topographic relief at the research area is less than 3 m over a horizontal distance of about 40 m (Delin and others, 1994a). The principal soil series is a Zimmerman fine sand, which is classified as a mixed, frigid, Argic Udipsamments. Greater than 92 percent (by weight) of the soil is composed of sand-sized particles at all depths in the upper 150 cm. The organic-carbon content of the soil is about 0.5 percent in the upper 35 cm and decreases to 0.1 percent below 150 cm. The surficial aquifer consists of an unsaturated zone of fine- to medium-grained sand and a saturated zone of medium- to coarse-grained sand to fine gravel. The unsaturated and saturated zones contain discontinuous layers of silt and very fine-grained sand up to 20 cm thick. Discontinuous layers cemented with iron oxides are present in the unsaturated zone between the 1- and 2-m depths in certain upland areas. The layers are 2- to 20-cm thick and contain an average of about 5 to 10 percent silt and clay compared to less than about 5 percent in adjacent horizons (Tomer and Anderson, 1995). A clayey till underlies the surficial sand and gravel aquifer; the till is less permeable than the sand. Geologic logs for the site are given in Delin and others (1994b), and Landon and others (1997).

During 1992, the average depth to the water table was about 3.3 m below land surface, and the saturated thickness ranged from 4 to 16 m across the study area. The average horizontal hydraulic conductivity is about 0.04 cm/s. Based on this hydraulic conductivity and horizontal hydraulic gradients of 0.0009 to 0.002, ground water generally moved from west to east (fig. 1) at a rate of 5-18 cm/d. Recharge ranged from 10 to 25 cm/yr during the study. Recharge water displaced older water in the surficial aquifer downward and laterally towards the discharge area along Battle Brook on the north edge of the research area or to the east. The measured vertical hydraulic gradient was less than 0.002. Most of the approximately 77.8 cm of mean annual precipitation (U.S. Department of Commerce, 1961-92) is rainfall during May through September. Annual precipitation amounts were 92 cm in 1991, 52 cm in 1992, 77 cm in 1993, 66 cm in 1994, and 70 cm in 1995 (Landon and others, 1997). The total amounts of irrigation water applied to the cropped areas during 1992-94 were 31 cm on A, 39 cm on B, 25 cm on C, 26 cm on D, and 40 cm on E (Landon and others, 1997). The differences in the amounts of irrigation water applied to each cropped area were small in the context of the overall water balance. Mean potential evapotranspiration calculated by the Thornthwaite method is about 61 cm per year (Baker and others, 1979, p. 8).

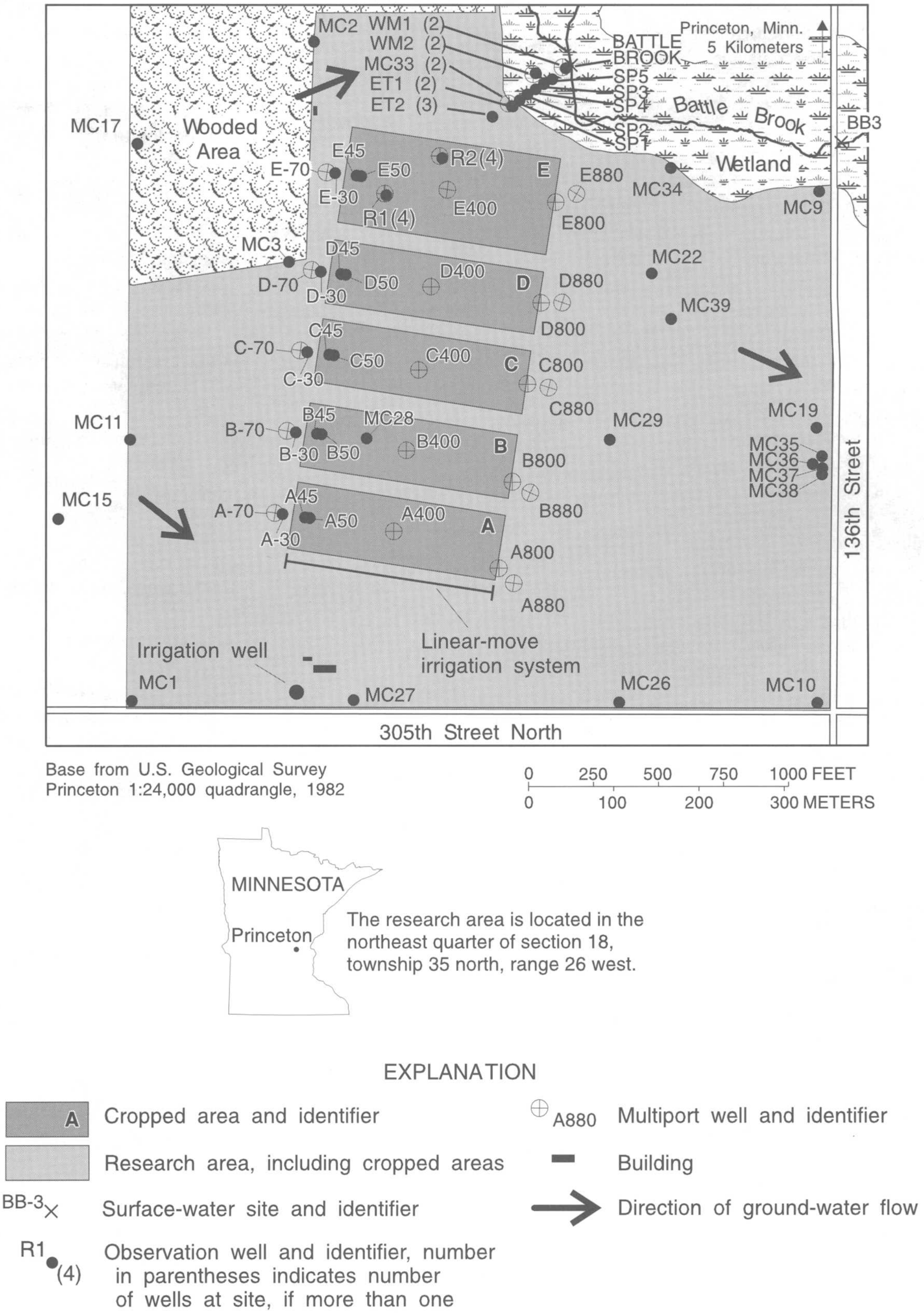
Acknowledgments

We are grateful to the many employees of the Minnesota Pollution Control Agency; U.S. Department of Agriculture-Agricultural Research Service; Department of Soil, Water, and Climate at the University of Minnesota; and the USGS who contributed to the data collection. We particularly thank Chuck Regan and Joe Magner (Minnesota Pollution Control Agency), Kurt Ault (U.S. Department of Agriculture-Agricultural Research Service), Dave Onken (Univ. of Minnesota), and Dan Rosemore and Wally Larson (USGS). We are also grateful to Lifeng Guo, Calvin Alexander, Scott Alexander, and Rick Knurr at the Department of Geology and Geophysics at the University of Minnesota for assistance with data collection and analysis. We also thank Berlinson and Associates for leasing the land to the University of Minnesota.

Methods of Investigation

MSEA Farming Systems

Five cropped areas (fig. 1) were established in 1991 to evaluate the effects of selected farming systems on ground-water quality (Anderson and others, 1991; Delin and others, 1994a). The 1.8- to 2.7-ha cropped areas were oriented approximately parallel to the predominant ground-water flow direction based on water-level data collected during October 1990 through March 1991. This orientation was preferred to minimize the mixing of leachates reaching the saturated zone



Base from U.S. Geological Survey
Princeton 1:24,000 quadrangle, 1982

Figure 1. Layout of the research area at the Princeton, Minnesota, Management Systems evaluation area

from the different farming systems being evaluated. Subsequent monthly water-level measurements during 1991-95 indicated that the cropped areas were correctly aligned with the predominant long-term ground-water flow direction.

The cropped areas were used to evaluate three cropping systems (Anderson and others, 1991): (1) a field corn (*Zea Mays L.*)-soybean (*Glycine max L.*), two-year rotation under ridge (conservation) tillage, split-nitrogen fertilizer application, nitrogen (N) credit for legumes, and banding of herbicides, which involves application only over the crop row (area 25.4 cm wide) rather than broadcast application over the row and furrow (91.4 cm wide) (fig. 1, areas B and D); (2) a potato (*Solanum tuberosum L.*)-sweet corn (*Zea Mays L.*), two-year rotation with conventional full-width (disk or chisel) tillage, split-N application, banding of herbicides for sweet corn, and broadcast application of herbicides for potatoes (fig. 1, areas A and C); and (3) field corn (*Zea Mays L.*) in consecutive years under conventional full-width tillage, split-N application, and broadcast application of herbicides (fig. 1, area E). Nitrogen was mainly applied in the form of urea on all of the cropped areas although lesser amounts of diammonium phosphate, ammonium sulfate, and ammonium nitrate were also sometimes applied (Landon and others, 1997). Sulfate was applied in the starter fertilizer to the corn and potato crops (Landon and others, 1997). Sulfate was mainly applied as ammonium sulfate with lesser amounts of zinc sulfate on all crops but the potatoes, where potassium magnesium sulfate was the main formulation applied with lesser amounts of ammonium and zinc sulfate (Landon and others, 1997).

A summary of crop activities, chemical, and irrigation applications to the cropped areas is given in Landon and others (1997). A buffer area around and between the cropped areas was planted with timothy and smooth brome grass in 1991 and was not treated with agricultural chemicals.

The research area was planted in alfalfa during 1981-89 and in corn during 1990, prior to the implementation of the MSEA farming systems in spring 1991. Detailed records of farming practices and chemical applications prior to 1991 were not available.

A linear-move irrigation system was used as necessary to supplement rainfall. The irrigation well was completed in a confined sand and gravel aquifer that is hydraulically separated from the surficial aquifer by a layer of clayey till (Delin and others, 1994a). Ground-water withdrawals from the irrigation well did not detectably affect water levels or ground-water flow patterns in the surficial aquifer during the study.

Water-Quality Monitoring Network

The on-site ground-water-quality monitoring network (fig. 1) consisted of 59 observation wells and 25 MPORTs. In addition, 14 observation wells were located off the 65-ha field (Delin and others, 1994a). Observation wells and MPORTs were used to measure water levels monthly and selected wells were used for determining concentrations of agricultural chemicals.

The observation wells and MPORTs were installed through 10.2-cm inside diameter (i.d.) hollow-stem augers. The augers were then removed and the natural formation was allowed to collapse around the well or MPORT.

Observation wells were constructed of 5.1-cm i.d. galvanized-steel or polyvinyl chloride (PVC) casing with 0.6-m to 1.5-m-long screens located at the water table or 0.15-m-long screens installed deeper in the aquifer. The MPORT wells were located 21 m upgradient (-70-series MPORTs), in the middle (400-series MPORTs), at the downgradient edge (800-series MPORTs), and 25 m downgradient of each cropped area (880-series MPORTs) (fig. 1). Each MPORT well consisted of six, 0.6-cm i.d. stainless-steel tubes (ports 1 through 6) housed in a 5.1-cm i.d. PVC casing; each tube had a 3-cm-long screened interval (port) external to the PVC casing (Delin and Landon, 1996b). In the upper 2-m of the saturated zone, the sampling ports were installed at 0.5-m intervals with the uppermost port 0.5 m above the water table to allow sample collection if the water table rose. MPORTs were also installed deeper in the aquifer at selected locations. These deep MPORTs (ports 7 through 11) were constructed similarly to the shallow MPORTs except that the interval between each sampling port varied from 1 to 2 m. Delin and others (1994a) provides a more detailed description of the ground-water-quality monitoring network; location and construction data for all wells are given in Landon and others (1997).

Recharge to the surficial aquifer was estimated by a method of hydrograph analysis described by Rasmussen and Andreason (1959). Estimates of annual recharge were determined for 28 locations in the research area for 1992-95, years for which complete sets of monthly water-level measurements were available (Landon and others, 1997). A more detailed description of the method and results are provided by Delin and others (1994a).

To compare ground-water quality between areas unaffected by the MSEA farming systems (background areas) and areas affected by the MSEA farming systems (cropped areas), observation and MPORT wells were classified with respect to land use or geographic setting. Only water-quality data from the upper 0.5 to 1.0 m of the saturated zone were used for classification purposes because they provided the most accurate characterization of the effects of the overlying land use on ground-water quality. These data included samples from observation wells screened at the water table and samples collected from ports 2 and 3 in MPORT wells. The depth below water table at which samples were collected fluctuated over time because of water-table fluctuations. Over the length of the study, the average depths below the water table were 0.1 m for port 2 and 0.6 m for port 3.

Wells within or near the research area, but not within the cropped areas, were classified based on land use and geographic setting as follows (fig. 1): (1) background setting: three MPORTs (A-70, B-70, and C-70) and ten observation wells (A-30, B-30, C-30, MC10, MC19, MC22, MC26, MC27, MC29, and MC39) affected by pre-MSEA land use but unaffected by MSEA farming systems, and (2) woodland setting: three observation wells (MC2, MC3, and MC15) located on the downgradient edge of wooded areas. The classification of these wells according to land use was based upon evaluation of the ground-water flow directions and rates (Delin and others, 1994a) and was consistent with measured differences in water-quality characteristics (Delin and others, 1995; Landon and others, 1996). Wells in areas influenced by more than one land use were excluded from this comparative analysis. For instance, wells D-30, D-70, E-30, and E-70 had anomalous concentrations of agricultural chemicals for background wells because they were located a short distance downgradient from the wooded area (fig. 1).

Ground-water quality in background areas changed during 1991-95 in response to the change from cultivated cropland to grassland. Thus, results from background areas were classified according to the year of sample collection. Water-quality data from 1992-95 were used to describe ground-water quality beneath the cropped areas. Data from 1991 were not used because they reflected the effects of pre-MSEA land use (Delin and others, 1995; Landon and others, 1996).

The 400- and 800-series MPORTs were the primary wells used to characterize the effects of cropped areas on ground-water quality because they were in the middle and downgradient edge of the cropped areas and were only influenced by land use on that cropped area. Data from the 50-series observation wells, located 15 m into the cropped areas from the upgradient edge, with 0.9 m screens intersecting the water table, were also used (fig. 1). These wells were installed in November 1994 and were only sampled four times before the end of data collection in August 1995. Because multiple wells were used for characterizing the water quality beneath each cropped area, the sampling results did not reflect anomalous contamination of a single well. Data from the 45-series observations wells, 1.5 m from the 50-series wells, were not included because these wells were screened approximately 2 m into the saturated zone and were primarily influenced by land use upgradient of the cropped areas. Data from observation well MC28, with a 0.6 m screen bisecting the water table, were also used to characterize the effects of cropped area B (fig. 1). Data from MPORTs R1 and R2 for 1992 and April 1993 were included with data from E400 and E800 to characterize the effects of cropped area E on water quality. After April 1993, data from R1 and R2 were not used because they were affected by tracer experiments (Delin and others, 1997). The 880-series MPORTs, 25 m downgradient (east) of the cropped areas, were not used for characterizing water quality related to the farming systems because the water quality in these wells was influenced by the grassland between the wells and the cropped areas (fig. 1).

Water-Quality Sampling Protocols and Procedures

Water samples were collected from all MPORTs and selected on-site observation wells four times per year (fig. 1). These samples were collected during April, before agricultural chemicals were applied, in June and August during the growing season, and in October-December after crops were harvested (Delin and others, 1994a). Water samples were collected more frequently from selected wells. Selected off-site observation wells were sampled at least once a year.

Sample-collection and laboratory-analysis quality-assurance/quality-control (QA/QC) protocols were followed and are described in detail by Delin and others (1994a) and Larson and others (1996). The QC results, discussed by Landon and others (1997) indicated that the water-quality data were of sufficient quality to fulfill the study objectives.

Chloride from potassium chloride fertilizer and bromide applied as an artificial (not part of the farming systems) tracer were used to identify ground water affected by MSEA chemical applications and to link concentrations of nitrate-N, sulfate, and herbicides to applications during particular years. Both chloride and bromide are generally considered to behave conservatively in water, that is, movement of these solutes is not retarded relative to movement of water by reactions or interaction with aquifer sediments. Because chloride was only applied to cropped areas, it was a tracer of ground-water affected by chemical application to the overlying cropped area (Delin and others, 1995; Landon and others, 1996). Chloride was useful as a tracer for those years and cropped areas where potassium chloride applications substantially exceeded applications during previous or subsequent years. The annually variable application rates of chloride on most cropped areas due to crop rotations made it possible to clearly relate changes in chloride concentrations to specific applications. Potassium bromide was applied on May 26, 1992, at a rate of 22 kg/ha, and on May 6, 1994, at a rate of 34 kg/ha to the eastern end of areas B, D, and E (Delin and others, 1995) (fig. 1). Potassium bromide was also applied to a 24- by 15-m area upgradient of the MPORT in the middle of these cropped areas. Potassium bromide was not applied to areas A and C as a precautionary measure to avoid possible human health risks of consuming sweet corn and potatoes containing trace levels of bromide.

Comparisons of changes in concentrations with application timing were used to estimate travel times of chemicals to the water table. Although data from sample collections four times a year cannot be used to precisely measure these travel times, the values could be constrained to within 2 months in best cases and 6 months in worst cases.

Mass Balance of Agricultural Chemicals

Mass-balance calculations were made for chloride, nitrogen, sulfur, bromide, atrazine plus metabolites, and metribuzin. The mass of a chemical detected in ground water was expressed as a percentage of the amount of chemical in the application. The masses of these chemicals in ground water derived from the MSEA farming systems were estimated during each year of the study by comparing concentrations beneath the cropped areas to those at similar depths at the same time in upgradient background areas. The concentrations beneath a cropped area that exceeded concentrations beneath the upgradient background area were interpreted to have recharged from the overlying cropped area and are herein called "excess concentrations" (Delin and others, 1995). Excess concentrations for each depth increment in the saturated zone were multiplied by the estimated water volume in that depth increment to determine the excess mass. The total excess mass of chemical in the saturated zone, which is attributed to the MSEA farming systems, equaled the sum of the excess masses in each depth increment.

Background concentrations were calculated as the average of concentrations in samples from MPORTs upgradient of areas A, B, and C (MPORTS A-70, B-70, and C-70, fig. 1). Average concentrations were computed for each sampling period for each depth increment using data from sampling ports 2 through 6. These average upgradient background concentrations are considered representative of concentrations that would have occurred beneath the MSEA cropped areas in the absence of effects of the MSEA farming systems.

Concentrations beneath each cropped area were determined by computing the average of the concentrations at the 400 and 800 series MPORTs for a given depth below the water table (fig. 1). Computations were based on data from ports 2 through 6 in the MPORTS because (1) sampling ports screened at greater depths in the saturated zone were not present in all MPORTS, and (2) excess concentrations of chemicals attributable to MSEA farming systems were mostly detected to the depth of port 6 (generally about 2 m below the water table) but usually not at greater depths (see figs. 4-9 in Landon and others, 1997). It was assumed that contributions of constituents from soils and precipitation were the same beneath the background areas as beneath the cropped areas and that the differences in mass concentrations between background and cropped areas were the result of recharge through the overlying cropped area.

Excess mass, defined as the mass of a constituent that reached the saturated zone as a result of chemical applications to a cropped area, was estimated using the following equation:

$$M = \Sigma(V \times C) \quad \text{(per hectare)} \qquad (1)$$

where

M = mass of chemical applied that reached the saturated zone (kg),

V = volume of water in each depth increment (usually 0.5 m) of the saturated zone beneath the cropped area (m^3);

C = average concentration beneath the cropped area in excess of average background concentration at a similar depth (mg/L, with appropriate factors to convert to kg/m^3).

All masses and volumes were computed for an area of 1 ha. A porosity of 0.40 (Delin and others, 1994a) was used in estimating the volume of water in the saturated zone beneath the cropped areas. Water-table fluctuations were incorporated in estimating the volume of water represented by the uppermost sample in the saturated zone.

There were a number of cases where the mass of chemical at a particular depth was a mixture related to applications from more than one year. This mixing was evident where concentrations increased as a result of more recent applications before concentrations from applications of the previous year had declined to pre-application levels. In these cases, the declining chemical concentration for the older application was linearly extrapolated to the date for the which the mass balance calculations were being done. All increases in concentrations above this extrapolated concentration for the older application were assumed to result from the most recent application.

