POSTFLOOD OCCURENCE OF SELECTED AGRICULTURAL CHEMICALS AND VOLATILE ORGANIC COMPOUNDS IN NEAR-SURFACE UNCONSOLIDATED AQUIFERS

IN THE UPPER MISSISSIPPI RIVER BASIN

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U.S. GEOLOGICAL SURVEY CIRCULAR 1120-G

Front cover—A scene from Minnesota shows the problems caused by the 1993 floods (Bernard Volker, Herman, Minnesota).

Back cover—View of Spirit of St. Louis Airport, Chesterfield, Mo. (Srenco Photography, St. Louis, Mo.)

Field Hydrologist making streamflow measurements (U.S. Geological Survey)

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By Dana W. Kolpin and E. Michael Thurman

Floods in the Upper Mississippi River Basin, 1993

U.S. GEOLOGICAL SURVEY CIRCULAR 1120-G

U.S. DEPARTMENT OF THE INTERIOR
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FOREWORD

During spring and summer 1993, record flooding inundated much of the upper Mississippi River Basin. The magnitude of the damages—in terms of property, disrupted business, and personal trauma—was unmatched by any other flood disaster in United States history. Property damage alone is expected to exceed $10 billion. Damaged highways and submerged roads disrupted overland transportation throughout the flooded region. The Mississippi and the Missouri Rivers were closed to navigation before, during, and after the flooding. Millions of acres of productive farmland remained under water for weeks during the growing season. Rills and gullies in many tilled fields are the result of the severe erosion that occurred throughout the Midwestern United States farmbelt. The hydrologic effects of extended rainfall throughout the upper Midwestern United States were severe and widespread. The banks and channels of many rivers were severely eroded, and sediment was deposited over large areas of the basin's flood plain. Record flows submerged many areas that had not been affected by previous floods. Industrial and agricultural areas were inundated, which caused concern about the transport and fate of industrial chemicals, sewage effluent, and agricultural chemicals in the floodwaters. The extent and duration of the flooding caused numerous levees to fail. One failed levee on the Raccoon River in Des Moines, Iowa, led to flooding of the city's water treatment plant. As a result, the city was without drinking water for 19 days.

As the Nation's principal water-science agency, the U.S. Geological Survey (USGS) is in a unique position to provide an immediate assessment of some of the hydrological effects of the 1993 flood. The USGS maintains a hydrologic data network and conducts extensive water-resources investigations nationwide. Long-term data from this network and information on local and regional hydrology provide the basis for identifying and documenting the effects of the flooding. During the flood, the USGS provided continuous streamflow and related information to the National Weather Service (NWS), the U.S. Army Corps of Engineers, the Federal Emergency Management Agency (FEMA), and many State and local agencies as part of its role to provide basic information on the Nation's surface- and ground-water resources at thousands of locations across the United States. The NWS has used the data in forecasting floods and issuing flood warnings. The data have been used by the Corps of Engineers to operate water diversions, dams, locks, and levees. The FEMA and many State and local emergency management agencies have used USGS hydrologic data and NWS forecasts as part of the basis of their local flood-response activities. In addition, USGS hydrologists are conducting a series of investigations to document the effects of the flooding and to improve understanding of the related processes. The major initial findings from these studies will be reported in this Circular series as results become available.

U.S. Geological Survey Circular 1120, *Floods in the Upper Mississippi River Basin, 1993*, consists of individually published chapters that will document the effects of the 1993 flooding. The series includes data and findings on the magnitude and frequency of peak discharges; precipitation; water-quality characteristics, including nutrients and man-made contaminants; transport of sediment; assessment of sediment deposited on flood plains; effects of inundation on ground-water quality; flood-discharge volume; effects of reservoir storage on flood peaks; stream-channel scour at selected bridges; extent of flood-plain inundation; and documentation of geomorphologic changes.

Director
January 11, 1995

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter
	Area	
acre	0.4047	hectares

Milligram per liter (mg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (milligrams) of solute per unit volume (liter) of water.
Microgram per liter (µg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (micrograms) of solute per unit volume (liter) of water.