The mass of chemical related to application(s) on a cropped area during a particular year was estimated from the maximum mass during the period when ground water in the upper 2 m of the saturated zone was affected by chemical applications from that year. The maximum mass was assumed to be the best estimate of chemical that reached the ground water for the following reasons: (1) following recharge at the water table, ground water mostly flows horizontally from recharge to discharge areas (Delin and others, 1994a); (2) recharge of agricultural chemicals from a particular application does not occur all at once, but is distributed over time; and (3) the masses computed for different sampling periods following an application typically showed that excess mass increased following first detection to a maximum value, then decreased until the effects of the next application were detected. Additional assumptions for these calculations are described by Landon and others (1997, p. 7 and 13).

Nitrogen uptake by crops was determined by collecting samples of aboveground corn-plant (grain plus stover) and soybean (whole plant) biomass at physiological maturity. Plant samples were collected from sixty 15-by-18-m grid areas within each cropped area. Plant nitrogen concentration was measured using Kjeldahl digestion techniques at the Research Analytical Laboratory of the University of Minnesota Agricultural Experiment Station, St. Paul, Minnesota. Whole-plant nitrogen uptake was then calculated by multiplying the biomass times the nitrogen concentration. Only average values of nitrogen uptake for each cropped area and year are discussed in this report. Crop nitrogen uptake results from the Minnesota MSEA are also discussed by Lamb and others (1995a).

Statistical Analyses

Wilcoxon rank-sum tests were used to determine if differences in chemical concentrations between land-use areas were statistically significant. The attained significance level (p-value) was compared to a predetermined significance level (α = 0.01) to determine when a difference was significant. All statistical test results are for two-sided tests unless otherwise noted. The p-value is the probability of obtaining the computed test statistic when the null hypothesis (no concentration difference between land-use areas) is true. The smaller the p-value, the less likely is the observed test statistic when the null hypothesis is true (Helsel and Hirsch, 1992). If the p-value was less than 0.01, the null hypothesis was rejected and the concentration differences between land-use areas were considered significant. All statistics were determined using SAS statistical software (SAS Institute Inc., 1989).

Effects of Farming Systems on Ground-Water Quality

Effects of the three farming systems evaluated at the Minnesota MSEA during 1991-95 are described in this section of the report. A statistical summary of selected chemical constituent concentrations during 1992-95 are presented in box plots for the cropped areas and the background areas (figs. 2 and 3). Table A (Appendix A at the back of the report) presents the statistical distribution of herbicide detections for the cropped areas and the background areas during 1991-95. The mass of selected chemicals in ground water derived from the MSEA farming systems are estimated (tables B1-B6, Appendix B at the back of the report). Figures 4a-f illustrate graphically how selected chemical concentrations beneath the cropped areas changed during the study in comparison to background concentrations. The times required for the selected chemical constituents to move through the unsaturated zone and be detected in ground water (travel times) are described. Vertical changes in ground-water quality beneath the cropped areas, a key indicator of the effects of the MSEA farming system, are presented.

Water Quality Beneath Background Areas

Background concentrations of nitrate-N in the upper 1 m of the saturated zone changed substantially during 1992-95. The median concentration of nitrate-N in background areas decreased from 16 mg/L during 1992, to 12 mg/L during 1993, to 2.6 mg/L during 1994-95 (fig. 2), which approaches the median concentration in woodland wells of 1.1 mg/L. This trend in background nitrate-N concentrations indicates that residual nitrate-N from pre-MSEA farming with alfalfa during 1981-89 and corn during 1990 moved out of the unsaturated zone in less than 5 years. Delin and others (1994a) discussed evidence indicating the primary source of the background nitrate-N concentrations was previous farming on the research area, rather than off-site sources.

Beneath background areas, there were widespread detections of atrazine plus metabolites in the upper 1 m of the saturated zone. The median concentration of atrazine plus metabolites in background areas decreased from 0.20 µg/L during 1991, to 0.10-0.12 µg/L during 1992-95 (table A, Appendix A at the back of the report). Atrazine, DEA, and DIA were detected in about 71, 72, and 23 percent, respectively, of the samples collected from background areas during 1991-95. DEA was the most frequently detected herbicide compound which was also present in the greatest concentrations with a median of 0.12 µg/L in 1991, and 0.06-0.09 µg/L during 1992-95 (table A, Appendix A at the back of the report). The median DAR was 1.9 in 1991, 5.5 in 1992, 7.0 in 1993, and 3.2 in 1994-95.

In woodland wells, atrazine, DEA, and DIA were detected in 34, 26, and 6 percent, respectively, of the samples (table A, Appendix A at the back of the report). Because atrazine was not applied, herbicide concentrations at the water table beneath woodland areas must be derived from another source. The concentrations and frequencies of detection of atrazine in woodland wells were similar to those measured in equipment blank samples (table A, Appendix A at the back of the report). Therefore, the trace levels of atrazine in the woodland wells are primarily attributed to trace contamination of sampling equipment and probably do not reflect environmental concentrations. Because the concentrations and frequencies of detection of DEA and DIA were greater in woodland wells than in equipment blanks, precipitation may be a secondary source of contamination. Concentrations of DEA and DIA were not measured in precipitation. However, Goolsby and others (1997) found that DEA was present in more than one-half of precipitation samples collected from across the midwest that contained atrazine. Analysis of weekly precipitation samples during May-September of 1993 and 1994 (Lin, 1997), and 1995 (Mitton and others, 1996) indicated that atrazine was detected above 0.01 µg/L in 81 percent of the samples, with a median concentration of 0.10 µg/L and a maximum concentration of 2.08 µg/L (table A, Appendix A at the back of the report).

Delin and others (1994a) discussed evidence indicating that the primary source of the background atrazine plus metabolite concentrations was farming on the research area prior to MSEA rather than upgradient sources. The most likely source was application of atrazine to the field corn grown on the research area in 1990, mainly based upon ground-water flow and age data. Atrazine would not have been applied during 1981-89 when alfalfa was grown. Ground-water age dating using the chlorofluorocarbon technique at MPORTs E-70, R1, R2, and MC33 indicated that ground water from the upper 1 m primarily recharged in the 1990's (J.K. Böhlke, U.S. Geological Survey, written commun., 1997). These age-dating results are consistent with the detection of chloride, bromide, and nitrate-nitrogen in the upper 1 m of the saturated zone within 0.5 to 2 years of application (Delin and others, 1995; Landon and others, 1996). Detection of these chemicals in the 400-series MPORTs indicates that the water in the upper 1 m of the saturated zone recharged no more than 120 m away from the MPORT, the distance from the 400-series MPORTs to the upgradient edge of the cropped area. These results are based upon an average ground-water velocity of 28 m/yr (Delin and others, 1994a). Ground water recharged from an upgradient field is an unlikely source. Water would have been displaced vertically downward by recharge that occurred along the flow path and would likely be greater than 1 m below the water table beneath the cropped area (Delin and others, 1994a).

Decreases in concentrations of atrazine and metabolites and increases in the DAR from 1991 to 1992 are consistent with the source of the atrazine being application in 1990. However, concentrations of atrazine plus metabolites changed very little during 1992-95. These results indicate that atrazine from pre-MSEA applications in 1990 had not fully moved out of the unsaturated zone 5 years after application. Thus, atrazine and atrazine metabolites have a relatively long residence time in the sandy unsaturated zone in

Text continues on page 16

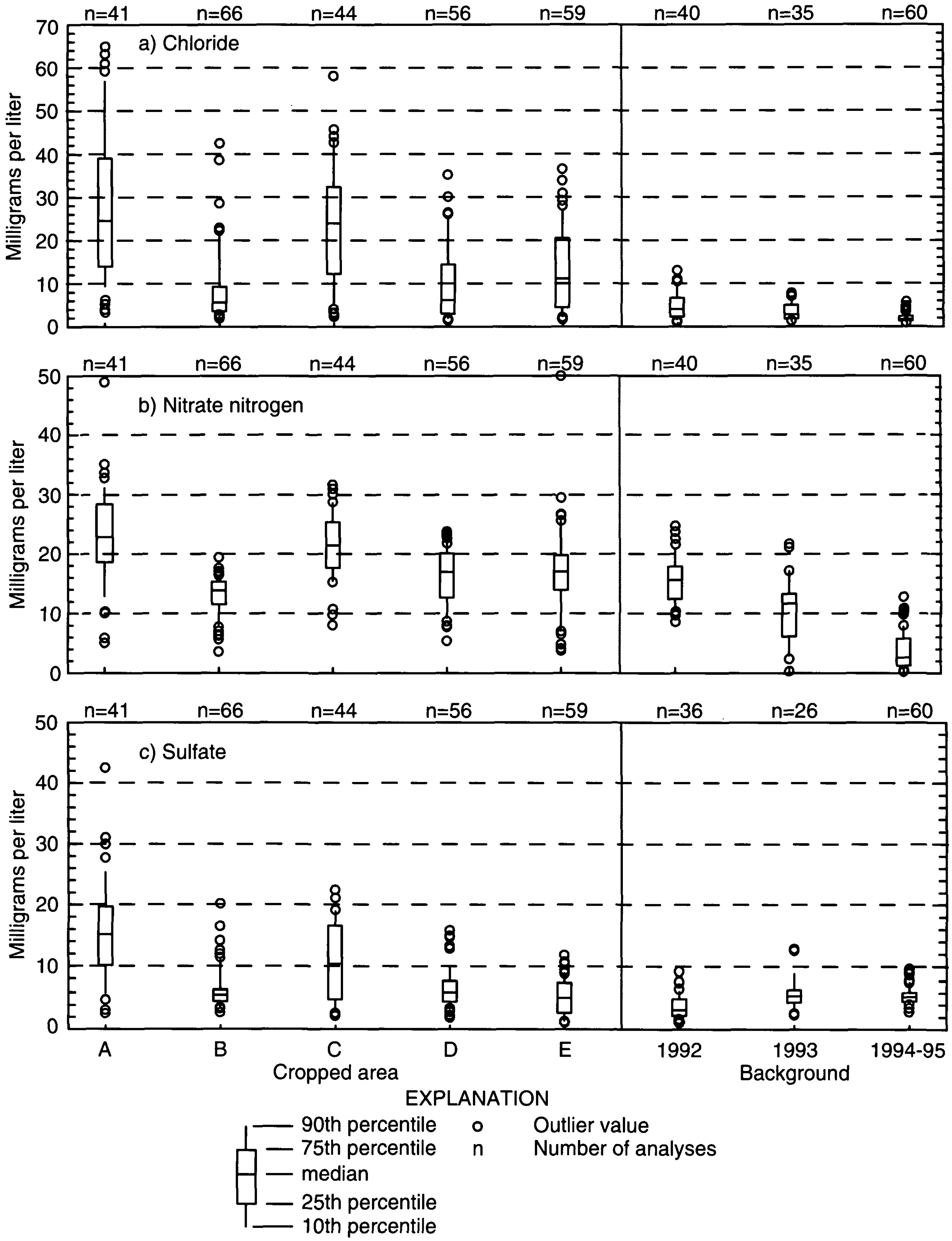


Figure 2. Statistical distribution of concentrations for chloride, nitrate nitrogen, and sulfate from the upper 1 meter of the saturated zone beneath each cropped area during 1992-95 and beneath background areas during 1992, 1993, 1994-95.

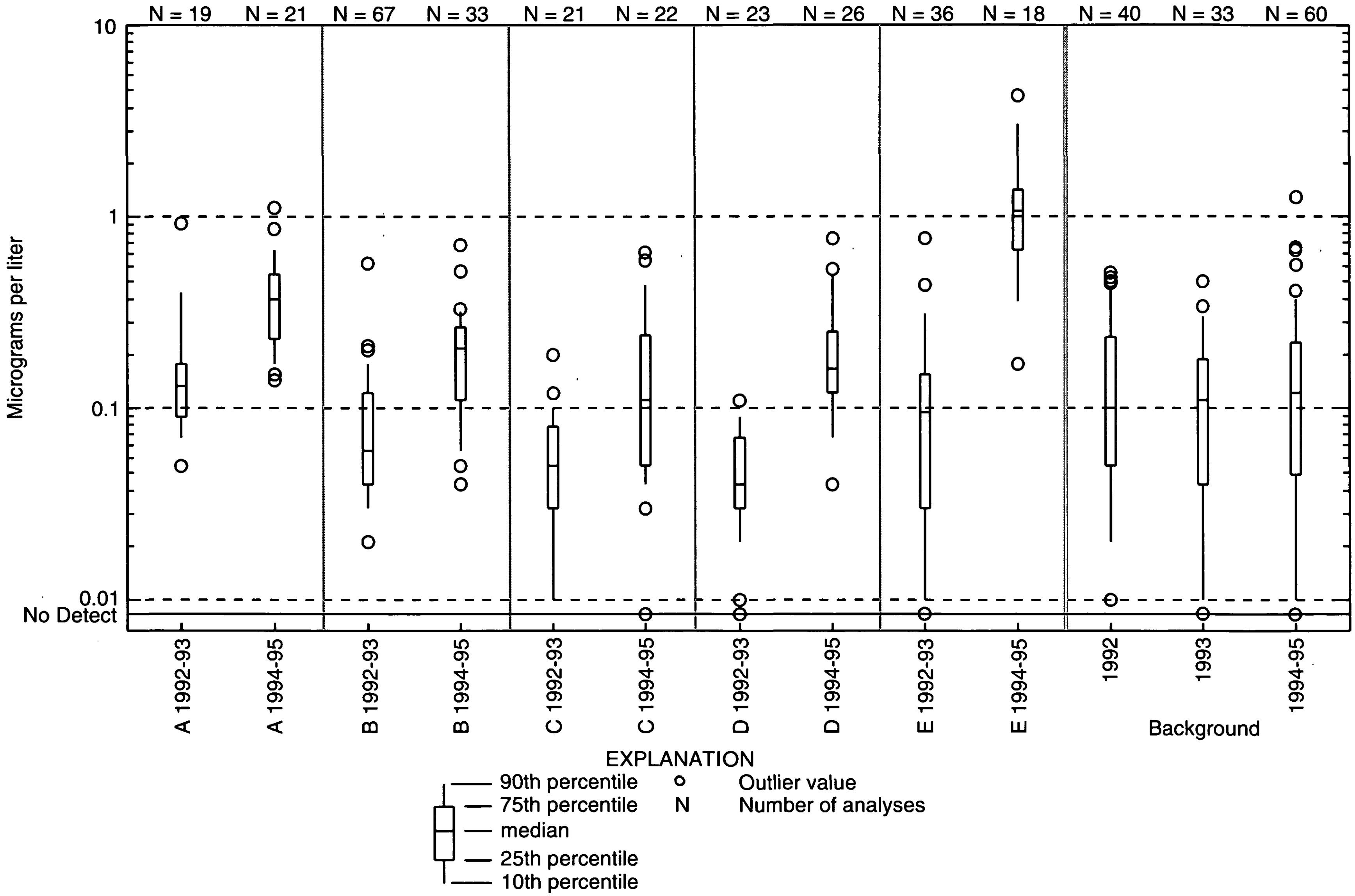


Figure 3. Distribution of concentrations of sum of atrazine plus metabolites de-ethylatrazine and de-isopropylatrazine from the upper 1 meter of the saturated zone beneath each cropped area during 1992-93 and 1994-95, and beneath background areas in 1992, 1993, and 1994-95.

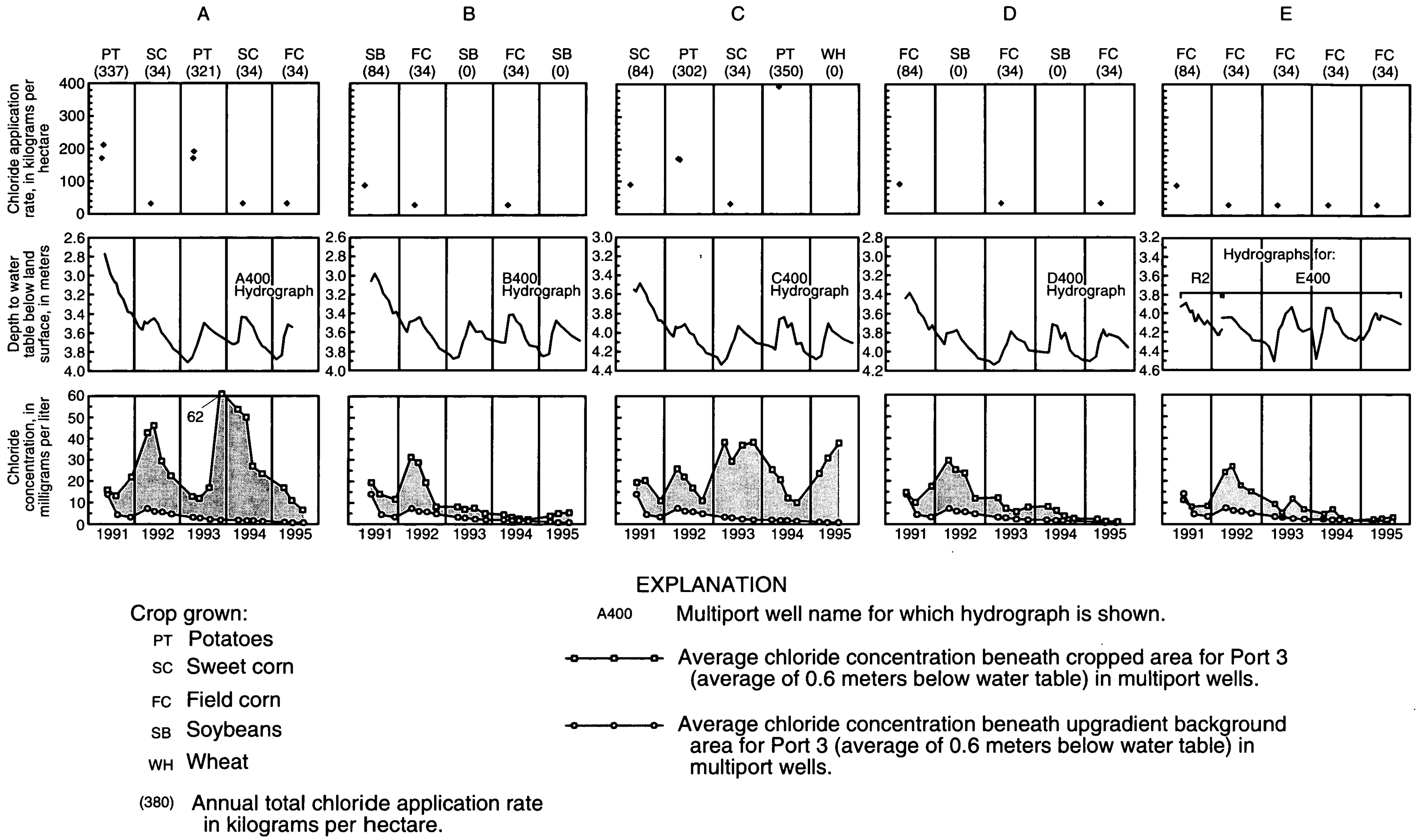
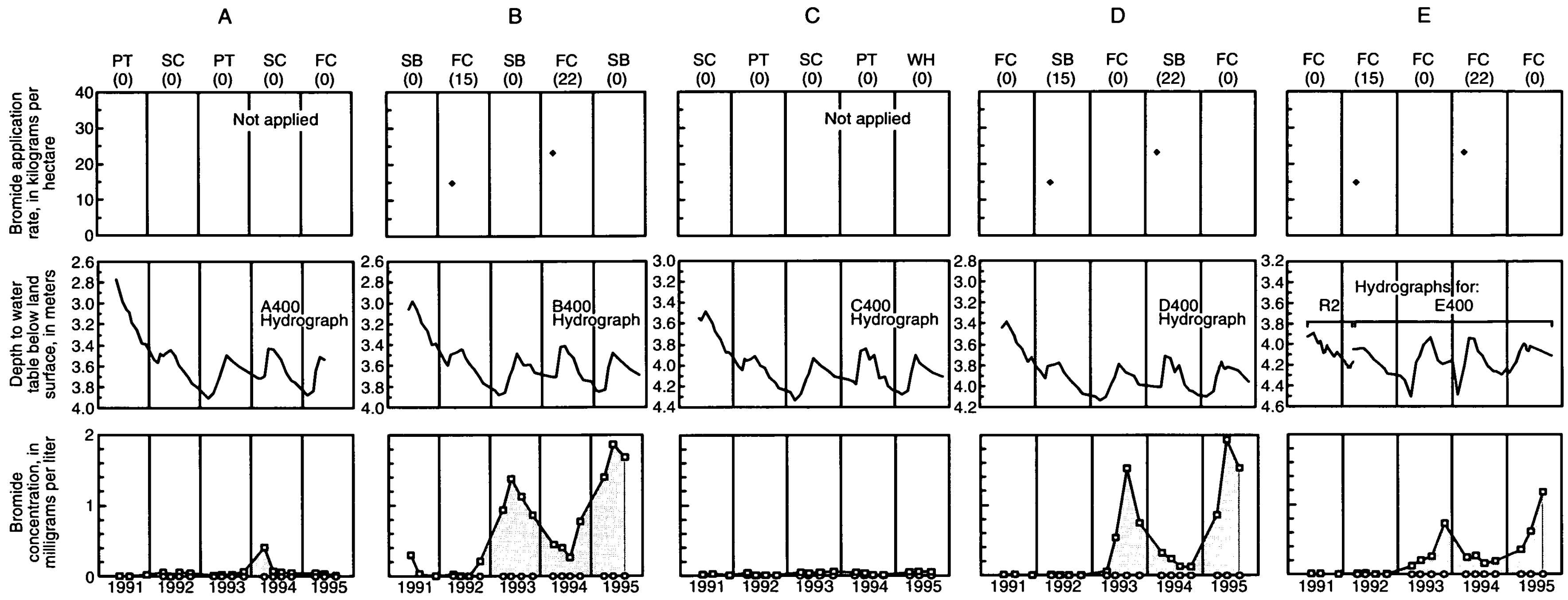


Figure 4a. Application rates, water-table hydrographs, and average concentrations beneath each cropped area compared to average background concentrations during June 1991-August 1995, for chloride.