Postflood Occurrence of Selected Agricultural Chemicals and Volatile Organic Compounds in Near-Surface Unconsolidated Aquifers in the Upper Mississippi River Basin, 1993

By Dana W. Kolpin *and* E. Michael Thurman

Abstract

The historic stream flooding and intense rainfall across the upper Mississippi River Basin during summer 1993 had an immediate effect on near-surface unconsolidated aquifers by raising the water levels closer to the land surface. The objective of this study was to determine if this flooding also had immediate effects on ground-water quality. Water samples were collected during September and October 1993 from 110 wells completed in near-surface unconsolidated aquifers and were analyzed for herbicides, herbicide metabolites, inorganic nutrients, and volatile organic compounds. The results of these samples were compared with those obtained during summer 1991 or 1992. The difference was not statistically significant in the frequency of herbicide detection, total herbicide concentration, nitrate concentration, or the frequency of volatile organic compound detection between water samples collected in 1991 and 1992 and those collected in 1993 when all 110 wells were considered collectively. However, water samples from the Missouri River alluvial aquifer had a fourfold increase in the frequency of herbicide detection. There also appears to be a relation between increases in total herbicide concentration and the occurrence of stream flooding near a well. Water samples from wells that had at least a 20-percent increase in dissolved-oxygen concentration had the greatest frequency of substantial changes in total herbicide concentration and substantial increases in nitrate concentration. Increased dissolved-oxygen concentration could indicate areas where recharge has increased as a result of extensive stream flooding and intense rainfall. An inverse relation was determined between well depth and changes (increase or decrease) in total herbicide concentration. Water in shallow wells more quickly reflect changes in water quality in response to changes in recharge. Significantly more urban residential and industrial land use was within a 30-meter radius of the well for wells in which volatile organic compounds were detected. Because water moves more slowly along ground-water flow paths compared with surface-water runoff, additional information is required to determine long-term effects of the 1993 flood on ground-water quality.

INTRODUCTION

Flooding was severe across large parts of the upper Mississippi River Basin during summer 1993 (fig. 1). This flooding was unprecedented in terms of its extent, long duration, and extensive damage. At 45 U.S. Geological Survey (USGS) streamflow-gaging stations in 8 Midwestern States, peak discharges exceeded 100-year recurrence intervals (Parrett and others, 1993). At 41 USGS streamflow-gaging stations, the peak discharge was greater than the previous maximum discharge. This record flooding during summer 1993 was facilitated by a wetter-than-normal spring that kept much of the soils in the upper Midwest saturated and a persistent weather pattern that created intense rainfall from June through August. Rainfall during July 1993 was more than 150 percent of normal (1961–90) over much of the upper Mid-

Figure 1. An example of damage caused when the Mississippi River breached a levee near the southern tip of Illinois.

west and more than 400 percent of the normal in several areas (Hillaker, 1993; Wahl and others, 1993).

The 1993 flood also affected the quality of surface waters in the upper Mississippi River Basin. Data collected from the Mississippi River and its tributaries during the flood showed that the large volumes of water did not have the anticipated dilutional effect on the concentrations of agricultural chemicals that were being transported in the river, but simply flushed increased amounts into the river systems (Goolsby and others, 1993). The concentrations of agricultural chemicals in 1993 were similar to those measured at much lower flows during 1991 and 1992, but the corresponding daily chemical loads that were being transported were substantially larger. The total atrazine load transported to the Gulf of Mexico from April through August 1993 was about 80 percent higher than that for the same period in 1991 and about 235 percent higher than that in 1992 (Goolsby and others, 1993).

Ground water is the major source of drinking water in the upper Midwest, and conventional water-treatment practices do not remove most agricultural chemicals. The large increases in the load of agricultural chemicals that were being transported in surface waters in the upper Mississippi River Basin from the 1993 flood raised the concern that transport of these chemicals to ground water, particularly alluvial aquifers, also could be increasing. Possible modes of chemical transport to ground water from flooding include reversed hydraulic gradients due to prolonged high river stages (fig. 2), infiltration of water from overbank flooding (fig. 3), and direct flow down the well casing through inundation of a well (fig. 4).