EXPLANATION

Crop grown:
PT Potatoes
SC Sweet corn
FC Field corn
SB Soybeans
WH Wheat

(0) Annual total bromide application rate in kilograms per hectare.

A400 Multiport well name for which hydrograph is shown.

-□-□-□- Average bromide concentration beneath cropped area for Port 3 (average of 0.6 meters below water table) in multiport wells.

-○-○-○- Average bromide concentration beneath upgradient background area for Port 3 (average of 0.6 meters below water table) in multiport wells.

Figure 4b. Application rates, water-table hydrographs, and average concentrations beneath each cropped area compared to average background concentrations during June 1991-August 1995, for bromide.

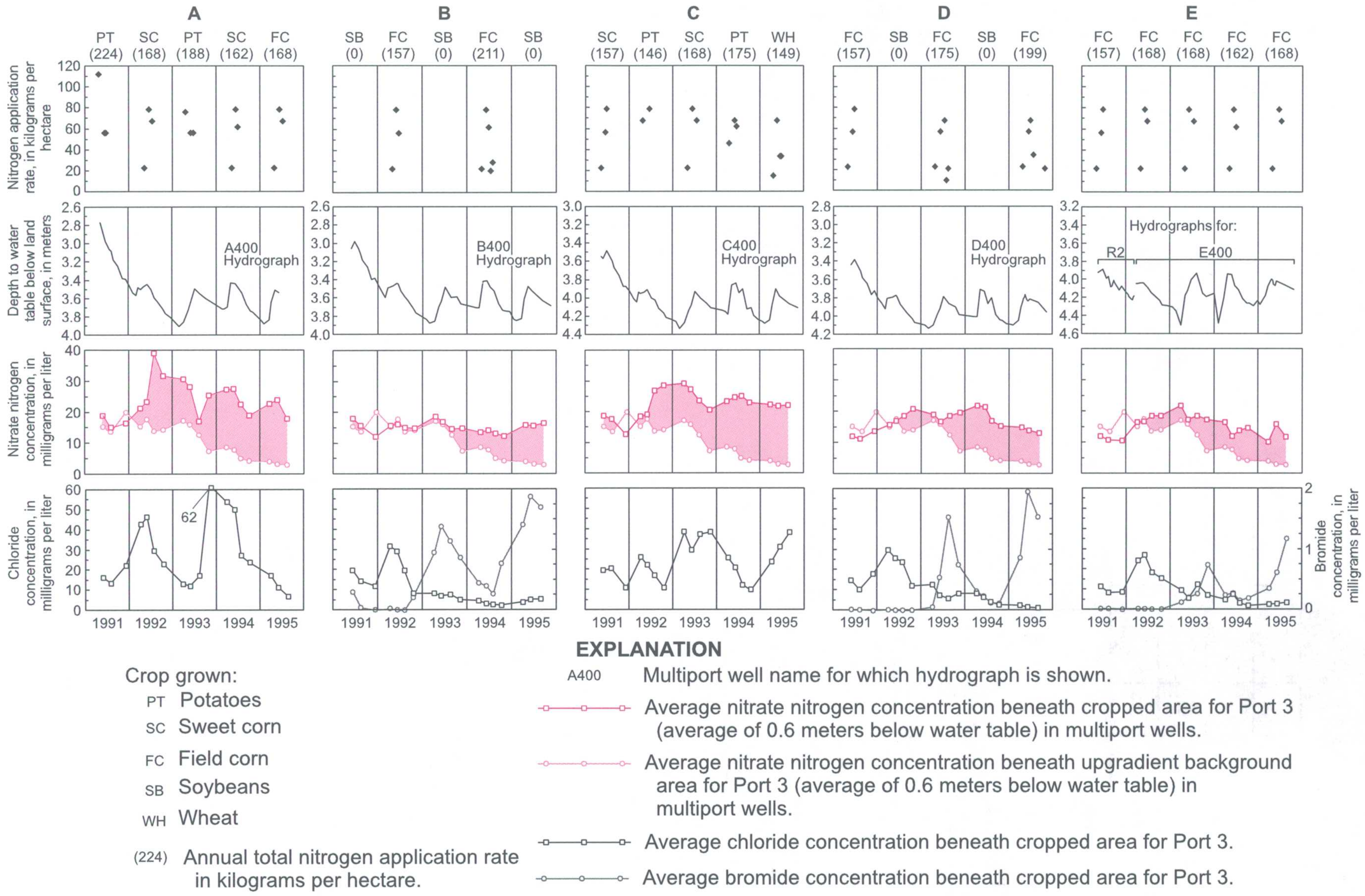


Figure 4c. Application rates, water-table hydrographs, and average concentrations beneath each cropped area compared to average background concentrations during June 1991-August 1995, for nitrate nitrogen.

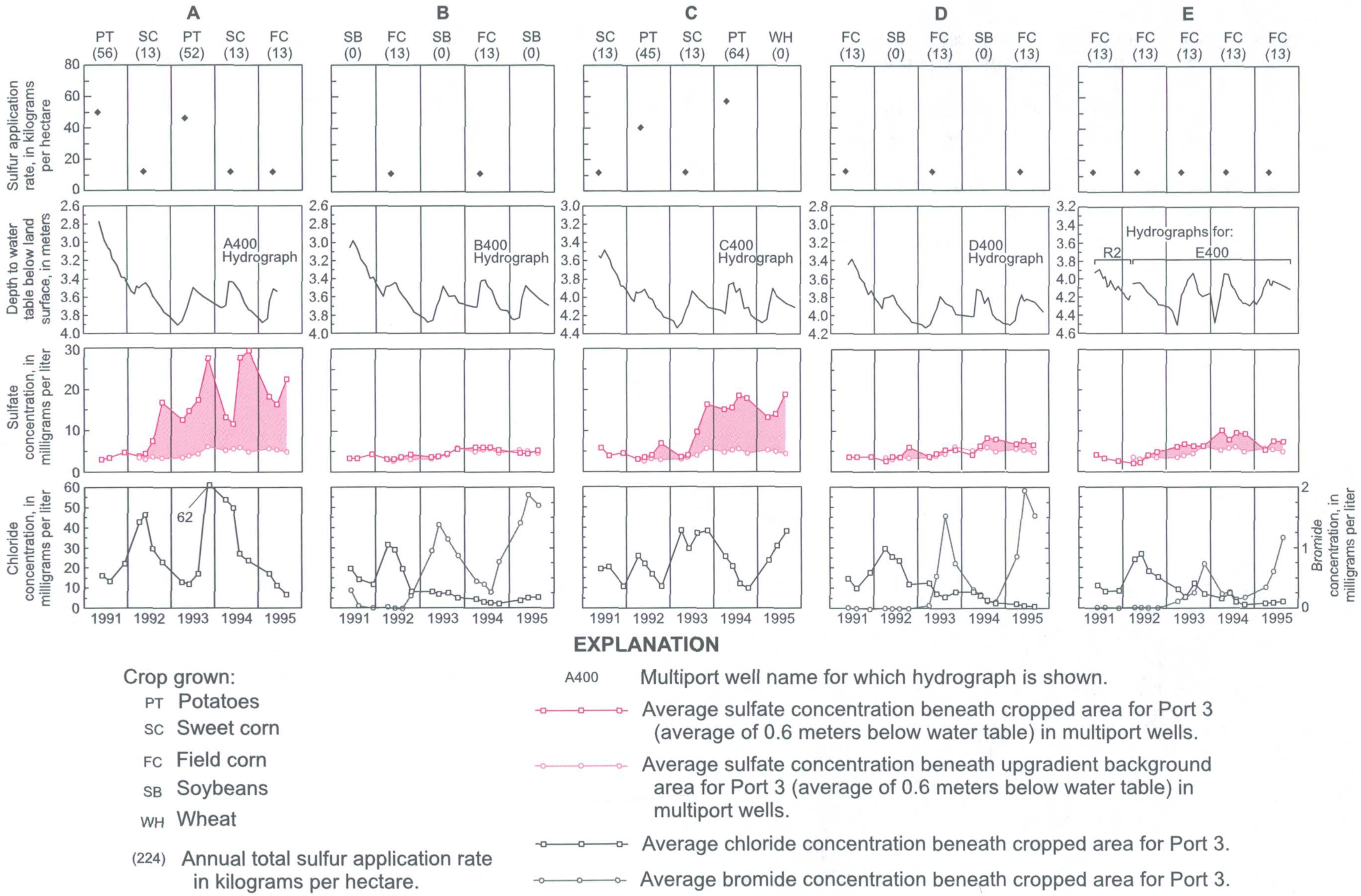
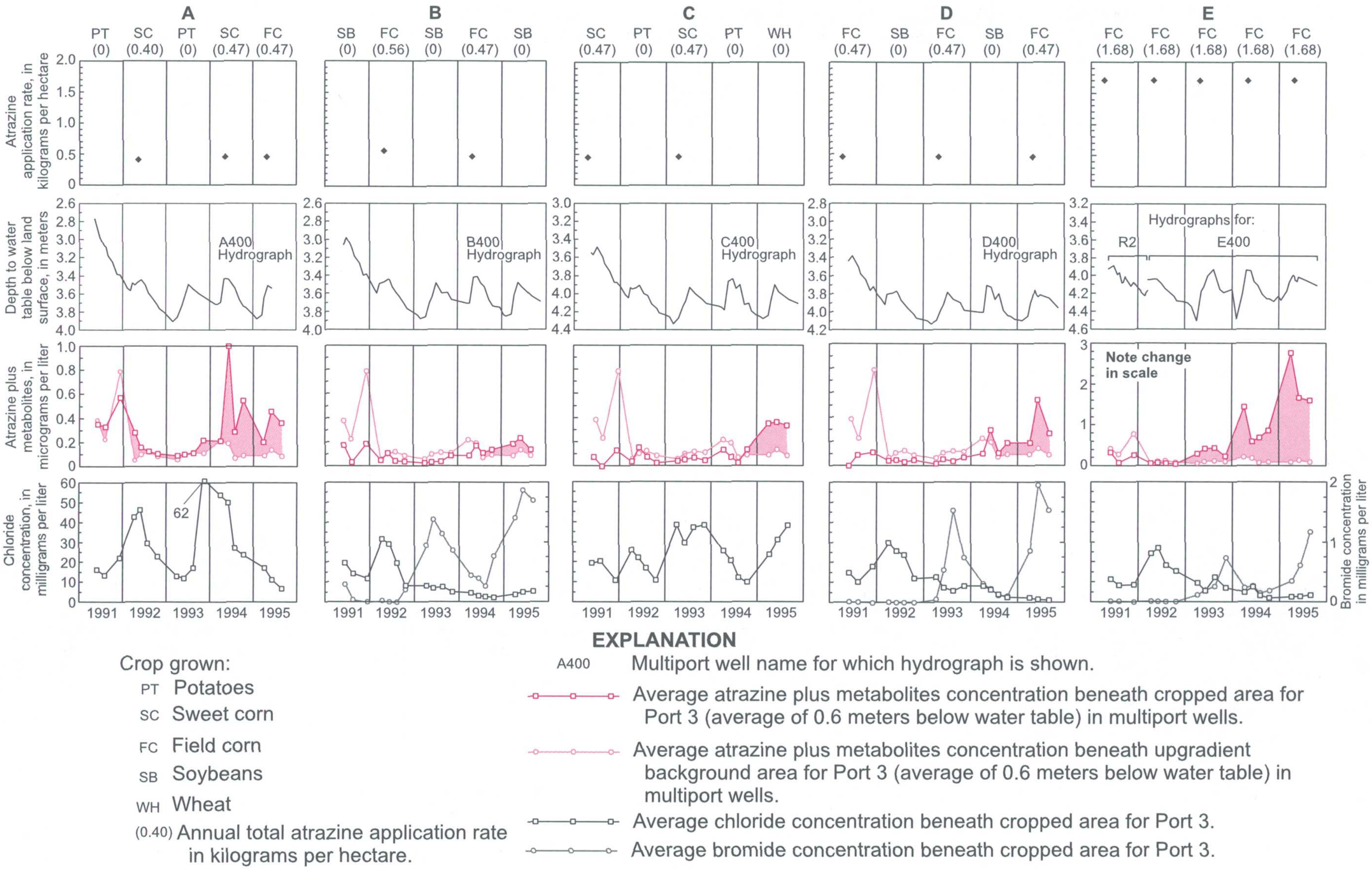


Figure 4d. Application rates, water-table hydrographs, and average concentrations beneath each cropped area compared to average background concentrations during June 1991-August 1995 for sulfate.



EXPLANATION

Crop grown:
- PT Potatoes
- SC Sweet corn
- FC Field corn
- SB Soybeans
- WH Wheat

(0.40) Annual total atrazine application rate in kilograms per hectare.

A400 Multiport well name for which hydrograph is shown.

Average atrazine plus metabolites concentration beneath cropped area for Port 3 (average of 0.6 meters below water table) in multiport wells.

Average atrazine plus metabolites concentration beneath upgradient background area for Port 3 (average of 0.6 meters below water table) in multiport wells.

Average chloride concentration beneath cropped area for Port 3.

Average bromide concentration beneath cropped area for Port 3.

Figure 4e. Application rates, water-table hydrographs, and average concentrations beneath each cropped area compared to average background concentrations during June 1991- August 1995, for atrazine plus atrazine metabolites de-ethylatrazine and de-isopropylatrazine.

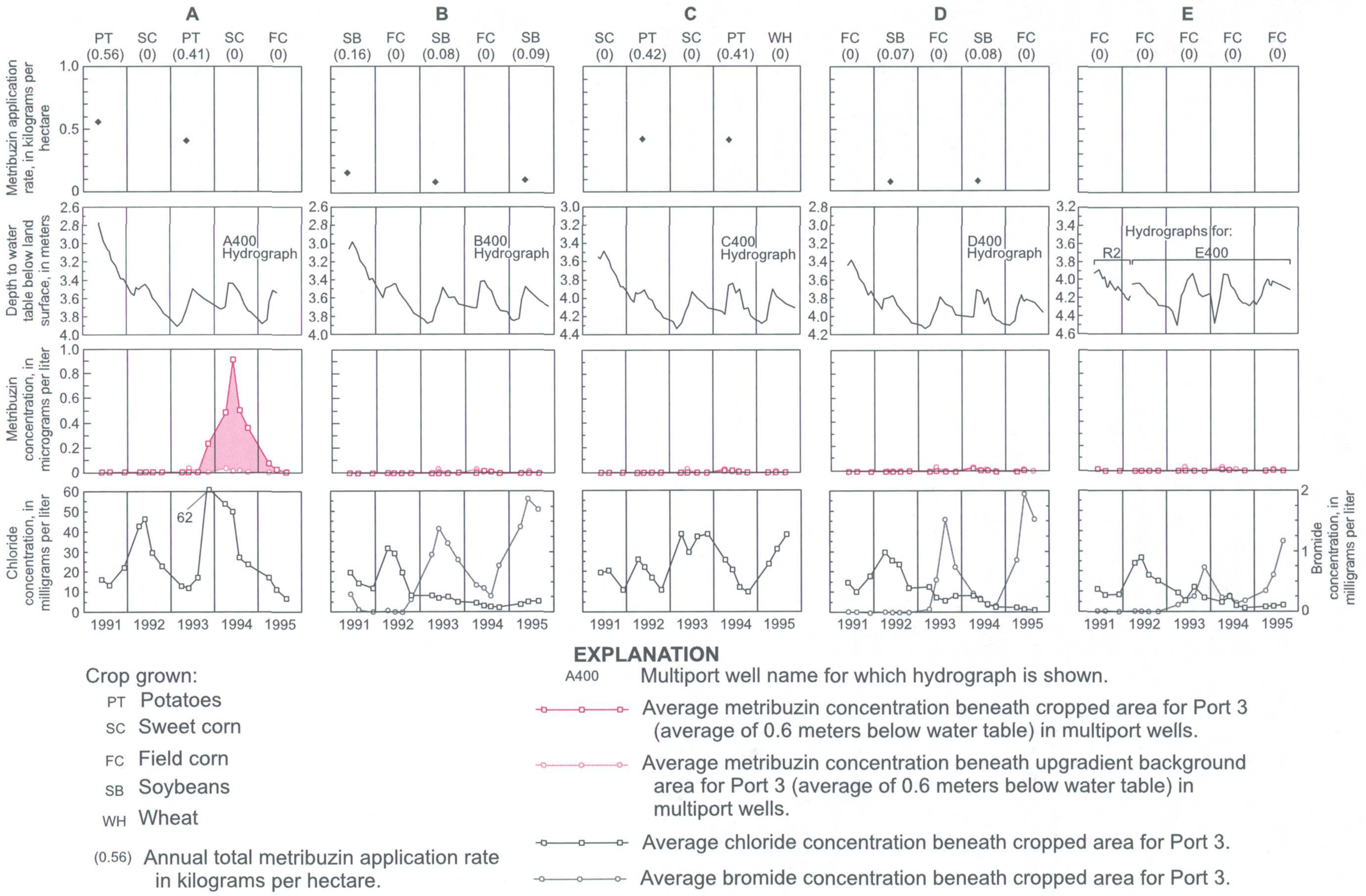


Figure 4f. Application rates, water-table hydrographs, and average concentrations beneath each cropped area compared to average background concentrations during June 1991-August 1995 for metribuzin.

sufficient quantities to add about 0.10 µg/L of atrazine plus metabolites to the underlying ground water.

Precipitation is likely a minor source of atrazine plus atrazine metabolites, as indicated by the trace detections in woodland wells where precipitation is the only plausible source. Because concentrations of atrazine plus metabolites in woodland wells were much less than concentrations in background areas (table A, Appendix A at the back of the report), precipitation was probably a minor source compared to atrazine application on the research area in 1990. However, it is possible that differences in organic matter, soil microbial activity, and recharge rates between wooded and non-wooded background areas could result in greater amounts of atrazine plus metabolites leaching to ground water beneath background areas than beneath wooded areas. Concentrations of atrazine in precipitation were generally similar to or greater than concentrations of atrazine plus metabolites in ground water (table A, Appendix A at the back of the report). However, given the small fraction of applied atrazine that typically leaches to ground water (Wehtje and others, 1984; Hall and others, 1989, 1991; Rutledge and Helgesen, 1990; Frank and others, 1991; Dousset and others, 1995) and the much greater amount of atrazine that is applied to fields than is dissolved in precipitation, it seems unrealistic that most or all of the atrazine dissolved in precipitation would leach to ground water.

Alachlor was detected in about 13 percent of the background wells and 17 percent of the woodland wells during 1991-95 (table A, Appendix A at the back of the report). However, with the exception of two detections of alachlor in background wells in 1991 at concentrations of 0.49 and 1.08 µg/L, concentrations and frequencies of detection of alachlor in background and woodland wells were similar to those in the blanks (table A, Appendix A at the back of the report). Landon and others (1997, p. 21-23) discussed the implications of the equipment-blank data for interpretations of alachlor concentrations and increased the effective reporting limit (ERL) for alachlor from 0.04 to 0.07 µg/L to account for the fact that alachlor concentrations less than 0.07 µg/L could be artifacts of sample contamination during collection and analysis. Therefore, most of the detections of alachlor in background and woodland wells could reflect trace level contamination of sampling equipment (Landon and others, 1997). Detections greater than 0.07 µg/L likely reflect environmental sources and comprised less than 2 percent of background samples. Alachlor exceeded the laboratory reporting limit of 0.04 µg/L in 49 percent of the precipitation samples and had a maximum concentration of 1.15 µg/L (table A, Appendix A at the back of the report). Therefore, precipitation was likely the source of some alachlor in ground water. Detection of the largest concentrations of alachlor in background wells in 1991 may indicate that alachlor was applied to the research area in 1990. Alachlor metabolite 2,6-diethylanaline was detected in about 2 percent of background and woodland wells at concentrations of 0.03 µg/L or less (table A, Appendix A at the back of the report).

There were few detections of metolachlor and metribuzin in ground water in background areas (table A, Appendix A at the back of the report). Metolachlor was detected above 0.01 µg/L in 60 percent of the precipitation samples collected during May-September 1993-95 and had a maximum concentration of 0.42 µg/L (table A, Appendix A at the back of the report). Metolachlor was only detected in one ground-water sample from the background areas at a concentration of 0.01 µg/L (table A, Appendix A at the back of the report). Thus, metolachlor in precipitation did not effect metolachlor concentrations in ground water. Metribuzin was detected in about 5 percent of the samples in background areas and 6 percent of samples in woodland wells. Metribuzin was detected above 0.01 µg/L in 30 percent of the precipitation samples (collected during May-September 1993-95) and had a maximum concentration of 0.10 µg/L (table A, Appendix A at the back of the report). These concentrations are in the same range as those found in the background area and woodland wells. This result suggests that precipitation is the primary source of the minor detections of metribuzin in shallow ground water in background areas.

Water Quality Beneath Farming Systems Cropped Areas

Concentrations of chloride were significantly greater beneath most cropped areas than background areas (figs. 2a and 4a, table 1) as a result of application of potassium chloride fertilizer. The greatest chloride concentrations occurred beneath areas A and C, having the potato-sweet corn farming system, which had median concentrations of 24 and 23 mg/L, respectively (fig. 2a). Four to ten times more potassium chloride fertilizer was applied to the potatoes than to other crops (fig. 4a) (Landon and others, 1997). Background concentrations of chloride declined from a median of 8 mg/L in 1991 to a median of 0.65 mg/L in 1994-95, as the effects of pre-MSEA applications of potassium chloride fertilizer decreased. The potassium chloride detected in 1991 was most likely applied to field corn grown in 1990 or to the alfalfa grown in 1981-89.

Chloride concentrations beneath the cropped areas were generally greatest following the greatest potassium chloride applications (fig. 4a). Chloride application rates of greater than about 80 kg/ha increased chloride concentrations substantially over background concentrations (fig. 4a). Chloride was applied at a rate of 34 kg/ha on several cropped areas (fig. 4a), resulting in concentrations only slightly in excess of background (fig. 4a, fields B, D, and E, 1993-95).

Because background bromide concentrations were at or below the detection limit of 0.01 mg/L, bromide in ground water as a result of applications of potassium bromide on the cropped areas was easily distinguished (fig. 4b). The small bromide peak in 1994 detected beneath area A (fig. 4b) was likely from potassium chloride fertilizer.

Measured concentrations of nitrate-N were greatest beneath areas A and C, having the potato-sweet corn rotation, *with* median concentrations of 23 and 22 mg/L, respectively (fig. 2b). The differences in concentrations between the potato-sweet corn cropped areas (A and C) and the other cropped areas were significant

Table 1. Results of statistical testing for significance of differences in concentrations of chloride, nitrate nitrogen, and sulfate between cropped and background areas

[Attained significance level (p-value) for two-sided Wilcoxon rank-sum tests are shown (for one-sided test, p/2). Significance criteria: p<p=0.01 (two-sided) (**bold indicates statistically significant difference**)]

Chloride

	Cropped area				Background		
	B	C	D	E	1992	1993	1994-95
A	**0.0001**	0.5352	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**
B		**0.0001**	0.8573	0.0113	**0.0031**	**0.0001**	**0.0001**
C			**0.0001**	**0.0002**	**0.0001**	**0.0001**	**0.0001**
D				0.0285	0.0145	**0.0001**	**0.0001**
E					**0.0001**	**0.0001**	**0.0001**
1992 - background						0.0623	**0.0001**
1993 - background							**0.0001**

Nitrate-N

	Cropped area				Background		
	B	C	D	E	1992	1993	1994-95
A	**0.0001**	0.3912	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**
B		**0.0001**	**0.0001**	**0.0001**	**0.002**	**0.0002**	**0.0001**
C			**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**
D				0.7371	0.3068	**0.0001**	**0.0001**
E					0.1063	**0.0001**	**0.0001**
1992 - background						**0.0001**	**0.0001**
1993 - background							**0.0001**

Sulfate

	Cropped area				Background		
	B	C	D	E	1992	1993	1994-95
A	**0.0001**	0.0169	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**
B		**0.0004**	0.3005	0.0707	**0.0001**	0.5968	0.3766
C			**0.0006**	**0.0001**	**0.0001**	**0.0016**	**0.0001**
D				0.021	**0.0001**	0.2377	0.047
E					0.028	0.2985	0.3037
1992 - background						**0.0007**	**0.0001**
1993 - background							0.9475

(table 1). Concentrations of nitrate-N were least beneath area B (median of 14 mg/L), one of the cropped areas having the corn-soybean rotation. Differences in concentrations between cropped area B and the other cropped areas were significant (table 1). Concentrations of nitrate-N were similar beneath areas D and E, the other corn-soybean rotation area and the continuous corn area, respectively, with median concentrations of 17 mg/L (fig. 2b). Concentrations beneath areas D and E were not significantly different (table 1). Eighty-nine percent of the samples from the upper 1 m of the saturated zone beneath the cropped areas had concentrations of nitrate-N that were greater than the U.S. Environmental Protection Agency (USEPA) MCL of 10 mg/L (U.S. Environmental Protection Agency, 1996).

Concentrations of nitrate-N beneath all cropped areas were greater than background concentrations during 1993-95 (fig. 2b and 4c), indicating that inputs of nitrate-N to ground water from the MSEA farming systems were detected above background levels once the effects of pre-MSEA farming activities decreased. Differences in concentrations beneath the cropped and background areas during 1993-95 were significant (table 1). Concentrations of nitrate-N beneath areas having the potato-sweet corn rotations (areas A and C) were significantly greater than background concentrations related to pre-MSEA farming practices (1992 background) (fig. 2b, table 1). Concentrations of nitrate-N beneath area B, having the corn-soybean rotation, were significantly less than those related to pre-MSEA farming practices. Concentrations of nitrate-N beneath the other area having the corn-soybean rotation (area D) and the continuous corn farming system (area E) were not significantly different from those related to pre-MSEA farming (background) (fig. 2b, table 1).

Concentrations of nitrate-N did not vary over time as much as chloride concentrations (fig. 4c). The lesser variability of nitrate-N concentrations probably reflects that nitrogen was applied multiple times per growing season compared to a single chloride application per year and that movement of nitrate-N in the unsaturated zone is affected by more processes and thus retarded relative to movement of chloride. The greatest nitrate-N concentrations occurred beneath area A in 1992, following the largest annual nitrogen application on the potatoes during 1991 (fig. 4c). The greatest temporal variation in nitrate-N occurred beneath area A, where concentrations varied from 15 to 40 mg/L. Lesser variability occurred beneath the other cropped areas with the least occurring beneath area B, where concentrations ranged from 12 to 18 mg/L. Beneath each cropped area (except D), the maximum nitrate-N concentrations occurred during August 1992 to April 1993, likely because the greatest amount of recharge occurred in 1991. After this time period, nitrate-N concentrations generally decreased or were similar during 1993-95. However, the decreases beneath cropped areas were less than the decreases in background areas. Nitrate-N concentrations in the upper 1 m of the saturated zone beneath all cropped areas began to consistently exceed background concentrations in 1992, except beneath area B, which consistently exceeded background concentrations beginning in 1993. The largest excess nitrate-N concentrations derived from MSEA farming systems on the cropped areas generally occurred in 1994 or 1995 (fig. 4c).

Concentrations of sulfate were significantly greater beneath areas having the potato-sweet corn rotation (areas A and C) than beneath background areas and areas having the field corn-soybean rotation (areas B and D) or continuous corn (area E) (figs. 2c and 4d, table 1). Areas A and C having the potato-sweet corn farming system had median sulfate concentrations of 15 and 10 mg/L, respectively (fig. 2c). These areas had the greatest sulfate concentrations because 3.5-5 times more sulfur was applied to potatoes than to corn (fig. 4d) (Landon and others, 1997). Concentrations of sulfate generally were similar, with median concentrations of 5 to 7 mg/L, beneath areas having the field corn-soybean rotation (areas B and D), the continuous corn system (area E), and beneath background areas (fig. 2c).

Concentrations of atrazine beneath the cropped areas in the upper 1 m of the saturated zone were always less than the USEPA MCL for atrazine (without metabolites) of 3 µg/L (USEPA, 1996). The maximum concentration of atrazine beneath the cropped areas was 0.14 µg/L (table A, Appendix A at the back of the report). However, concentrations of the atrazine plus metabolites did exceed the atrazine MCL of 3 µg/L in 2 samples from beneath area E.

Other studies (Thurman and others, 1992, 1996) have demonstrated that the DAR can be a useful tool for evaluating the history and pathways of atrazine. Because degradation of atrazine into DEA mostly takes place in the soil (Adams and Thurman, 1991; Mills and Thurman, 1994), DAR values of less than 1.0 indicate rapid transport of atrazine to ground water (Thurman and others, 1996). The relatively large DAR values detected in ground water at the site indicate that atrazine is predominantly being degraded to DEA in the soil and that the transport of atrazine through the unsaturated zone is probably not occurring rapidly along preferential pathways. The median DARs for the cropped areas were: 8 for A, 20 for B, undefined for C, 20 for D, and 45 for E. These DAR values were greater than medians for background areas, which ranged from 1.9 to 7.0 during 1991-95. The average DAR for the entire research area was 8.0. Annual median values of D^2R were 0.04 to 0.08 beneath the cropped areas during 1992-95; whereas, annual median values were 0 to 0.5 beneath background areas during 1991-95. These values are typical of those found in ground water because atrazine mostly degrades to DEA rather than DIA in the soil.

Concentrations of atrazine plus metabolites were significantly greater during 1994-95 than during 1992-93 beneath all cropped areas in the upper 1 m of the saturated zone (table 2, fig. 3, fig. 4e). In contrast, background concentrations in 1991, 1992, 1993, and 1994-95 were not significantly different (table 2). These results indicate that the effects of MSEA atrazine applications on the underlying ground-water quality changed over time.

Concentrations of atrazine plus metabolites beneath areas A, B, and E

Table 2. Results of statistical testing for significance of differences in concentrations of sum of atrazine plus metabolites, de-ethylatrazine and de-isopropylatrazine, between the cropped and background areas

[Attained significance level (p-value) for two-sided Wilcoxon rank-sum tests are shown (for one-sided test, p/2); Significance criteria: $p<\alpha= 0.01$ (two-sided) (**bold indicates statistically significant difference**); --, comparison not made]

		Cropped area												
		A	B	B	C	C	D	D	E	E	Background			
		1994-95	1992-93	1994-95	1992-93	1994-95	1992-93	1994-95	1992-93	1994-95	1991	1992	1993	1994-95
A	1992-93	**0.0001**	**0.0012**	--	**0.0001**	--	**0.0001**	--	0.0425	--	--	0.2522	--	--
A	1994-95		--	**0.0002**	--	**0.0001**	--	**0.0004**	--	**0.0002**	0.0582	**0.0001**	--	**0.0001**
B	1992-93			**0.0001**	0.1536	--	0.0453	--	0.5246	--	--	0.0755	--	--
B	1994-95				--	0.0618	--	0.7723	--	**0.0001**	0.9671	0.0273	--	0.0190
C	1992-93					**0.0059**	0.6023	--	0.0704	--	--	**0.0051**	0.0455	--
C	1994-95						--	0.0700	--	**0.0001**	0.3907	0.8079	--	0.9624
D	1992-93							**0.0001**	0.0182	--	--	**0.0010**	0.0138	--
D	1994-95								--	**0.0001**	0.8916	0.0297	--	0.0350
E	1992-93									**0.0001**	--	0.3172	--	--
E	1994-95										**0.0001**	**0.0001**	--	**0.0001**
Background	1991											0.2909	0.1268	0.2704
Background	1992												0.4471	0.9383
Background	1993													0.4427

during 1992-93 were not significantly different from background areas during 1992 (table 2); concentrations beneath areas C and D were significantly less than background areas in 1992 (fig. 3) and not significantly different during 1993 (table 2). Significantly greater concentrations beneath area A than areas B, C, and D during 1992-93 likely are an artifact of anomalously high pre-MSEA concentrations beneath area A. Landon and others (1996, fig. 4) found that concentrations of atrazine and DEA beneath area A were greater than beneath other cropped areas in April 1992, even though atrazine was not applied to area A in 1991 (fig. 4e). Concentrations of atrazine and DEA generally were greater in MPORT A-70, upgradient of area A (fig. 1), than in other background wells (Landon and others, 1996, fig. 4; Delin and others, 1995, fig. 4; Landon and others, 1997). The reason for these greater than average background concentrations in the vicinity of area A is unknown but is probably related either to (1) anomalous pre-MSEA application rates in this part of the research area or (2) greater leaching potential due to differing soil or hydrologic characteristics.

Area E (continuous corn) had the largest concentrations of atrazine plus metabolites, with about 10 percent of the samples exceeding the maximum concentration of about 1.3 µg/L found elsewhere in the research area during 1992-95 (fig. 3; table A, Appendix A at the back of the report). Area E also had the greatest atrazine application rates (fig. 4e). Concentrations of atrazine plus metabolites beneath area E began to exceed upgradient background concentrations in 1993 and increased during 1994-95. These results indicate that some transport of atrazine and metabolites to ground water occurred as a result of atrazine applications on area E. Some loading of atrazine plus metabolites to ground water as a result of MSEA farming activities likely occurred beneath area A during 1994-95, when concentrations were significantly greater than background levels (table 2, fig. 4e).

Concentrations of atrazine plus metabolites also increased beneath areas B, C, and D during 1994-95 (fig. 4e). The greater concentrations beneath these cropped areas than in upgradient background areas indicate that some atrazine plus metabolites reached ground water as a result of the MSEA farming activities, although the amounts were less than on areas E and A. However, the concentrations during 1994-95 were not significantly different from all background concentrations (table 2).

Metribuzin was not detected beneath the cropped areas in concentrations or frequencies greater than those found in background areas except beneath area A (table A, Appendix A at the back of the report). Metribuzin was applied to potato and soybean crops (Landon and others, 1997) and was detected in concentrations of 0.14 to 1.24 µg/L during November 1993 to June 1995 beneath area A (fig. 4f). These concentrations presumably resulted from application of metribuzin during April 1993 to the potato crop (fig. 4f). Metribuzin likely was not detected beneath the other cropped areas due to differing soil and hydrologic characteristics. There are no USEPA primary drinking water standards for metribuzin.

Metolachlor and alachlor generally were not detected beneath the cropped areas in concentrations or frequencies greater than those found in background areas (Table A, Appendix A at the back of the report). Metolachlor was only applied to the potato crops grown on area A during 1991 and 1993 and on area C during 1992 and 1994 (Landon and others, 1997). Metolachlor was detected above the detection limit of 0.01 µg/L in 18 percent of the samples beneath area A, compared to detections in the background areas of 0 to 2 percent (table A, Appendix A at the back of the report). However, the maximum concentration of 0.05 µg/L was the only sample in which metolachlor was present above the reporting limit of 0.04 µg/L; most of the other detections were at the detection limit of 0.01 µg/L and did not exceed concentrations in background areas (table A, Appendix A at the back of the report). There are no USEPA primary drinking water standards for metolachlor. Concentrations of alachlor were always much less than the USEPA MCL of 2 µg/L (U.S. Environmental Protection Agency, 1996). Alachlor was only detected at or above the effective reporting limit (ERL) of 0.07 µg/L in three samples: 0.07 µg/L in area A, 0.14 µg/L in area B, and 0.22 µg/L in area C (table A, Appendix A at the back of the report). However, these concentrations were similar to the greatest background concentration of 0.18 µg/L detected in 1994-95. Similarly, concentrations and detection frequencies of alachlor metabolite 2,6-diethylanaline beneath the cropped areas were not distinguishable above those in background samples (table A, Appendix A at the back of the report).

Constituent Travel Times

The first detection of excess chloride or bromide at the water table very rarely occurred during the first sampling period following application. Rather, the first detection at the water table was 2 to 15 months after application with an average of about 7 to 9 months (tables B1 and B2, Appendix B at the back of the report). The peak chloride and bromide concentrations in the upper 2 m of the saturated zone occurred 11 to 19 months after application with an average of 14 to 16 months.

The travel times for chloride and bromide to ground water were longer than originally expected given the fine-to-medium grained sand texture, relatively high hydraulic conductivity, and shallow depth to water of about 2.5- to 4.5-m. However, these travel times were not anomalous when compared to travel times of recharge water determined by measuring the oxygen and hydrogen stable-isotopic compositions of precipitation, soil water, and ground water. The isotopic data were used to track movement of precipitation that fell during different seasons, which have unique isotopic compositions, through the unsaturated zone (Landon and others, 1997; Delin and others, 1997)). The travel times of these seasonal isotopic signals through the unsaturated zone to the water table were a minimum (first detection) of 1.5 to 6 months and a maximum (end of detection) of up to 12 months in upland settings (R2 and MC22, fig. 1). Travel times for seasonal isotopic signals through the unsaturated zone of shorter than one week were measured only during focused recharge of snowmelt in the spring in a topographic depression (site R1, fig. 1). In the absence of evaporative effects, which were found to have very little affect on the isotopic composition of soil water in this study (Komor and Emerson, 1994; Landon and others, 1997; Delin and others, 1997), stable isotopes of oxygen and hydrogen are conservative tracers of water movement (International Atomic Energy Agency, 1981; Payne, 1988; Coplen, 1993). The relatively long travel times of recharge water, despite the thin and highly permeable unsaturated zone, reflect that the volume of water entering the soil during most infiltration events was generally small, 5 to 30 percent of the total volume of water stored in the unsaturated zone. As a result, several infiltration events, occurring over a period of several months, were required to replace the total volume of water in the unsaturated zone.

The ranges of travel times for chloride, bromide, and the isotopic signals overlapped, but the travel times for chloride and bromide generally were longer. This result is tempered by the fact that the travel times of the isotopic signals and the chloride and bromide tracers were mostly measured at different wells and times. However, isotopic signal travel times at well R2 during 1993 and 1994 were directly comparable to chloride travel times during 1993 and chloride and bromide travel times during 1994 on area E. Minimum travel times of isotopic signals indicating recharge of summer (May-September) precipitation were 6 months in 1993 and 1.5 months in 1994. These travel times were much shorter than the first detections for 1993 applied chloride of 13 months and for 1994 applied chloride and bromide of 11 months. These results imply that chloride and bromide did not move as rapidly as recharge water. Although samples were collected more frequently (monthly) for isotopes than for chloride and bromide (four times a year), the longer travel times for chloride and bromide than the isotopic signals were not simply an artifact of the differences in sampling frequency.