The 1993 flood increased ground-water recharge and caused an immediate increase in water levels in unconsolidated aquifers. For example, the increase in water level in a well completed in the Mississippi River alluvium in eastern Iowa, is shown in figure 5. About 40 percent of the USGS water-level monitoring wells completed in unconsolidated aquifers in Iowa had the highest water level for their period of record (D. Sneck-Fahrer, U.S. Geological Survey, oral commun., 1994).

Purpose and Scope

The purpose of this study was to determine whether the 1993 flood affected the water quality of near-surface aquifers in the upper Mississippi River Basin. This report presents and summarizes information on the concentrations of agricultural chemicals and volatile organic compounds in water samples from near-

Figure 2. Flood conditions along the Missouri River in west-central Missouri, July 1993.

Figure 3. Aerial view of the Iowa River in eastern Iowa after floodwaters had receded (September 1993). The recent sediment deposition clearly denotes the maximum extent of floodwater inundation. Note the amount of water left behind in the low-lying areas.

Figure 4. An inundated municipal well along the Cedar River in eastern Iowa.

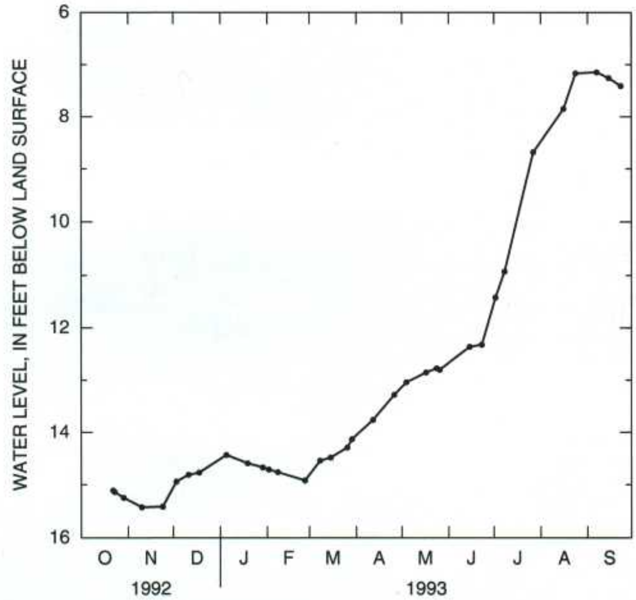

Figure 5. Water level during the 1993 water year for a well completed in the Mississippi River alluvium in eastern Iowa.

surface unconsolidated aquifers in the upper Mississippi River Basin collected during September and October 1993, which was shortly after the worst of the flooding.

Ground water moves slowly compared with surface water. The rate of ground-water movement can vary greatly depending on the materials through which the water passes, the hydraulic conductivity of the unsaturated zone, and the distance from the land surface to the saturated zone. Consequently, additional information is required to determine long-term effects of the 1993 flood on the water quality of near-surface aquifers. For example, changes in the nitrate concentrations of ground water lagged behind changes in the amounts of nitrogen fertilizer usage by about 4 to 19 months (Hall, 1992).

Results of Previous Studies

During 1991, the USGS performed a reconnaissance study to determine the hydrogeologic, seasonal, and geographic distribution of herbicides and nitrate in near-surface aquifers of the midcontinental United States (Kolpin and Burkart, 1991; Burkart and Kolpin, 1993; Kolpin, Burkart, and Thurman, 1993, 1994). Near-surface aquifers were defined as having the top of the aquifer material about 15 m below land surface. A statistical design was used to select 303 wells from which water samples were collected in March or April (preplanting) and July or August (postplanting) 1991. However, seven of these wells could only be sampled once during the 1991 study and 10 water samples could not be analyzed because of lost or broken bottles. Samples were analyzed for 11 herbicides, 2 triazine herbicide metabolites, and 4 inorganic nutrients.