The reason chloride did not move as rapidly as seasonal stable-isotopic signals is unknown. Some of the factors that may have contributed are the lag time between application and the first subsequent precipitation event that led to recharge and any delays resulting from dissolution of the chloride from the granular fertilizer applied.

The slower movement of bromide than seasonal isotopic signals is consistent with recent tracer studies that have indicated low recoveries and non-conservative behavior of bromide (Lange and others, 1996), uptake of bromide by plants (Owens and others, 1985), and effects of solute concentrations and soil chemistry on bromide transport in alluvial soils (Seaman and others, 1996).

Increased concentrations of nitrate-N were first detected at the water table 3 to 17 months after application with an average of 12 months (table B3, Appendix B at the back of the report). Peak concentrations of nitrate-N in the upper 2 m of the saturated zone generally occurred 13 to 27 months after application with an average of 18 months. Increases in nitrate-N concentrations generally occurred a few months after increases in the concentrations of chloride and bromide applied during the same crop year (fig. 4c). For example, the peak chloride concentration related to 1991 applications occurred in June 1992 beneath area A (table B1, Appendix B at the back of the report), whereas the peak nitrate-N concentration occurred in August 1992 (fig. 4c; table B3, Appendix B at the back of the report). These travel times indicate that nitrate-N did not move as rapidly as chloride and bromide.

Maximum sulfate concentrations occurred 13 to 23 months after application with an average of 17 months (table B4, Appendix B at the back of the report). Increases in sulfate concentrations occurred a few months after increases in the concentrations of chloride and bromide applied during the same year (fig. 4d).

Increases in concentrations of atrazine plus metabolites were first detected at the water table 11 to 23 months after application with an average of 18 months (table B5, Appendix B at the back of the report). Peak atrazine plus metabolite concentrations in the upper 2 m of the saturated zone were generally detected about 2 years after application beneath all of the cropped areas. These travel times were determined by comparing the timing of increases in atrazine plus metabolite concentrations to increases in chloride and bromide concentrations. For example, beneath area E the first atrazine plus metabolite peak occurred in 1993 after the chloride peak in 1992 (related to 1991 applications), but before the late 1993 bromide peak (related to 1992 applications) (fig. 4e). Because atrazine and metabolites were expected to have a slower travel time through the unsaturated zone than chloride and bromide due to sorption, the atrazine plus metabolite peak detected in 1993 must be related to atrazine applied in 1991, not 1992. Travel times of about 25 months were indicated for the other cropped areas (table B5, Appendix B at the back of the report).

Excess metribuzin was detected beneath area A during November 1993 through June 1995 with the peak concentration occurring in June 1994 (fig. 4f). The peak chloride concentration related to 1993 chloride applications occurred in November 1993. Because metribuzin is expected to have a slower travel time through the unsaturated zone than chloride due to sorption, the metribuzin detection probably was related to the 1993 application. If the metribuzin detections are linked to the 1993 application, the first detection occurred 3 months after application and the peak concentrations were detected 13 months after application (table B6, Appendix B at the back of the report). It is also possible that these detections are linked to the 1991 application. This would imply that there was greater than a 3 year delay between when metribuzin was applied in 1991 and the peak concentrations were detected in 1994.

Constituent Mass Balances

The excess mass of chloride detected in ground water ranged from 34 to 135 percent of the applied amount with an average of 80 percent (table B1). The mass balance calculations for 1991 chloride applications indicate that essentially all of the chloride applied was detected in the underlying ground water within 14 to 19 months. The values of greater than 100 percent beneath areas E and particularly D reflect detection of anomalously large chloride concentrations and may also reflect uncertainties in the method. The reason for the anomalously high mass balance percentages is not known. Chloride detection percentages near 100 percent are conceptually reasonable given that chloride is not effected by biochemical reactions (Hem, 1992). The large recoveries indicate that most or all of the applied chloride was eventually mobilized by soil water and leached to ground water. The chloride mass balances for 1991 applications were the most reliable values because the application rates were the highest during the study period on all cropped areas except C, and resulted in the most discernible increase in chloride concentrations above background concentrations (fig. 4a). There was greater uncertainty associated with the mass-balance estimates during 1992-94 because of the difficulty of separating excess concentrations related to applications during these years from relatively large applications in 1991 on all cropped areas. There is also greater uncertainty in 1992 on area C, and in 1993 on area A. Values for 1994 applications may also underestimate mass-balance percentages in cases where the peak masses in ground water were detected during the last sampling period in August 1995. It is possible that there was incomplete breakthrough of the 1994 mass in August 1995 and that the mass in ground water continued to increase after sampling ceased. Chloride detected during 1992-94 ranged from 34 to 96 percent of applied amounts (table B1). Lower values likely reflect the above mentioned uncertainty in separating chloride related to applications during different years.

The mass of bromide detected in ground water ranged from about 15 to 60 percent with an average of 36 percent of the applied amount (table B2, Appendix B at the back of the report). These percentages were less than those for chloride and probably reflect greater bromide uptake by plants, which can be considerable (Owens and others, 1985). Bromide transport may also be affected by adsorption or ion exchange with soil depending upon soil mineralogy and soil water pH, ionic strength, and predominant counter ion (Seaman and others, 1996). Percentages were greater for the 800-series MPORTs than for the 400-series MPORTs. A smaller percentage of the bromide may have been intercepted by the 400-series MPORTs because of the much smaller application area than for the 800-series MPORTs (Delin and others, 1995, fig. 1). As a result of this smaller application area, the local ground-water flow paths from the bromide application may not have intersected the 400-series MPORTs.

The mass of nitrogen detected as nitrate-N in ground water ranged from 13 to 50 percent with an average of 30 percent of the applied amount (table B3, Appendix B at the back of the report). Beneath areas A and C, with the potato-sweet corn rotation, the mass of nitrogen detected was greater than 35 percent, up to a maximum of 50 percent, of the applied amount in 6 of 8 cases. Beneath field corn grown in areas B and D, the mass of nitrogen detected was about 20 percent of the amount applied in 3 of 4 cases, with the exception being a value of 45 percent following the field corn grown on area D in 1993 (table B3, Appendix B at the back of the report). Beneath field corn grown in area E, the mass of nitrogen detected was about 20 percent of the amount applied during all 4 years. These masses are in the range of those reported in other studies on sandy soils (Rutledge and Helgesen, 1990; Wang and Alva, 1996) and regional studies of surface water in the Mississippi River Basin (Battaglin and Goolsby, 1997).

The mass of applied nitrogen that reached ground water appears to be reasonable in comparison to nitrogen uptake values by the field corn crops. The mass of nitrate-N in ground water beneath field corn crops ranged from 16 to 45 percent of applied nitrogen with an average of 24 percent. In comparison, values of total plant nitrogen (stover plus grain) taken up by field corn crops, ranged from 28 to 89 percent of applied nitrogen with an average of 65 percent (table B3, Appendix B at the back of the report). Nitrogen uptake by grain, which is an estimate of the nitrogen removed from the field when the grain is harvested and is a portion of total plant nitrogen uptake, ranged from 21 to 70 percent of applied nitrogen with an average of 46 percent for field corn. Nitrogen taken up by the plants but not harvested with the grain is presumably left in residual plant material on the field or is returned to the organic fraction of soil nitrogen after harvest. The sum of nitrogen taken up by grain and nitrogen detected as nitrate-N in ground water ranged from 42 to 91 percent of applied nitrogen and averaged 69 percent. While there are many uncertainties both in the mass balance determinations for nitrogen taken up by plants and leaching to ground water, the mass-balance analysis indicates that plant uptake and leaching, in order of importance, were the predominant sinks for nitrogen at the research site. This result was expected since other mechanisms in the nitrogen cycle should have little influence at the research area. Nitrogen mineralization or immobilization through interaction with the pool of organic-nitrogen in the soil is a major component of the nitrogen cycle in soils (Hallberg and Keeney, 1993). These processes should have a very minor effect on the nitrogen mass balance at this site, however, because of the low organic content of the soils (1 percent or less). This small pool of mineralizable soil organic matter is not likely to be a substantial source or sink of nitrogen when soils are cultivated. Soil analyses for nitrate-N indicated that concentrations everywhere in the research area were less than the detection limit of 6 milligrams per kilogram. Volatilization of nitrogen fertilizer should be minor since the large majority of the fertilizer was in granular form and was incorporated into the soil. Because the coarse sandy soil texture permits aerobic conditions, denitrification should not be a major factor in the removal of nitrogen from these soils.

The nitrogen mass balances for other crops either could not be calculated or had greater uncertainty than for field corn. Uncertainties associated with nitrogen uptake by sweet corn are greater than those for field corn because nitrogen uptake by the grain was not measured. For sweet corn, nitrogen uptake was measured in whole plant samples collected just prior to harvest. Total plant nitrogen taken up by sweet corn accounted for 33 to 51 percent of the applied amount with an average of 39 percent. The mass of nitrate-N in ground water beneath sweet corn crops ranged from 24 to 50 percent of applied nitrogen with an average of 40 percent. These results imply that plant uptake and leaching were the primary sinks for nitrogen applied to sweet corn and field corn. Because soil nitrogen concentrations and organic matter are low at the site, much of the nitrogen taken up by soybeans was probably fixed from the atmosphere. Therefore, it was not possible to estimate a mass balance for nitrogen on soybean fields since the amount of nitrogen entering the soil from the atmosphere was unknown. For potatoes, the mass of nitrogen taken up by the tubers was not measured. Therefore, comparisons with other crops are not possible.

The mass of sulfur detected as sulfate in ground water ranged from about 9 to 51 percent with an average of 27 percent of the amount applied (table B4, Appendix B at the back of the report). The maximum mass of 51 percent was detected beneath area A in 1993 and the minimum mass of about 10 percent was detected beneath area B in 1992 and 1994.

The mass of atrazine plus metabolites in ground water ranged from 0 to about 1 percent with an average of 0.37 percent of the applied amount (table B5, Appendix B at the back of the report). Most of this mass was composed of DEA, with much lesser amounts of atrazine and DIA. These leaching percentages are similar to those found in other studies, which generally detected less than 2 percent of applied atrazine in ground water (Wehtje and others, 1984; Hall and others, 1989, 1991; Rutledge and Helgesen, 1990; Frank and others, 1991; Dousset and others, 1995) or surface water (Schottler and others, 1994; Larson and others, 1995; Battaglin and Goolsby, 1997).

Atrazine transport was predominantly affected by processes occurring in the soil such as adsorption and degradation based on: (1) the 2-year travel times to reach ground water, (2) small proportions of applied atrazine that reached ground water, and (3) persistence of atrazine metabolites (predominantly DEA) in background areas over the 5-year period of monitoring. The general absence of DAR values less than 1, which have been interpreted as evidence of rapid transport or preferential flow of atrazine to ground water (Adams and Thurman, 1991), is consistent with the lengthy travel times of atrazine metabolites observed. While adsorption and degradation in the soil have prevented most atrazine from reaching ground water in the research area, some atrazine metabolites have persisted for at least 5 years in the unsaturated zone and have resulted in DEA concentrations of about 0.1 μg/L in shallow ground water.

The mass of metribuzin applied to area A in 1993 that reached ground water was 0.9 percent of the applied amount (table B6, Appendix B at the back of the report). This was the only detection of metribuzin above background concentrations in cropped areas during the study. Because relatively few samples from beneath cropped areas had concentrations of alachlor or metolachlor larger than from background areas (table A, Appendix A at the back of the report), no mass balances of these constituents were calculated.

Vertical Changes in Water-Quality

Concentrations of selected constituents for all sampling periods during 1992-95 were plotted against depth from all sites with deep MPORTs (A400, B400, C400, D400, and shallow MPORT E400 combined with deep MPORT R2 (1991 and 1992 data only), fig. 5). These data illustrate vertical changes in ground-water quality beneath the cropped areas.

Concentrations of nitrate-N generally decreased with depth in the saturated zone (fig. 5). Concentrations were mostly greater than 10 mg/L in the upper 2.5 m, 1 to 10 mg/L from 2.5 to 4.5 m, and mostly less than 1 mg/L, and frequently below the detection limit of 0.05 mg/L, at depths greater than 4.5 m. The decrease in nitrate-N concentrations with depth corresponded with a decrease in DO concentrations (fig. 5). Concentrations of DO were mostly 5-10 mg/L near the water table, nearly at equilibrium with the atmosphere. Concentrations of DO were mostly 3-10 mg/L in the upper 2.5 m, were mostly 1-6 mg/L between 2.2 and 4.5 m, and were mostly less than 1 mg/L below 4.5 m. These trends in concentrations with depth were generally observed at each of the sites where vertical chemical profiles could be measured, although minor variations were observed. The decrease in DO and nitrate-N concentrations with depth indicate that the ground water becomes chemically more reduced with depth, following a common sequence of biochemical reactions in ground water (Champ and others, 1979). The occurrence of higher concentrations of manganese in some samples at depths greater than about 5 m are also consistent with more reduced ground water (fig. 5).

Excess concentrations of nitrate-N from the MSEA farming systems were mostly detected in the upper 2 m of the saturated zone, although in a few cases excess concentrations extended to about 3 m below the water table (Landon and others, 1997, figs. 4-9). Because the upper 2-3 m of the saturated zone was predominantly oxic, concentrations of nitrate-N at these shallow depths were likely influenced predominantly by nitrate-N loading rates at the water table and advective-dispersive transport.

The transition from oxidized to reduced ground water and the decrease in nitrate-N between about 2 and 6 m below the water table are consistent with the occurrence of denitrification, a biochemical reaction in which nitrate-N is converted through a series of reaction steps to nitrogen gas (Korom, 1992). Evidence of denitrification at the site was obtained by Böhlke and others (1994). Nitrogen and argon gas analyses and nitrogen isotopic analyses of the products and reactants of the denitrification reaction indicated that partial to complete denitrification occurred along the flow paths from area E to Battle Brook. It is likely that denitrification is also occurring beneath other areas of the MSEA as well. There can be a complex interaction between the effects of changing agricultural practices, ground-water residence times, and geologic features that will affect the distribution of nitrate-N in an aquifer (Böhlke and Denver, 1995).

The exact mechanism of denitrification at the site remains unclear. Denitrification requires an electron donor, a

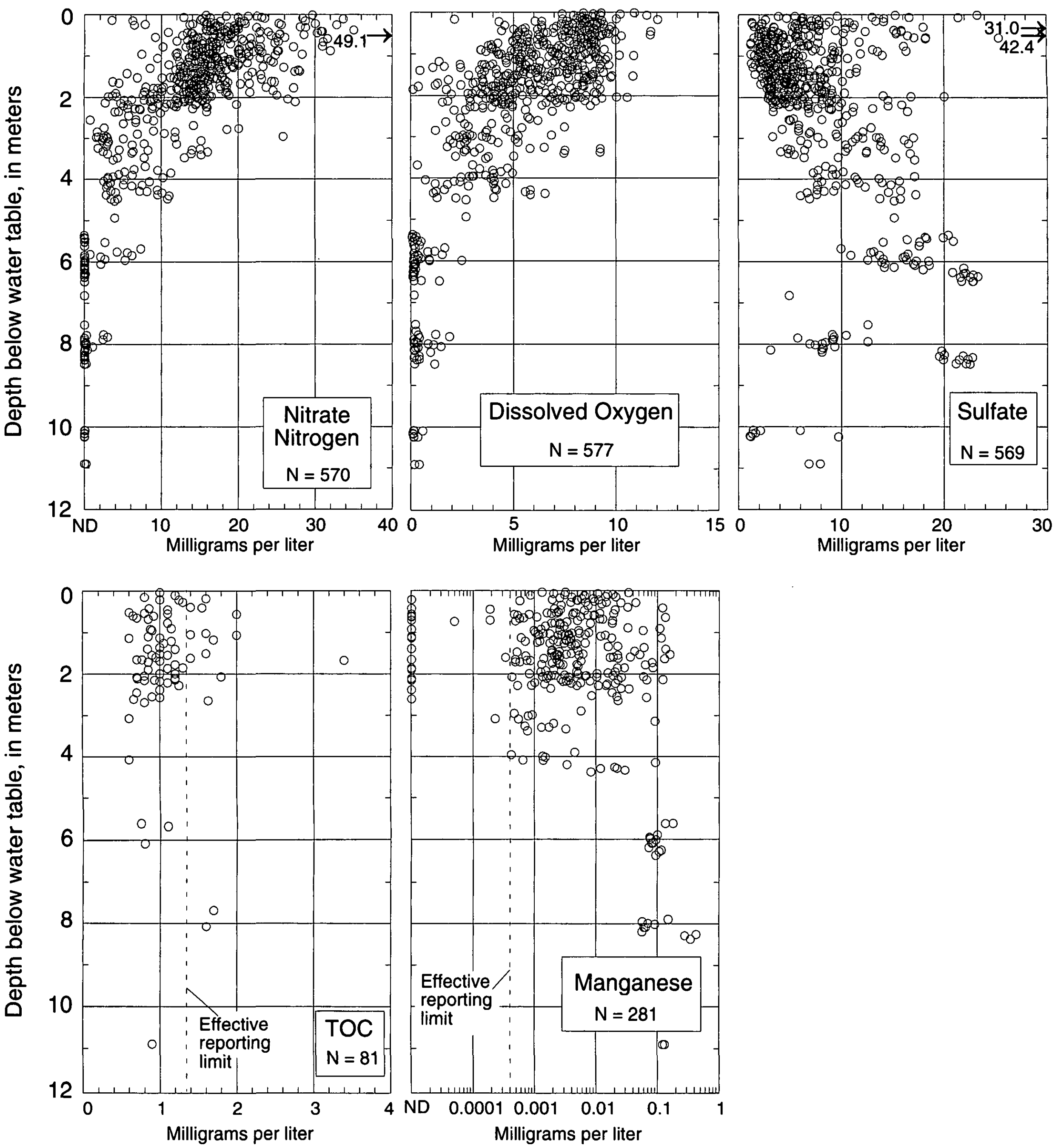
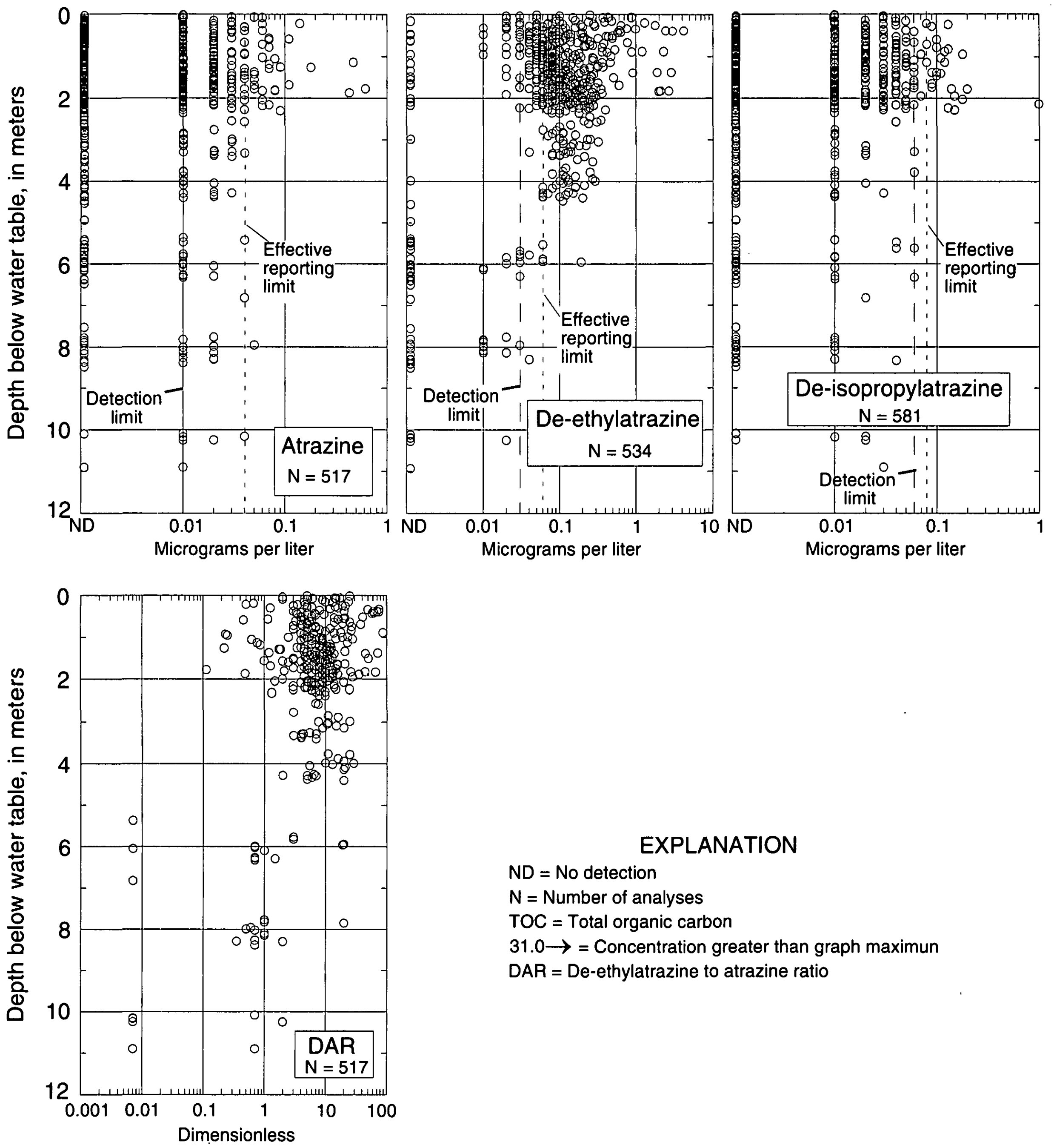