Herbicides or triazine metabolites were detected in about 24 percent of the 589 samples collected for analysis during 1991. Results of this study showed that water from unconsolidated aquifers is more likely to contain herbicides than water from bedrock aquifers (frequency of detection 34 percent compared with 18 percent). Recharge rates generally are faster and recharge sources are in closer proximity to the unconsolidated aquifers than to the bedrock aquifers because of such differences as aquifer geometry and the likelihood of confining conditions (Kolpin and others, 1994). Ground-water samples from wells located within 30 m of a stream had more than twice the frequency of herbicide detection than of wells with no streams nearby (48 percent compared with 22 percent). Because almost all sampled wells within 30 m of a stream were completed in alluvial aquifers, this difference in frequency of herbicide detection could be caused by a hydraulic connection between aquifers and streams. Frequencies of detection and concentrations of herbicides are much larger in streams than in aquifers of the midcontinent (Thurman and others, 1992; Goolsby and Battaglin, 1993). Therefore, recharge to an aquifer by a stream could be a source of herbicide contamination to the aquifer (Squillace and others, 1993).

During 1992, the USGS conducted a follow-up study to investigate why herbicides were not detected in greater than 70 percent of the samples from near-surface aquifers sampled in 1991. By using a stratified-random procedure, 101 wells were selected from the 1991 study network and were resampled once during July or August 1992. The same 13 herbicide compounds and 4 inorganic nutrients were analyzed as in the 1991 study, as well as an additional 45 herbicides, insecticides, and metabolites. A subset of these 101 wells also was sampled for 63 volatile organic compounds.

A pesticide or pesticide metabolite was detected in ground water from about 62 percent of the 101 wells sampled (Kolpin, Goolsby, and others, 1993). The greater frequency of detection during 1992 was the result of an increased number of pesticides and metabolites analyzed and a more sensitive analytical method that had reporting limits that were about an order of magnitude less than those used in 1991.

Ground water from 117 wells were analyzed for tritium concentrations during either the 1991 or 1992 study. The combination of tritium's short half-life (12.3 years), low rate of natural production, and large inputs caused by nuclear testing makes it a useful tool for determining water that has recharged aquifers since 1953 (Bradbury, 1991). For this study, no pesticide or pesticide metabolite concentrations were determined (at 0.05 μg/L reporting limits) in wells containing "old" water. Because agricultural chemicals, such as atrazine, have been used to enhance crop yields only during the last 40 years, the absence of pesticide detection in wells that contain water recharged before 1953 ("old" water) was expected.

STUDY DESIGN AND METHODS

Because the greatest effect on water quality of near-surface aquifers was expected in the areas with the greatest rainfall and stream flooding, the study region was defined as the area with more than 150 percent of normal rainfall from April 1 to July 31, 1993, (Climate Analysis Center, National Weather Service, written commun., 1993) (fig. 6). Information from the 1991–1992 studies was used to select wells that would have the greatest potential for determining the immediate effects of the 1993 flood on ground-water quality. The initial well selection identified 114 wells from the network that were completed in unconsolidated aquifers that contained "new" (post-1953) water and were located in the high-rainfall region. However, six of these wells could not be sampled as a result of either the well owner declining to participate in the study or continued inundation by flood water; two of these wells were replaced with alternative sampling wells known to be in an area with flood problems during 1993. One of these alternative wells happen to reside outside the study region. The 110 wells selected for study were sampled during September or October 1993.

Data-Collection Methods

Methods to collect and process the water samples were the same as those used for the 1991 and 1992 studies (Kolpin and Burkart, 1991; Kolpin, Goolsby, and others, 1993). All samples were collected by USGS personnel with equipment constructed of materials, such as glass and stainless steel, that would not leach or adsorb organic compounds. Decontamination procedures were implemented to prevent cross-contamination of water between wells and samples. Wells were purged before sampling until pH, water temperature, and specific conductance stabilized. Where possible, water levels were measured before purging. However, water levels could be measured in only 25 of the 110 wells sampled. Well owners were interviewed to determine how the flooding and intense rainfall may have affected the area that surrounds the sampled wells.

The concentrations of 11 herbicides (alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, propazine, prometryn, simazine, and terbutryn) and 2 triazine herbicide metabolites [deethylatrazine (DEA), deisopropylatrazine (DIA)] were determined by extraction on disposable C-18 solid-phase extraction cartridges followed by gas chromatography/mass spectrometry (GC/MS) (Thurman and others, 1990; Meyer and others, 1993). The analytical reporting limit for these herbicides and her-

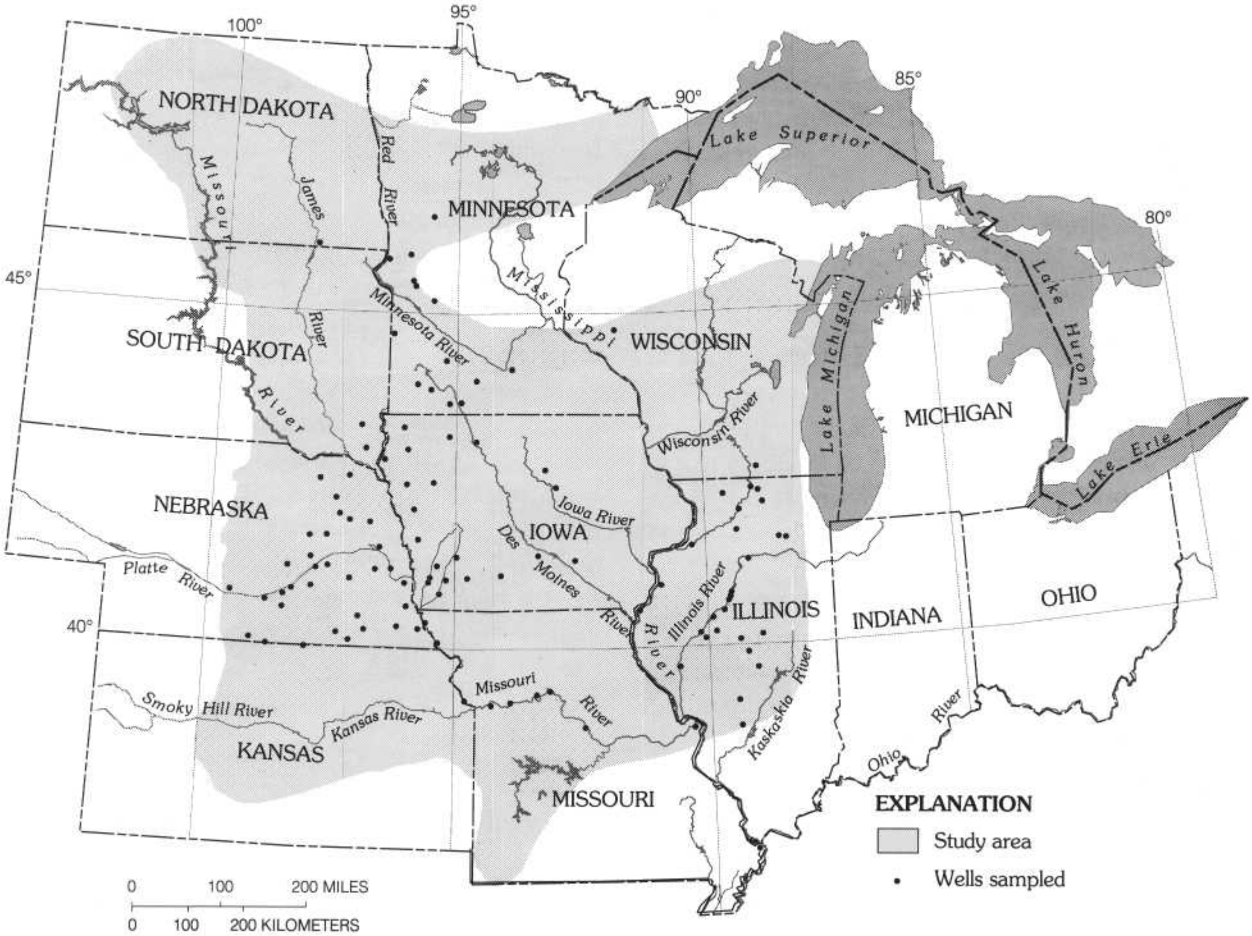

Figure 6. Location of study region in the upper Mississippi River Basin and the 110 wells sampled for this study. The shaded region represents an area with greater than 150 percent of normal rainfall from April 1 to July 31, 1993 (Climate Analysis Center, National Weather Service, written commun., 1993).

bicide metabolites was 0.05 µg/L. The total herbicide concentration, which was defined here as the sum of the concentrations of the 11 herbicides and 2 triazine metabolites determined by GC/MS, was calculated for each sample. In addition, an alachlor metabolite, ethanesulfonic acid (ESA), was extracted and isolated by solid-phase extraction and analyzed by immunoassay (Aga and others, 1994). The analytical reporting limit for ESA was 0.10 µg/L.

The concentrations of dissolved nitrite, nitrite plus nitrate (hereafter referred to as "nitrate"), ammonium, and orthophosphate were determined by colorimetric methods (Fishman and Friedman, 1989). The analytical reporting limit for these nutrient compounds was 0.01 mg/L, except for nitrate which was 0.05 mg/L.

The concentrations of the 63 volatile organic compounds were analyzed in unacidified water samples according to U.S. Environmental Protection Agency (USEPA) method 524.2. All these water samples were analyzed within 14 days of the time of collection.

Quality Assurance