Figure 5. Relation between depth below water table and concentrations of selected water-quality



EXPLANATION
ND = No detection
N = Number of analyses
TOC = Total organic carbon
31.0⟶ = Concentration greater than graph maximun
DAR = De-ethylatrazine to atrazine ratio

constituents for all samples collected during 1992-95 from the middle of each cropped area.

constituent that can give up electrons to other reactants. Two common electron donors for denitrification are organic carbon, and reduced inorganic compounds such as sulfides (Korom, 1992). TOC concentrations in ground water were generally less than 2 mg/L and were usually less than the effective reporting limit of 1.35 mg/L (fig. 5). These concentrations are generally considered too low to be a feasible electron donor source for denitrification (Korom, 1992; Starr and Gillham, 1993), although solid organic carbon in the aquifer sediments could also be a source. Analyses of aquifer solids did not indicate detectable amounts of reduced sulfide minerals in core samples (Richard Wanty, U.S. Geological Survey, oral communication, 1995). Only small amounts of reduced sulfide minerals are required, however, so this electron donor source is still a possibility. In addition, sulfate concentrations generally increased between about 2 and 6 m (fig. 5), the depth over which ground water changed from an oxidized to reduced chemical state. An increase in sulfate concentrations has been identified in other aquifer settings in which denitrification occurred with reduced sulfide minerals as the electron donor (Postma and others, 1991; Korom, 1992). Therefore, the increase in sulfate concentrations are consistent with the presence of reduced sulfide minerals as the electron donor. However, this denitrification reaction mechanism cannot be confirmed with the available evidence.

The greatest concentrations of atrazine, DEA, and DIA occurred in the upper 2 m of the saturated zone (fig. 5). Concentrations of atrazine below about 2.2 m were at or below the reporting limit of 0.04 µg/L, but were sometimes detected above the detection limit of 0.01 µg/L at depths to 11 m below the water table. Concentrations of DIA were at or below the detection limit of 0.06 µg/L below depths of about 2.2 m. Concentrations of DEA greater than 0.10 µg/L were often detected to a depth of about 4.5 m below the water table. Below about 4.5 m, DEA concentrations were mostly below the detection limit, with a few samples at concentrations between the detection limit of 0.03 µg/L and the reporting limit of 0.06 µg/L.

It could not be determined whether atrazine was degrading to form DEA in the saturated zone based upon vertical changes in concentrations through the saturated zone. Most conversion of atrazine to DEA and DIA occurs in the soil zone (Adams and Thurman, 1991). However, conversion of atrazine to DEA in ground water has been shown to occur (McMahon and others, 1992). For the depths of 2 to 5 m, more samples had concentrations of DEA greater than the ERL than concentrations of atrazine greater than the ERL (fig. 5). This could simply reflect greater historical loading of DEA than atrazine from the unsaturated zone to ground water or could also indicate that some degradation of atrazine to DEA occurred in the saturated zone. However, below 4.5 m, DAR values decreased (fig. 5). This decrease is inconsistent with conversion of atrazine to DEA, which should cause DAR values to increase. However, because concentrations of atrazine and DEA were just above the detection limit, there may be large uncertainties in the DAR values.

Factors Affecting Ground-Water Quality

Substantial differences in agricultural chemical concentrations in ground water between cropped areas resulted from differences in the timing and quantity of recharge and in the quality of recharge water, which is influenced by land-use practices and soils. The discussion below describes evidence relating differences in chemical concentrations between the cropped areas to several important physical factors. The effects on ground-water quality of specific farming practices used as part of the farming systems such as the fertilizer or pesticide formulation, the method of application, and cultivation practices, are difficult to isolate and will not be discussed. Other research at the site evaluated the effects of some of these specific agricultural practices (Dowdy and others, 1995a, 1995b; Lamb and others, 1995a, 1995b).

Application Rate

Figure 6 shows average annual chemical application rates and chemical concentrations, averaged over the 4-year period (two complete crop rotation cycles) for which complete data were available. The periods for the average application (1991-94) and the average concentrations (1992-95) are different because the effects of chemical applications were usually not fully evident in ground water until a year or more after application. The figure shows one summary data point for each constituent for each cropped area. These simplified graphs showing 4-year averages were used to clarify the relation of application rate and concentrations.

The application rate strongly and directly influenced the concentrations of chloride, nitrate-N, sulfate, and atrazine plus metabolites in ground water in many, but not all, cases (fig. 6). Large differences in application rates resulted in large differences in concentrations. Concentrations of chloride, nitrate-N, and sulfate were greatest beneath areas A and C (potato-sweet corn rotation). The larger application rates on these areas mostly resulted from larger applications to the potatoes than to the sweet corn. The average annual application rate of chloride was approximately 4 to 6 times larger on areas A and C than on the other areas and average concentrations were approximately 2 to 3 times greater (fig. 6). The average annual application rate of sulfur was approximately 2.5 to 5 times larger on areas A and C than on the other areas and average concentrations were approximately 2 to 3 times greater (fig. 6).

The average annual application rate of atrazine on area E (continuous corn) was approximately 7 times greater than on the other areas and the average concentration was approximately 2 to 5 times greater (fig. 6). The greater application rate on area E reflects that atrazine was broadcast applied every year on this area; whereas, it was band applied in alternating years on the other areas.

The average annual application rate of nitrogen was approximately twice as great on areas A and C as on areas B and D, and average nitrate-N concentrations beneath areas A and C were approximately 1.4 to 1.8 times greater than beneath areas B and D (fig. 6). The differ-

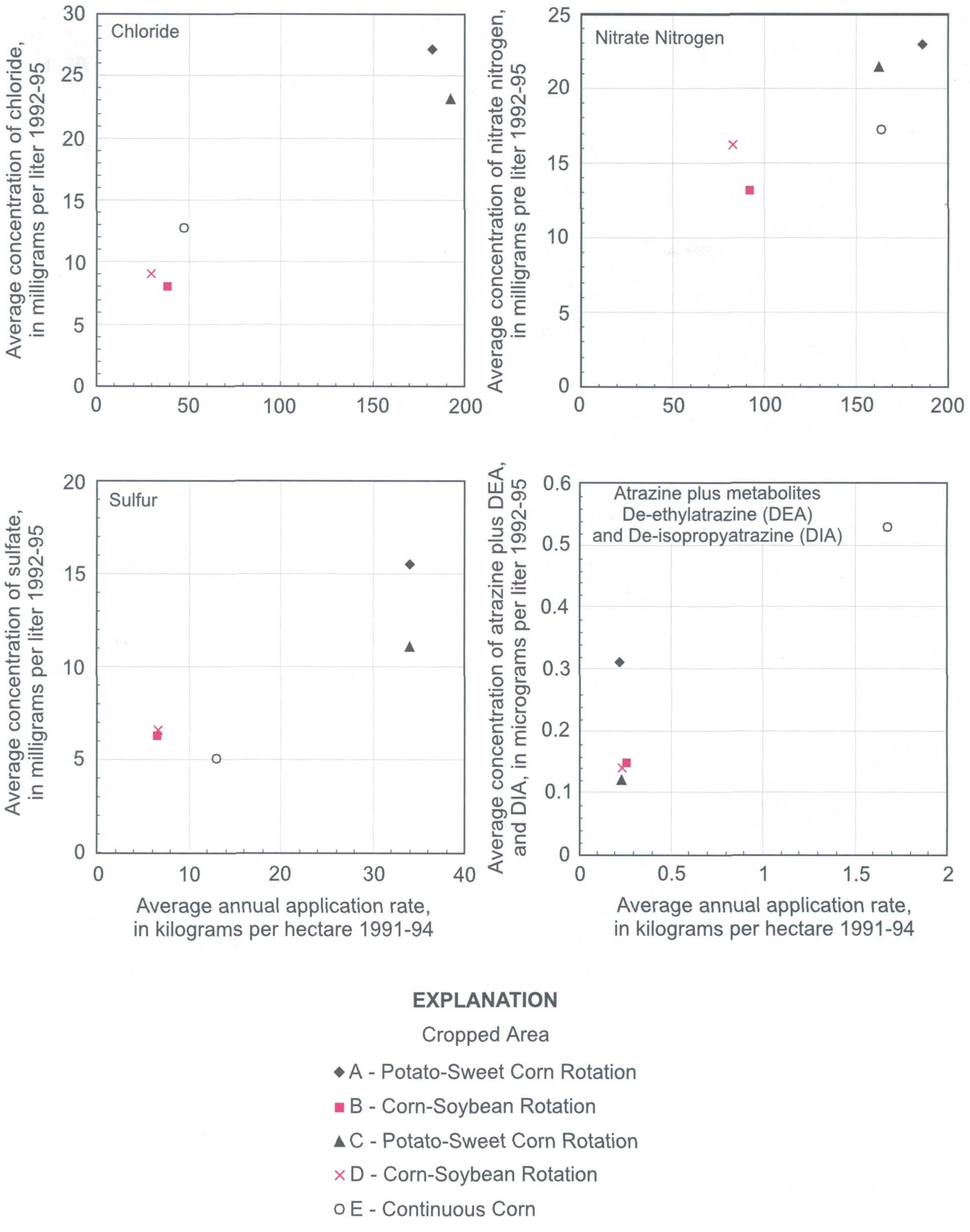


Figure 6. Relation of 4-year average application rates and 4-year average concentrations of chloride, nitrate nitrogen, sulfate, and atrazine plus metabolites, de-ethylatrazine and de-isopropylatrazine, in ground water beneath the cropped areas.

ences in average annual application rates reflected that nitrogen was only applied to areas B and D every other year, when field corn was grown, and was not applied to the soybeans. In contrast, areas A and C had nitrogen fertilizers applied to them every year because of the potato-sweet corn rotation, and application rates to potatoes were sometimes greater than for the corn crops (table B3, Appendix B at the back of the report).

Differences in application rate cannot account for all of the observed differences in concentrations, particularly for nitrogen. For instance, average annual nitrogen application rates on areas C and E were very similar, but the average nitrate-N concentration beneath area C was about 5 mg/L greater (fig. 6). In addition, the average annual application rate on area E was about twice that on area D (fig. 6), yet nitrate-N concentrations beneath these two cropped areas were not significantly different (table 1). Conversely, the average annual application rates on areas B and D were very similar, yet the average nitrate-N concentration beneath area D was about 3 mg/L greater than beneath area B (fig. 6) and the difference was significant (table 1). Similar discrepancies between average application rate and average concentration were notable, to a slightly lesser extent than for nitrogen, for chloride, sulfate, and atrazine. Factors in addition to application rate are required to explain the observed differences in concentrations between cropped areas.

One complicating variable with respect to nitrogen application rate is the effect of nitrogen fixation from the atmosphere by soybeans. The management system credited nitrogen fixation from the atmosphere by soybeans at about 22 kg/ha based upon estimated values for the soils and climate at the site. However, it is unknown how much nitrogen was actually fixed to the soil; the quantities of nitrogen fixed by soybeans can vary greatly (Wall and Montgomery, 1991). Due to nitrogen fixation by soybeans, differences in nitrogen added to the soil were not as great between areas D and E as indicated by the nitrogen fertilizer application rates alone. Some of the nitrogen fixed to the soil by soybeans may have also leached to ground water. This unaccounted for nitrogen may contribute to the similarity of nitrate-N concentrations beneath cropped areas D and E, although nitrogen applications were twice as great on area E.

Timing of Application

The timing of nitrogen application may have contributed to the generally greater nitrate-N concentrations beneath areas A and C. These areas were planted with potatoes every other year. Although the annual application totals on potatoes and corn were often similar, nitrogen was applied to potatoes earlier in the spring, generally in mid-April, than to corn, early-to-mid May. Nitrogen was also applied to the potatoes at rates approximately 2 to 3 times greater than those for corn during the first application each year. Greater amounts of nitrogen fertilizer were typically applied to the corn during the fertilizer applications in June-July than to the potatoes, to bring the annual application totals for the corn and potatoes to similar values. During late April and early May, relatively little uptake of nitrogen by plants would be expected due to small plant size. In contrast, during May-July, when greater amounts of nitrogen were applied to corn than to potatoes, plant uptake likely was greater because of larger plant size and increased growth rate. In addition, relatively large amounts of ground-water recharge typically occurred during April and May; whereas, in June and July, greater water uptake by plants and warmer temperatures resulted in greater evapotranspiration and less ground-water recharge (Delin and others, in press). Thus, because of the greater susceptibility of nitrogen applied earlier in the spring to leach through the soil, it is reasonable that there would be greater amounts of nitrate-N leaching from areas planted in potatoes than in corn. This hypothesis is consistent with the fact that the average nitrate-N concentration was greater beneath area C than area E despite similar average annual application rates (figs. 2b and 6). Similarly, early spring chloride and sulfur applications to the potatoes were larger than to corn crops. These larger applications early in the spring may have exposed the fertilizers to greater opportunities for leaching, which may explain the generally greater chloride and sulfate concentrations beneath areas A and C. Atrazine was applied at approximately the same time on all of the corn crops, so the timing of application did not likely influence differences in the leaching of atrazine plus metabolites among the cropped areas.

Timing of Recharge in Relation to Crop Rotation

Average annual recharge varied by a factor of about two, with approximately 21 cm in 1991, 9 cm in 1992, 15 cm in 1993, and 14 cm in 1994. Because greater amounts of recharge occurred in 1991 and 1993 than in 1992 and 1994, greater amounts of leaching of the applied nitrogen fertilizer may have occurred in 1991 and 1993. Area D was planted in corn and treated with nitrogen during 1991 and 1993. In contrast, area B was planted in soybeans with no nitrogen applied in 1991 and 1993 (table B3, Appendix B at the back of the report). Area B was planted with corn and had nitrogen applied during the dryer years of 1992 and 1994. Greater fertilizer application rates on area D during the years with greater recharge rates may have resulted in greater nitrate-N concentration beneath area D than area B despite having the same farming system with very similar 4-year average application rates. The greater recharge during 1991 and 1993 than during 1992 and 1994 may have also been a factor in causing nitrate-N concentrations to be greater beneath area A than area C. Similar reasoning may explain slightly higher chloride and sulfate concentrations beneath area A than area C (fig. 6). The similarity of nitrate-N concentrations beneath areas D and E despite dissimilar application rates could be influenced by the fact that both cropped areas had similar nitrogen application rates and farming practices during 1991 and 1993, when the greatest recharge occurred. It may be that the effects of this greater recharge in 1991 and 1993 masked the effects in years with lesser recharge, 1992 and 1994. There was no evidence that greater leaching of atrazine plus metabolites to ground water occurred as a result of applications during wetter years.

Plant Uptake

Differences in nitrogen uptake by crops may have contributed to differences in nitrate-N concentrations beneath the cropped areas. In 1991, total plant nitrogen uptake by sweet corn on area C was approximately 62 kg/ha, less than one-half the total plant uptake by field corn of 137 kg/ha on area E and 140 kg/ha on area D, despite the same application rate of 157 kg/ha (table B3, Appendix B at the back of the report). For the field corn, analysis of the grain indicated that approximately 65 to 70 percent of the nitrogen taken up by the plants was in the grain, which was removed from the fields at harvest. For sweet corn, the quantity of nitrogen in the grain, as compared to the rest of the plant, was not measured. The considerably small amount of total plant uptake of nitrogen by the sweet corn implies that more nitrogen would potentially be available for leaching from area C than area E. This factor may help explain why the nitrate-N concentration was greater beneath area C than area E, in spite of the same application rates. Similarly in 1992, total nitrogen uptake by sweet corn grown on area A, approximately 52 kg/ha, was much less than uptake by field corn, 150 kg/ha on area E and 121 kg/ha on area B (table B3, Appendix B at the back of the report). The smaller amount of nitrogen taken up by sweet corn than field corn in 1992 could be a contributing factor to the greater nitrate-N concentration beneath area A than areas D and E. Nitrogen uptake by sweet corn and field corn crops during 1993 and 1994 were not substantially different. Substantially greater total plant nitrogen uptake on area B during 1992 than on area D during 1993 may also be a contributing factor to the significantly greater nitrate-N concentrations beneath area D than area B, despite the same farming system and similar 1991-94 nitrogen application rates (table B3, Appendix B at the back of the report). Total plant nitrogen uptake by field corn on area B during 1992 (121 kg/ha) was substantially greater than by soybeans on area D (54 kg/ha). Total plant nitrogen uptake by soybeans on area B (96 kg/ha) during 1993 was also greater than that by field corn on area D (62 kg/ha). Also, the total plant nitrogen uptake by soybeans on area D during 1992 was much smaller than total plant nitrogen uptake by field corn on area E (150 kg/ha). The smaller nitrogen uptake by crops on area D could have resulted in relatively greater leaching of nitrate-N to ground water during 1992 and 1993 on area D than area E. This result would be consistent with the similarity of nitrate-N concentrations beneath areas D and E, despite total 1991-94 nitrogen application rates being twice as much on area E as on area D.

Soil Properties and Topographic Setting

It is possible that differences in topographic setting and variations in soil properties as a function of topography may have influenced differences in chemical concentrations in ground water between the cropped areas. However, the effects of this factor on water quality cannot be determined with the available data. The topographic map of the site (Delin and others, 1994a, fig. 5, p. 7) indicates some upland areas in each of the cropped areas and some lowland areas in areas A, D, and E. Areas B and C have more uniform elevation. Differences in topography are reflected in differences in average depth to water table between the cropped areas (table 3). The median depth to the water table was greatest beneath areas C and B and was least beneath area E.

Topographic setting and unsaturated zone properties are closely linked in the research area. Tomer and Anderson (1995) determined that the distribution of soil-water storage in area E and an area near well MC22 (fig. 1) was closely linked to the topographic setting. Similar variations presumably occur elsewhere in the research area.

Delin and others (in press) identified greater recharge in a topographic lowland (R1) than a topographic upland (R2) located 78 m away with an elevation difference of 1.4 m (area E, fig. 1). The investigators attributed greater recharge in the lowland area to three factors: (1) surface runoff, (2) fine-grained laminations found between 1 and 2 m below the upland site that reduced recharge, and (3) coarser grained sediments at the lowland site, particularly at depths greater than about 1 m. Delin and Landon (1996a) estimated that fluxes of nitrate-N and atrazine at R1 were 3.5 and 5 times greater, respectively, than corresponding fluxes at R2. In addition, elevated nitrate-N, chloride, and sulfate concentrations extended 2-3 meters deeper into the saturated zone at R1 than at R2 (Delin and others, 1997).

Concentrations of nitrate-N and chloride were not greater beneath areas with thin unsaturated zones than areas with thicker unsaturated zones. Comparison of chemical concentrations from approximately the upper 1 m of the saturated zone between MPORTs located within the same cropped area showed that concentrations of chloride and nitrate-N were significantly greater at the 400-series MPORT than at the 800-series MPORT regardless of whether the 800-series MPORT was in a similar or lower topographic setting. This probably reflects the fact that the 800-series MPORTs were on the downgradient edge of the cropped areas and likely sometimes collected a mixture of water that recharged both through the cropped areas and surrounding buffer areas.

Recharge rates based on hydrograph analysis were very similar in the different cropped areas. Average annual recharge for 1992-95 for each cropped area was 12 to 14 cm, approximately the same as the research site average of 14 cm.

Table 3. Summary statistics for depth to water table

[All data is for depth of water level below land surface in meters; Data for each cropped area includes measurements for 1991-95 for the 400- and 800-series multiport wells and 50-series observation wells]

Statistic	Cropped Area				
	A	B	C	D	E
Maximum	4.61	4.33	4.49	4.14	4.51
90th percentile	3.86	4.04	4.25	4.01	4.21
75th percentile	3.66	3.88	4.11	3.86	4.07
Median	3.34	3.71	3.95	3.41	3.00
25th percentile	3.07	3.53	3.79	2.59	1.89
10th percentile	2.94	3.40	3.65	2.50	1.8
Minimum	2.55	2.98	3.28	2.10	1.45
Number of measurements	103	107	106	120	123
Mean	3.40	3.72	3.94	3.23	2.95
Standard deviation	0.44	0.29	0.25	0.67	1.10

Summary

Ground-water quality in an unconfined sand-and-gravel aquifer was monitored during 1991-95 at the Minnesota Management Systems Evaluation Area (MSEA) near Princeton, Minnesota. The objectives of the study were to (1) describe the effects of three farming systems on ground-water quality, and (2) evaluate the factors affecting the ground-water quality and transport of agricultural chemicals at the site.

Five cropped areas were established in 1991 to evaluate the effects of three farming systems on ground-water quality: (1) a field corn-soybean, two-year rotation under ridge (conservation) tillage, split-nitrogen fertilizer application, nitrogen (N) credit for legumes, and banding of herbicides, (2) a potato-sweet corn, two-year rotation with conventional full-width (disk or chisel) tillage, split-N application, banding of herbicides for sweet corn, and broadcast application of herbicides for potatoes, and (3) field corn in consecutive years under conventional full-width tillage, split-N application, and broadcast application of herbicides.

Median background nitrate-N concentrations of 16 mg/L in 1992, reflect the effects of pre-MSEA farming activities at the site. Nitrate-N declined to a median of 2.6 mg/L by 1994-95 because of suspension of agricultural activity in the background area. Median concentrations of the sum of atrazine plus metabolites, mostly de-ethylatrazine (DEA), in the upper 1 m of the saturated zone in the background areas were 0.10 to 0.12 μg/L during 1992-95, indicating that atrazine and metabolites from pre-MSEA applications in 1990 had not fully moved out of the unsaturated zone 5 years after application. Precipitation was likely a minor source of atrazine plus metabolites and metribuzin in ground water, as indicated by the trace detections in woodland wells.

Concentrations of nitrate-N in the upper 1 m of the saturated zone were greatest beneath areas having a potato-sweet corn annual rotation (median concentrations of 23 and 22 mg/L). Concentrations of nitrate-N were least beneath one area having a field corn-soybean annual rotation (median of 14 mg/L); another area having the field corn-soybean rotation had nitrate-N concentrations similar to those beneath a continuous corn area (medians of 17 mg/L). Concentrations of nitrate-N beneath the cropped areas in the upper 1 m of the saturated zone were greater than 10 mg/L, the USEPA MCL, in 89 percent of the samples. Concentrations of nitrate-N beneath all cropped areas were greater than background concentrations during 1993-95, indicating that inputs of nitrate-N to ground water from MSEA farming systems could be detected above background levels once the effects of pre-MSEA farming activities decreased. Concentrations of nitrate-N beneath areas having the potato-sweet corn rotations were significantly greater than concentrations related to pre-MSEA farming (1992 background). Concentrations of nitrate-N beneath area B, having the corn-soybean rotation, were significantly less than those related to pre-MSEA farming. Concentrations of nitrate-N beneath the other area (D) having the corn-soybean rotation and the continuous corn farming system (area E) were not significantly different from those related to pre-MSEA farming.

Concentrations of atrazine plus metabolites, DEA, and de-isopropylatrazine (DIA), were significantly greater during 1994-95 than during 1992-93 beneath all cropped areas in the upper 1 m of the saturated zone. Concentrations of atrazine plus metabolites during 1994-95 were greatest beneath the continuous corn (median of 1.07 μg/L), intermediate beneath one cropped area

with the potato-sweet corn rotation (median of 0.37 µg/L), and least beneath the other cropped area with the potato-sweet corn rotation, the field corn-soybean rotation, and background areas (medians ranging from 0.11 to 0.21 µg/L), for which concentrations were not significantly different. Concentrations of atrazine plus metabolites during 1992-93 were mostly similar beneath the different cropped areas and background areas. Concentrations of atrazine plus metabolites were significantly greater than background concentrations related to pre-MSEA farming practices only beneath area E during 1994-95.

Concentrations of atrazine in the upper 1 m of the saturated zone beneath the cropped areas were always less than the USEPA MCL of 3 µg/L. The maximum concentration of atrazine found beneath the cropped areas was 0.14 µg/L. However, concentrations of the atrazine plus metabolites did exceed the atrazine MCL of 3 µg/L in 2 samples from beneath cropped area E. DEA was the predominant atrazine metabolite detected in ground water; the average DAR for the research area was 8.0.

The herbicides metribuzin, alachlor, and metolachlor were rarely detected in ground water and only at trace levels. These trace detections could not be linked to the MSEA farming systems with the exception of metribuzin from November 1993 to June 1995 at concentrations of 0.14-1.24 µg/L beneath area A where metribuzin was applied to potatoes.

Chloride from potassium chloride fertilizer and bromide applied to the cropped areas were used as tracers of ground water affected by chemical applications and to link concentrations of nitrate-N, sulfate, and herbicides to applications. First detection of increased chloride and bromide concentrations at the water table occurred 2 to 15 months after application. Peak chloride and bromide concentrations were measured in the upper 2 m of the saturated zone 11 to 19 months after application. First detection of increased concentrations of nitrate-N followed application by 3 to 17 months. Peak concentrations of nitrate-N in the upper 2 m of the saturated zone lagged behind application by 13 to 27 months. Increases in nitrate-N concentrations generally lagged behind increases in the concentrations of chloride and bromide tracers by a few months. Increases in concentrations of atrazine plus metabolites were first detected at the water table 11 to 23 months after application. Peak atrazine plus metabolites concentrations in the upper 2 m of the saturated zone were generally detected about 2 years after application beneath all of the cropped areas.

The travel times for chloride and bromide to ground water were longer than originally expected given the fine-to-medium grained sand texture, relatively high hydraulic conductivity, and shallow depth to water of about 2.5- to 4.5-m. These travel times overlapped with but were generally longer than travel times of seasonal oxygen and hydrogen stable-isotopic signals through the unsaturated zone. These isotopic signals, conservative indicators of water movement, indicated first detections at the water table in 1.5 to 6 months, with maximum transit times of up to 12 months in upland settings. The travel times indicate that the volume of water entering the soil during most infiltration events was generally small, 5 to 30 percent of the total volume of water stored in the unsaturated zone. Consequently, several infiltration events occurring over a period of several months were required to replace the volume of water in the unsaturated zone. Chloride and bromide apparently did not move as rapidly as recharge water.

Mass balance calculations indicated that approximately 100 percent of the chloride applied in 1991 reached ground water. The mass of bromide detected ranged from about 15 to 60 percent with an average of 36 percent of the applied amount. The mass of applied nitrogen detected as nitrate-N ranged from 13 to 50 percent with an average of 30 percent. In 6 of 8 cases, more than 35 percent of applied nitrogen was detected beneath cropped areas with the potato-sweet corn rotation. The mass of nitrogen detected beneath field corn grown in the field corn-soybean rotation was about 20 percent in 3 of 4 cases. The mass of nitrogen detected beneath field corn grown in the continuous corn system was about 20 percent during all 4 years. The mass of applied sulfur detected as sulfate ranged from about 9 to 51 percent with an average value of 27. The mass of applied atrazine that was detected as atrazine or metabolites DEA or DIA in ground water beneath cropped areas ranged from 0 to about 1 percent with an average of 0.37 percent. The percentage of metribuzin applied to area A in 1993 that reached ground water was 0.9 percent.

The masses of applied nitrogen that reached ground water appear to be reasonable in comparison to nitrogen uptake values by crops. Plant uptake and leaching, in order of importance, are the predominant sinks for nitrogen at the research site. Concentrations of nitrate-N in the oxic upper 2 to 3 m of the saturated zone were predominantly influenced by nitrate-N loading rates at the water table and by advective-dispersive transport. Between about 2 and 6 m below the water table there was a transition from oxidized to reduced ground water; the disappearance of nitrate-N at these depths is consistent with denitrification. Long travel times to ground water, small proportions of applied atrazine detected in ground water, and greater concentrations of DEA than atrazine indicate that atrazine was predominantly affected by processes occurring in the soil such as adsorption and degradation.

Concentrations of chloride, nitrate-N, sulfate, and atrazine plus metabolites in ground water were strongly a function of chemical application rate. Differences in the concentrations of nitrate-N, chloride, and sulfate were also related to the timing of chemical application and the timing of recharge in relation to crop rotation. Differences in nitrate-N concentrations were also related to differences in nitrogen uptake by crops. Other factors may have influenced the concentrations beneath different cropped areas, but their effects could not be identified.

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Appendix A

Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks

Table A. Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks[3]

[µg/L, micrograms per liter; DL, laboratory detection limit; RL, laboratory reporting limit; ≥ greater than or equal to; <, less than]

Atrazine [DL = 0.01 µg/L; RL = 0.04 µg/L]

	Cropped area					Background							
Statistic	A	B	C	D	E	1991	1992	1993	1994-95	Wood-land	Precipi-tation[1]	Equip-ment blanks	Equip-ment blanks
Maximum	0.07	0.07	0.11	0.07	0.14	0.54	0.14	0.13	1.1	0.05	2.08	0.03	0.02
99th percentile	0.07	0.07	0.11	0.07	0.14	0.54	0.14	0.13	1.1	0.05	2.05	0.02	0.01
95th percentile	0.06	0.04	0.02	0.04	0.06	0.46	0.12	0.07	0.12	0.02	1.58	0.02	0.01
90th percentile	0.05	0.03	0.01	0.03	0.04	0.27	0.08	0.07	0.08	0.01	1.09	0.01	0.01
75th percentile	0.03	0.01	0.01	0.01	0.02	0.18	0.04	0.02	0.03	0.01	0.28	0.01	<0.01
Median	0.02	0.01	<0.01	0.01	0.01	0.02	0.01	0.01	0.02	<0.01	0.1	<0.01	<0.01
25th percentile	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.02	<0.01	<0.01
10th percentile	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
5th percentile	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1st percentile	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Minimum	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Number of samples	40	67	43	49	54	31	39	33	60	47	43	58	58
Mean[2]	0.03	0.01	0.01	0.01	0.02	0.1	0.03	0.02	0.05	0.01	0.32	<0.01	<0.01
Standard Deviation[2]	0.01	0.02	0.02	0.01	0.02	0.14	0.04	0.03	0.16	0.01	0.54	0.01	<0.01
Number of samples ≥ DL	40	41	20	26	31	19	24	23	50	16	35	16	7
Percentage of samples ≥ DL	100	61	47	53	57	61	62	70	83	34	81	28	12
Number of samples ≥ RL	7	4	2	3	7	14	11	7	11	1	28	0	0
Percentage of samples ≥ RL	18	6	5	6	13	45	28	21	18	2	65	0	0

Table A. Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks[3] -- continued

[µg/L, micrograms per liter; DL, laboratory detection limit; RL, laboratory reporting limit; ≥ greater than or equal to; <, less than]

De-ethylatrazine [DL = 0.03 µg/L; RL = 0.06 µg/L]

Statistic	Cropped area					Background				Wood-land	Precipi-tation[1]	Equip-ment blanks	Equip-ment blanks
	A	B	C	D	E	1991	1992	1993	1994-95				
Maximum	1.01	0.64	0.63	0.72	4.2	1	0.3	0.32	0.44	0.22	Not Analyzed	0.21	0.02
99th percentile	1.01	0.64	0.63	0.72	4.2	1	0.3	0.32	0.44	0.22		0.11	0.01
95th percentile	0.82	0.31	0.41	0.44	2.45	0.95	0.27	0.24	0.26	0.06		<0.01	<0.01
90th percentile	0.55	0.25	0.25	0.3	1.3	0.6	0.21	0.21	0.21	0.05		<0.01	<0.01
75th percentile	0.37	0.17	0.09	0.15	0.76	0.32	0.13	0.14	0.12	0.03		<0.01	<0.01
Median	0.17	0.07	0.05	0.08	0.09	0.12	0.06	0.09	0.07	0.01		<0.01	<0.01
25th percentile	0.09	0.03	0.02	0.03	0.04	<0.01	0.03	0.02	0.01	<0.01		<0.01	<0.01
10th percentile	0.06	0.02	0.01	0.01	0.02	<0.01	0.01	<0.01	0.01	<0.01		<0.01	<0.01
5th percentile	0.05	0.02	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
1st percentile	0.04	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Minimum	0.04	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Number of samples	40	67	43	49	54	31	40	33	60	47		58	59
Mean[2]	0.26	0.12	0.09	0.12	0.5	0.23	0.08	0.09	0.09	0.02		<0.01	<0.01
Standard Deviation[2]	0.23	0.12	0.14	0.14	0.81	0.28	0.08	0.08	0.09	0.04		0.03	<0.01
Number of samples ≥ DL	40	60	31	39	44	22	30	23	43	12		2	0
Percentage of samples ≥ DL	100	90	72	80	81	71	75	70	72	26		3	0
Number of samples ≥ RL	37	39	17	30	34	21	20	19	37	3		1	0
Percentage of samples ≥ RL	93	58	40	61	63	68	50	58	62	6		2	0

Table A. Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks[3] -- continued

[µg/L, micrograms per liter; DL, laboratory detection limit; RL, laboratory reporting limit; ≥ greater than or equal to; <, less than]

De-isopropylatrazine [DL = 0.06 µg/L; RL = 0.08 µg/L]

	Cropped area					Background							
Statistic	A	B	C	D	E	1991	1992	1993	1994-95	Wood-land	Precipi-tation[1]	Equip-ment blanks	Equip-ment blanks
Maximum	0.1	0.13	0.09	0.04	0.1	0.66	0.18	0.07	0.14	0.06	Not Analyzed	<0.01	<0.01
99th percentile	0.1	0.13	0.09	0.04	0.1	0.66	0.18	0.07	0.14	0.06		<0.01	<0.01
95th percentile	0.06	0.06	0.06	0.03	0.06	0.58	0.15	0.07	0.12	0.06		<0.01	<0.01
90th percentile	0.06	0.04	0.03	0.03	0.04	0.28	0.13	0.05	0.09	0.02		<0.01	<0.01
75th percentile	0.04	0.02	0.02	0.02	0.03	0.01	0.08	0.02	0.06	0.01		<0.01	<0.01
Median	0.02	0.01	0.01	0.01	0.02	<0.01	0.03	0.01	0.02	<0.01		<0.01	<0.01
25th percentile	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	0.01	<0.01		<0.01	<0.01
10th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
5th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
1st percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Minimum	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Number of samples	40	67	43	49	54	31	40	33	60	47		58	59
Mean[2]	0.02	0.02	0.01	0.01	0.02	0.08	0.05	0.01	0.04	0.01		<0.01	<0.01
Standard Deviation[2]	0.02	0.02	0.02	0.01	0.02	0.17	0.05	0.02	0.04	0.02		<0.01	<0.01
Number of samples ≥ DL	4	5	3	0	5	7	13	2	16	3		0	0
Percentage of samples ≥ DL	10	7	7	0	9	23	33	6	27	6		0	0
Number of samples ≥ RL	1	2	2	0	1	6	10	0	11	0		0	0
Percentage of samples ≥ RL	3	3	5	0	2	19	25	0	18	0		0	0

Table A. Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks[3] -- continued

[µg/L, micrograms per liter; DL, laboratory detection limit; RL, laboratory reporting limit; ≥ greater than or equal to; <, less than]

	Sum of atrazine plus metabolites, in µg/L												
	Cropped area					Background				Wood-land	Precipi-tation[1]	Equip-ment blanks	Equip-ment blanks
	A	B	C	D	E	1991	1992	1993	1994-95				
Maximum	1.12	0.71	0.65	0.77	4.28	2.12	0.51	0.46	1.26	0.22	Not Analyzed	0.22	0.02
99th percentile	1.12	0.71	0.65	0.77	4.28	2.12	0.51	0.46	1.26	0.22		0.12	0.02
95th percentile	0.9	0.33	0.44	0.49	2.52	2.07	0.47	0.34	0.62	0.08		0.02	0.01
90th percentile	0.61	0.28	0.27	0.35	1.32	0.85	0.44	0.3	0.37	0.07		0.01	0.01
75th percentile	0.43	0.21	0.12	0.16	0.77	0.59	0.24	0.18	0.22	0.05		0.01	<0.01
Median	0.21	0.11	0.06	0.09	0.15	0.2	0.1	0.11	0.12	0.02		<0.01	<0.01
25th percentile	0.14	0.05	0.04	0.04	0.06	0.02	0.05	0.04	0.05	0.01		<0.01	<0.01
10th percentile	0.09	0.03	0.03	0.03	0.02	<0.01	0.02	0.01	0.01	<0.01		<0.01	<0.01
5th percentile	0.08	0.03	0.01	0.02	0.01	<0.01	0.02	<0.01	0.01	<0.01		<0.01	<0.01
1st percentile	0.05	0.02	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Minimum	0.05	0.02	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Number of samples	40	67	43	49	54	31	40	33	60	47		58	59
Mean[2]	0.31	0.15	0.12	0.14	0.53	0.4	0.16	0.13	0.18	0.03		0.01	<0.01
Standard Deviation[2]	0.25	0.13	0.14	0.15	0.82	0.56	0.15	0.12	0.21	0.04		0.03	<0.01
Number of samples ≥ 0.01	40	67	42	48	52	26	24	23	50	37		17	8
Percentage of samples ≥ 0.01	100	100	98	98	96	84	62	70	83	79		29	14
Number of samples ≥ 0.04	40	59	35	42	44	23	11	7	11	17		2	0
Percentage of samples ≥ 0.04	100	88	81	86	81	74	28	21	18	36		3	0

Table A. Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks[3] -- continued

[µg/L, micrograms per liter; DL, laboratory detection limit; RL, laboratory reporting limit; ≥ greater than or equal to; <, less than]

Alachlor [DL = 0.01 µg/L; RL = 0.04 µg/L; ERL = 0.07 µg/L]

Statistic	Cropped area					Background				Wood-land	Precipi-tation[1]	Equip-ment blanks	Equip-ment blanks
	A	B	C	D	E	1991	1992	1993	1994-95				
Maximum	0.07	0.14	0.22	0.06	0.02	1.08	<0.01	<0.01	0.18	0.05	1.15	0.31	0.01
99th percentile	0.07	0.14	0.22	0.06	0.02	1.08	<0.01	<0.01	0.18	0.05	0.98	0.17	0.01
95th percentile	0.03	0.02	0.02	0.01	0.01	0.49	<0.01	<0.01	0.03	0.02	0.52	0.03	<0.01
90th percentile	0.02	0.01	0.01	0.01	0.01	<0.01	<0.01	<0.01	0.01	0.01	0.31	0.01	<0.01
75th percentile	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.13	<0.01	<0.01
Median	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01
25th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01
10th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
5th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1st percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Minimum	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Number of samples	40	67	43	49	54	31	40	33	60	47	43	58	59
Mean[2]	0.01	<0.01	0.01	<0.01	<0.01	0.05	<0.01	<0.01	0.01	<0.01	0.12	0.01	<0.01
Standard Deviation[2]	0.01	0.02	0.03	0.01	<0.01	0.21	<0.01	<0.01	0.02	0.01	0.22	0.04	<0.01
Number of samples ≥ DL	11	10	7	8	9	2	0	0	19	8	30	7	3
Percentage of samples ≥ DL	28	15	16	16	17	6	0	0	32	17	70	12	5
Number of samples ≥ RL	2	2	1	1	0	2	0	0	1	2	21	3	0
Percentage of samples ≥ RL	5	3	2	2	0	6	0	0	2	4	49	5	0