A quality-assurance program was implemented to determine the effect, if any, of field and laboratory equipment and procedures on the herbicide, nutrient, and volatile organic compound concentrations detected in water samples. Field blanks, which are made from organic-free water, were submitted as water-quality samples from seven predetermined sites. Field blanks were subject to the same sample processing, handling, and equipment as the regular samples. Field duplicate samples were collected at seven predetermined sites to determine the reproducibility of sample processing and analytical methods. Field duplicates were water samples collected along with the regular samples and processed as if they had been obtained at a specific site. Sixteen blind spike samples of known herbicide concentration were submitted to the laboratory; concentrations were 0.07 and 0.70 µg/L.

Although results of the field blanks indicated no reportable concentrations of nitrate, concentrations of chloroform, methylenechloride, and xylene were reported in two of the blank samples, and alachlor was reported in two blank samples. The cause of the volatile organic compounds in the two field blanks was determined to be the result of laboratory-grade organic-free water not being used in producing the blanks as directed. The cause of the alachlor detection in two of the field blanks was determined not to be the result of the analytical methods used. The back-up herbicide sample (all regular and quality-assurance herbicide samples were collected in duplicate) for the two herbicide blanks in question were analyzed and also were found to contain alachlor.

The results of the field duplicates indicated that no concentrations differed by more than 20 percent from the regular sample for nitrate or volatile organic compounds. In only 5 of the 98 herbicide determinations did the duplicate sample differ from that of the regular sample by more than 20 percent. Of these five cases, four had concentrations near the reporting limit; for example, 0.07 µg/L of metolachlor in the regular sample and 0.10 µg/L of metolachlor in the duplicate sample.

Median percent recoveries for the blind herbicide spikes were as follows: alachlor (143), atrazine (128), cyanazine (144), DEA (102), DIA (98), metolachlor (150), metribuzin (128), prometon (109), and simazine (114). ESA was below the reporting limit for all alachlor spike samples submitted for analysis.

Statistical Methods

Nonparametric statistical methods were used to analyze the data collected. These methods were appropriate because the data were not normally distributed, and a large percentage of the data were censored; that is, many of the concentrations were less than the reporting limit. Nonparametric statistics have the advantage over parametric statistics of not being overly affected by outliers in the data because the ranks of the data are used in the analysis rather than the actual concentrations. The nonparametric statistical methods included the Wilcoxon signed-rank and Kruskal-Wallis tests (Helsel and Hirsch, 1992). The Wilcoxon signed-ranked test is used to determine whether the median difference between paired observations equals zero. Because this study was undertaken to determine if the flooding increased the transport of agricultural chemicals to unconsolidated aquifers, a one-tailed Wilcoxon signed-rank test was used. The Kruskal-Wallis test can be used to analyze for statistical differences of two or more groups.

A significance level of 0.05 was applied for all statistical tests in this study. This acceptable probability of error ($\alpha = 0.05$) means that the chance is 1 in 20 that results of the statistical test indicated a significant difference when one did not exist. Reporting the p value associated with a test shows the level of certainty that a statistical difference exists. The smaller the p value, the greater the certainty that a reported statistical difference resulted.

EXTENT OF FLOODING PROBLEMS

Well owners were interviewed to determine how flooding and intense rainfall may have affected the area that surrounds the sampled wells (figs. 7, 8). Of the 110 wells sampled during 1993, 30 were reported to be unaffected by flooding or intense rainfall; 15 were somewhat affected by nearby stream flooding (floodwaters nearby, but not in the immediate vicinity of the well); 30 were severely affected by stream flooding (12 of which were inundated at least to the base of the well); and 35 were not affected by stream flooding, but were affected by standing water

Figure 7. A farmstead in Minnesota, July 1993. The 1993 flood affected many rural areas in the upper Midwest (Bernard Volker, Herman, Minnesota).

from intense rainfall. Of the 25 wells where a water-level measurement was made, 17 were found to have had a rise in water level since the previous measurement. Because the 25 wells were not spatially distributed across the study area and were not representative of any specific type of flooding, the changes reported might not represent the entire study area.

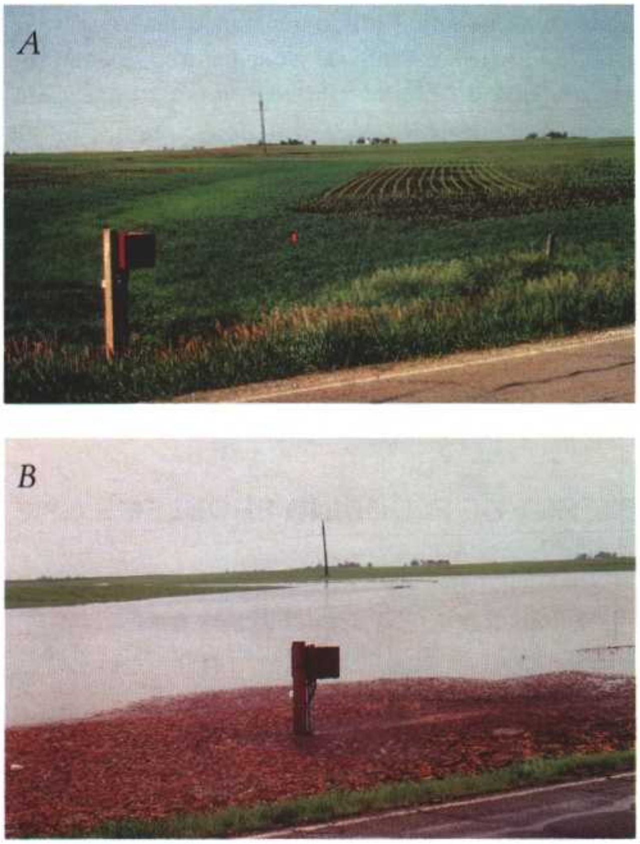

Figure 8. Water problems caused by heavy rains in 1993. Agricultural area in central Iowa under normal conditions (*A*) and during July 1993 (*B*).

CHEMICAL OCCURRENCE AND DISTRIBUTION

Concentrations of 11 herbicides, 3 herbicide metabolites, 4 nutrients, and 63 volatile organic compounds were determined by using water samples collected during 1993 from 110 wells from the well network utilized in the 1991 and 1992 studies.