Table A. Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks[3] -- continued

[µg/L, micrograms per liter; DL, laboratory detection limit; RL, laboratory reporting limit; ≥ greater than or equal to; <, less than]

2,6-Diethylanaline [DL = 0.01 µg/L; RL = 0.04 µg/L]

Statistic	Cropped area					Background				Wood-land	Precipi-tation[1]	Equip-ment blanks	Equip-ment blanks
	A	B	C	D	E	1991	1992	1993	1994-95				
Maximum	<0.01	<0.01	0.01	0.01	<0.01	0.03	<0.01	<0.01	0.02	0.01	Not Analyzed	<0.01	0.01
99th percentile	<0.01	<0.01	0.01	0.01	<0.01	0.03	<0.01	<0.01	0.02	0.01		<0.01	0.01
95th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
90th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
75th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Median	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
25th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
10th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
5th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
1st percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Minimum	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Number of samples	40	67	43	54	54	31	40	33	60	47		58	59
Mean[2]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Standard Deviation[2]	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01		<0.01	<0.01
Number of samples ≥ DL	0	0	1	1	0	1	0	0	2	1		0	3
Percentage of samples ≥ DL	0	0	2	2	0	3	0	0	3	2		0	5
Number of samples ≥ RL	0	0	0	0	0	0	0	0	0	0		0	0
Percentage of samples ≥ RL	0	0	0	0	0	0	0	0	0	0		0	0

Table A. Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks[3] -- continued

[µg/L, micrograms per liter; DL, laboratory detection limit; RL, laboratory reporting limit; ≥ greater than or equal to; <, less than]

Metolachlor [DL = 0.01 µg/L; RL = 0.04 µg/L]

	Cropped area					Background							
Statistic	A	B	C	D	E	1991	1992	1993	1994-95	Woodland	Precipitation[1]	Equipment blanks	Equipment blanks
Maximum	0.05	<0.01	0.02	<0.01	0.02	<0.01	<0.01	<0.01	0.01	<0.01	0.42	<0.01	<0.01
99th percentile	0.05	<0.01	0.02	<0.01	0.02	<0.01	<0.01	<0.01	0.01	<0.01	0.41	<0.01	<0.01
95th percentile	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.33	<0.01	<0.01
90th percentile	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.25	<0.01	<0.01
75th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.08	<0.01	<0.01
Median	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01
25th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
10th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
5th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1st percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Minimum	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Number of samples	40	67	43	54	54	31	40	33	60	47	42	58	59
Mean[2]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	<0.01	<0.01
Standard Deviation[2]	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.11	<0.01	<0.01
Number of samples ≥ DL	7	0	3	0	1	0	0	0	1	0	25	0	0
Percentage of samples ≥ DL	18	0	7	0	2	0	0	0	2	0	60	0	0
Number of samples ≥ RL	1	0	0	0	0	0	0	0	0	0	14	0	0
Percentage of samples ≥ RL	3	0	0	0	0	0	0	0	0	0	33	0	0

Table A. Herbicide detections and statistical distribution of concentrations for cropped areas during 1992-95, background areas during 1991, 1992, 1993, 1994-95, woodland wells during 1991-95, precipitation during 1993-95, and blanks[3] -- continued

[µg/L, micrograms per liter; DL, laboratory detection limit; RL, laboratory reporting limit; ≥ greater than or equal to; <, less than]

Metribuzin [DL = 0.03 µg/L; RL = 0.06 µg/L]

	Cropped area					Background							
Statistic	A	B	C	D	E	1991	1992	1993	1994-95	Wood-land	Precipi-tation[1]	Equip-ment blanks	Equip-ment blanks
Maximum	1.24	0.02	0.03	0.03	0.03	<0.01	<0.01	0.09	0.05	0.07	0.1	0.09	0.05
99th percentile	1.24	0.02	0.03	0.03	0.03	<0.01	<0.01	0.09	0.05	0.07	0.1	0.04	0.05
95th percentile	0.62	0.01	0.02	0.02	0.02	<0.01	<0.01	0.02	0.04	0.03	0.07	<0.01	<0.01
90th percentile	0.5	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.02	0.04	<0.01	<0.01
75th percentile	0.14	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01
Median	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
25th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
10th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
5th percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1st percentile	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Minimum	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Number of samples	40	67	43	54	52	31	40	33	60	47	44	58	59
Mean[2]	0.13	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01
Standard Deviation[2]	0.26	0.01	0.01	0.01	0.01	<0.01	<0.01	0.02	0.01	0.01	0.02	0.01	0.01
Number of samples ≥ DL	15	0	1	2	2	0	0	1	7	3	13	1	2
Percentage of samples ≥ DL	38	0	2	4	4	0	0	3	12	6	30	2	3
Number of samples ≥ RL	14	0	0	0	0	0	0	1	0	1	4	1	0
Percentage of samples ≥ RL	35	0	0	0	0	0	0	3	0	2	9	2	0

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[1] Sources of data on herbicide concentrations in precipitation at Princeton, Minnesota, MSEA: 1993-94 from Lin (1997), 1995 from Mitton and others (1996).

[2] For the purpose of calculating mean and standard deviation, concentrations below the detection limit were either assigned the below detection limit values reported by the laboratory or, when reported as <0.01 µg/L, were assigned a value of 0.00 µg/L.

[3] Values shown in the table are based upon those reported by the analytical laboratory, even if the reported values were less than the reporting and detection limits. The reported concentrations are the best estimate of the actual concentration even though the uncertainty associated with the quantifying concentrations below the reporting and detection limits is much greater than for values above the reporting limit. The detection limit is defined as the minimum concentration at which the analyte can be routinely identified by the GC/MS. The reporting limit is defined as the concentration at which the analyte can be reliably and consistently quantified by GC/MS.

Appendix B

Mass balances for each cropped area for chloride, bromide, nitrogen, sulfur, atrazine, and metribuzin

Table B1. Mass balances for each cropped area for chloride

[--, no data]

Year	Field	Crop	Amount applied (kg/ha)	Mass detected in ground water (kg/ha)	Percent of applied detected in ground water	Time of peak mass	Time between first application and peak mass (months)	Time of first detection in ground water	Time between first application and first detection (months)
1991	A	Potatoes	337	318	95	June 92	14	Aug. 91	4
1991	B	Soybeans	84	82	97	June 92	14	Aug. 91	4
1991	C	Sweet corn	84	82	98	Oct. 92	18	Aug. 91	4
1991	D	Field corn	84	114	135	June 92	16	Dec. 91	8
1991	E	Field corn	84	96	114	June 92	14	Dec. 91	8
1992	A	Sweet corn	34	Not detectable	--	--	--	--	--
1992	B	Field corn	34	Not detectable	--	--	--	--	--
1992	C	Potatoes	302	215	71	Nov. 93	19	Apr. 93	12
1992	D	Soybeans	Not applied	--	--	--	--	--	--
1992	E	Field corn	34	32	96	Nov. 93	19	Aug. 93	15
1993	A	Potatoes	321	218	68	June 94	14	Aug. 93	4
1993	B	Soybeans	Not applied	--	--	--	--	--	--
1993	C	Sweet corn	34	Not detectable	--	--	--	--	--
1993	D	Field corn	34	14	42	June 94	14	Nov. 93	7
1993	E	Field corn	34	18	52	June 94	14	June 94	13
1994	A	Sweet corn	34	Not detectable	--	--	--	--	--
1994	B	Field corn	34	30	[1]90	Aug. 95	16	Apr. 95	11
1994	C	Potatoes	350	167	[1]48	Aug. 95	16	Apr. 95	12
1994	D	Soybeans	Not applied	--	--	--	--	--	--
1994	E	Field corn	34	11	[1]34	Aug. 95	16	Apr. 95	11
		Maximum			135		19		15
		Average			80		16		9
		Minimum			34		14		4

Table B2. Mass balances for each cropped area for bromide (400-series MPORTS/800-series MPORTS)
[MPORTS, multiport wells; --, no data]

Year	Field	Crop	Amount applied (kg/ha)	Mass detected in ground water (kg/ha)	Percent of applied detected in ground water	Time of peak mass	Time between first application and peak mass (months)	Time of first detection in ground water	Time between first application and first detection (months)
1991	A	Potatoes	Not applied	--	--	--	--	--	--
1991	B	Soybeans	Not applied	--	--	--	--	--	--
1991	C	Sweet corn	Not applied	--	--	--	--	--	--
1991	D	Field corn	Not applied	--	--	--	--	--	--
1991	E	Field corn	Not applied	--	--	--	--	--	--
1992	A	Sweet corn	Not applied	--	--	--	--	--	--
1992	B	Field corn	15 / 15	4.1 / 6.0	27 / 40	June 93 / June 93	12/12	Aug. 92 / Oct. 92	2/4
1992	C	Potatoes	Not applied	--					
1992	D	Soybeans	15 / 15	4.9 / 9.0	33 / 60	Aug. 93 / Aug. 93	14 / 14	Oct. 92 / Apr. 93	4/10
1992	E	Field corn	15 / 15	3.6 / 5.0	27 / 33	Nov. 93 / Nov. 93	17 / 17	Apr. 93 / June 93	10/12
1993	A	Potatoes	Not applied	--	--	--	--	--	--
1993	B	Soybeans	Not applied	--	--	--	--	--	--
1993	C	Sweet corn	Not applied	--	--	--	--	--	--
1993	D	Field corn	Not applied	--	--	--	--	--	--
1993	E	Field corn	Not applied	--	--	--	--	--	--
1994	A	Sweet corn	Not applied	--	--	--	--	--	--
1994	B	Field corn	22 / 22	7.6 / 7.8	34 / 35	June 95 / Apr. 95	13 / 11	Aug. 94 / Aug. 94	3/3
1994	C	Potatoes	Not applied	--	--	--	--	--	--
1994	D	Soybeans	22 / 22	3.5 / 11.9	15 / 53	June 95 / June 95	13 / 13	Apr. 95 / Apr. 95	11/11
1994	E	Field corn	22 / 22	5.8 / 10.9	[1]26 / [1]48	Aug. 95 / Aug. 95	16 / 16	Apr. 95 / Oct. 94	11/6
		Maximum			34 / 60		17 / 17		11/12
		Average			27 / 45		14 / 14		6/8
		Minimum			15 / 33		12/11		2/3

Table B3. Mass balances for each cropped area for nitrogen

[--, no data]

Year	Field	Crop	Amount applied (kg/ha)	Mass detected in ground water (kg/ha)	Percent of applied detected in ground water[2]	Time of peak mass	Time between first application and peak mass (months)	Time of first detection in ground water	Time between first application and first detection (months)
1991	A	Potatoes	224	106	47	Aug. 92	17	Dec. 91	7
1991	B	Soybeans	Not applied	--	--	--	--	--	--
1991	C	Sweet corn	157	72	46	Oct. 92	17	Aug. 92	15
1991	D	Field corn	157	33	21	Aug. 93	27	Oct. 92	17
1991	E	Field corn	157	38	24	June 93	25	Aug. 92	15
1992	A	Sweet corn	168	44	24	Aug. 93	15	Apr. 93	11
1992	B	Field corn	157	27	17	Nov. 93	18	Aug. 93	15
1992	C	Potatoes	146	52	36	Nov. 93	18	June 93	13
1992	D	Soybeans	Not applied	--	--	--	--	--	--
1992	E	Field corn	168	38	23	June 94	25	Aug. 93	15
1993	A	Potatoes	188	77	41	June 94	13	Nov. 93	7
1993	B	Soybeans	Not applied	--	--	--	--	--	--
1993	C	Sweet corn	168	85	50	Oct. 94	17	Apr. 94	11
1993	D	Field corn	175	80	45	June 94	13	Nov. 93	6
1993	E	Field corn	168	36	21	Apr. 95	23	Aug. 94	15
1994	A	Sweet corn	162	63	[1]39	Aug. 95	16	Apr. 95	11
1994	B	Field corn	211	48	[1]23	Aug. 95	16	Aug. 94	3
1994	C	Potatoes	175	24	[1]13	Aug. 95	16	Apr. 95	11
1994	D	Soybeans	Not applied	--	--	--	--	--	--
1994	E	Field corn	162	26	[1]16	June 95	13	June 95	13
		Maximum			50		27		17
		Average			30		18		12
		Minimum			13		13		3

Table B3. Mass balances for each cropped area for nitrogen -- continued

[--, no data]

Year	Field	Crop	Total plant nitrogen uptake (grain plus stover) (kg/ha)	Percent of applied total plant uptake	Nitrogen uptake by grain (kg/ha)	Percent of applied uptake by grain	Percent sum of total uptake plus detected in ground water	Percent sum of uptake by grain plus detected in ground water
1991	A	Potatoes	--	--	--	--	--	--
1991	B	Soybeans	--	--	--	--	--	--
1991	C	Sweet corn	62	39	--	--	85	--
1991	D	Field corn	140	89	110	70	110	91
1991	E	Field corn	137	87	102	65	111	89
1992	A	Sweet corn	52	33	--	--	57	--
1992	B	Field corn	121	77	84	54	94	71
1992	C	Potatoes	--	--	--	--	--	--
1992	D	Soybeans	--	--	--	--	--	--
1992	E	Field corn	150	89	79	47	112	70
1993	A	Potatoes	--	--	--	--	--	--
1993	B	Soybeans	--	--	--	--	--	--
1993	C	Sweet corn	56	33	--	--	83	
1993	D	Field corn	62	35	46	26	80	71
1993	E	Field corn	47	28	36	21	49	42
1994	A	Sweet corn	83	51	--	--	90	--
1994	B	Field corn	101	58	78	37	81	60
1994	C	Potatoes	--	--	--	--	--	--
1994	D	Soybeans	--	--	--	--	--	--
1994	E	Field corn	95	59	73	45	75	61
		Maximum	150			70	112	91
		Average	92			46	86	69
		Minimum	47			21	49	42

Table B4. Mass balances for each cropped area for sulfur

[--, no data]

Year	Field	Crop	Amount applied (kg/ha)	Mass detected in ground water (kg/ha)	Percent of applied detected in ground water[3]	Time of peak mass	Time between first application and peak mass (months)	Time of first detection in ground water	Time between first application and first detection (months)
1991	A	Potatoes	56	14	25	Oct. 92	17	Aug. 92	15
1991	B	Soybeans	Not applied	--	--	--	--	--	--
1991	C	Sweet corn	13	2.7	20	Oct. 92	17	Oct. 92	17
1991	D	Field corn	13	2.2	16	Oct. 92	17	Oct. 92	17
1991	E	Field corn	13	2.3	17	June 93	25	Oct. 92	17
1992	A	Sweet corn	13	Not detectable	--	--	--	--	--
1992	B	Field corn	13	1.5	11	Nov. 93	18	Nov. 93	18
1992	C	Potatoes	45	13	29	Nov. 93	18	Aug. 93	15
1992	D	Soybeans	Not applied	--	--	--	--	--	--
1992	E	Field corn	13	3.4	26	Apr. 94	23	Apr. 94	23
1993	A	Potatoes	52	26	51	Aug. 94	15	June 93	13
1993	B	Soybeans	Not applied	--	--	--	--	--	--
1993	C	Sweet corn	13	4.4	33	Aug. 94	15	June 94	13
1993	D	Field corn	13	4.6	34	June 94	13	June 94	13
1993	E	Field corn	13	5.2	39	Oct. 94	17	Aug. 94	17
1994	A	Sweet corn	13	6.8	[1]51	Aug. 95	15	Aug. 95	15
1994	B	Field corn	13	1.1	9	June 95	13	June 95	13
1994	C	Potatoes	64	7.5	[1]12	Aug. 95	15	June 95	13
1994	D	Soybeans	Not applied	--	--	--	--	--	--
1994	E	Field corn	13	3.2	[1]24	Aug. 95	15	June 95	13
		Maximum			51		25		23
		Average			27		17		17
		Minimum			9		13		13

Table B5. Mass balances for each cropped area for atrazine plus metabolites

[--, no data]

Year	Field	Crop	Amount applied (kg/ha)	Mass detected in ground water (kg/ha)	Percent of applied detected in ground water[4]	Time of peak mass	Time between first application and peak mass (months)	Time of first detection in ground water	Time between first application and first detection (months)
1991	A	Potatoes	Not applied	--	--	--	--	--	--
1991	B	Soybeans	Not applied	--	--	--	--	--	--
1991	C	Sweet corn	0.47	0.0007	0.13	June 93	25	Apr. 93	23
1991	D	Field corn	0.47	0	0	--	--	--	--
1991	E	Field corn	1.68	0.0012	0.08	June 93	25	Apr. 93	23
1992	A	Sweet corn	0.4	0.0041	1.01	June 94	25	Aug. 93	15
1992	B	Field corn	0.56	0.0019	0.34	June 94	25	Nov. 93	18
1992	C	Potatoes	Not applied	--	--	--	--	--	--
1992	D	Soybeans	Not applied	--	--	--	--	--	--
1992	E	Field corn	1.68	0.0041	0.24	Apr. 94	23	Apr. 94	23
1993	A	Potatoes	Not applied	--	--	--	--	--	--
1993	B	Soybeans	Not applied	--	--	--	--	--	--
1993	C	Sweet corn	0.47	0.0014	0.3	June 95	25	Oct. 94	17
1993	D	Field corn	0.47	0.001	0.21	June 95	25	Oct. 94	17
1993	E	Field corn	1.68	0.0167	1	Apr. 95	23	Aug. 94	15
1994	A	Sweet corn	0.47	0.0018	0.36	June 95	13	June 95	13
1994	B	Field corn	0.47	0.0021	0.44	June 95	13	Apr. 95	11
1994	C	Potatoes	Not applied	--	--	--	--	--	--
1994	D	Soybeans	Not applied	--	--	--	--	--	--
1994	E	Field corn	1.68	Not detected before end of sampling					
		Maximum			1.01		25		23
		Average			0.37		22		18
		Minimum			0		13		11

Table B6. Mass balances for each cropped area for metribuzin

[--, no data]

Year	Field	Crop	Amount applied (kg/ha)	Mass detected in ground water (kg/ha)	Percent of applied detected in ground water	Time of peak mass	Time between first application and peak mass (months)	Time of first detection in ground water	Time between first application and first detection (months)
1991	A	Potatoes	0.56	0	0	--	--	--	--
1991	B	Soybeans	0.16	0	0	--	--	--	--
1991	C	Sweet corn	Not applied	--	--	--	--	--	--
1991	D	Field corn	Not applied	--	--	--	--	--	--
1991	E	Field corn	Not applied	--	--	--	--	--	--
1992	A	Sweet corn	Not applied	--	--	--	--	--	--
1992	B	Field corn	Not applied	--	--	--	--	--	--
1992	C	Potatoes	0.42	0	0	--	--	--	--
1992	D	Soybeans	0.07	0	0	--	--	--	--
1992	E	Field corn	Not applied	--	--	--	--	--	--
1993	A	Potatoes	0.41	0.0038	0.9	June 94	13	Aug. 93	3
1993	B	Soybeans	0.08	0	0	--	--	--	--
1993	C	Sweet corn	Not applied	--	--	--	--	--	--
1993	D	Field corn	Not applied	--	--	--	--	--	--
1993	E	Field corn	Not applied	--	--	--	--	--	--
1994	A	Sweet corn	Not applied	--	--	--	--	--	--
1994	B	Field corn	Not applied	--	--	--	--	--	--
1994	C	Potatoes	0.41	0	0	--	--	--	--
1994	D	Soybeans	0.08	0	0	--	--	--	--
1994	E	Field corn	Not applied	--	--	--	--	--	--

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