Herbicides and Metabolites

The results of the herbicide analyses from the 110 wells sampled during September or October 1993 are summarized in table 1. The most frequently detected herbicide compound was ESA followed by atrazine, DEA, and DIA. A reportable concentration of at least one herbicide compound was found in 55.4 percent of the wells (37.3 percent if ESA is not included). One sample contained a concentration of alachlor (4.27 µg/L) that exceeded the USEPA maximum contaminant level (MCL) for treated drinking water (U.S. Environmental Protection Agency, 1992). Of the almost 800 samples that have been collected since the ground-water studies began in 1991, this was the first and only sample in which a herbicide concentration was greater than an MCL for drinking water. Water from this same well exceeded one-half of the MCL for alachlor several times during the previous studies.

The frequencies of detection from previous water-quality samples collected from the same 110 wells are summarized in table 2 and generally are similar to the results from this study (table 1). Differences for either the frequency of herbicide detection ($p = 0.395$; one-tailed Wilcoxon signed-rank test) or the total herbicide concentration ($p = 0.164$; one-tailed Wilcoxon signed-rank test) were not significant between the previous samples (summer 1991 or, where available, summer 1992) and those from this study.

The total herbicide concentrations measured in this study (postflood) were compared with the data collected in either 1991 or 1992 (preflood) from each of the 110 wells. A difference of 20 percent or more was used to define a substantial change in total herbicide concentration of each well. This threshold was selected because an examination of the quality-assurance results indicated that differences of greater than 20 percent are beyond that caused by analytical error (Kolpin and others, 1994). Total herbicide concentration did not substantially change in 81 wells, 63 of which had no herbicide detection in the postflood or the preflood samples. Of the remaining 29 wells, total herbicide concentration substantially increased in 16 wells and substantially decreased in 13 wells. Because information is not available on herbicide concentrations in the water that recharges the aquifers, increases or decreases in total herbicide concentration cannot be determined in any given well.

When the data were separated according to the severity of flooding effects (somewhat affected by stream flooding, severely affected by stream flooding, affected by intense rainfall, or not affected by stream flooding or intense rainfall), samples from 10

Table 1. Summary of 1993 herbicide and herbicide metabolite data for the 110 wells completed in near-surface unconsolidated aquifers, upper Mississippi River Basin, sampled for this study

[μg/L, micrograms per liter, - - -, no data or none available]

Chemical compound	Frequency of detection (percent)	Reporting limit (μg/L)	Maximum concentration (μg/L)	Maximum contaminant level[1] (μg/L)	Health advisory level[1] (μg/L)
Alachlor	4.5	0.05	4.27	2	- - -
Ametryn	0	.05	- - -	- - -	2,000
Atrazine	23.6	.05	1.80	3	3
Cyanazine	3.6	.05	.88	- - -	1
Deethylatrazine (DEA)	23.6	.05	1.67	- - -	- - -
Deisopropylatrazine (DIA)	13.6	.05	.48	- - -	- - -
Ethanesulfonic acid (ESA)	40.0	.10	7.31	- - -	- - -
Metolachlor	6.4	.05	.59	- - -	100
Metribuzin	1.8	.05	.22	- - -	200
Prometon	8.2	.05	1.07	- - -	100
Prometryn	0	.05	- - -	- - -	- - -
Propazine	0	.05	- - -	- - -	10
Simazine	1.8	.05	.07	4	4
Terbutryn	0	.05	- - -	- - -	- - -

[1]U.S Environmental Protection Agency (1992).

of the 16 wells that had a substantial increase in total herbicide concentration were found to be severely affected by stream flooding (fig. 9); inundation by floodwater was noted for four of these wells. Thus, the relation may be direct between the occurrence of stream flooding in the immediate vicinity of a sampled well and increases in total herbicide concentration in the aquifer. The flood waters could be sources of herbicides in the aquifer as a result of reversed hydraulic gradients caused by prolonged high river stages (fig. 2), from infiltration of herbicide-laden floodwater through the soil matrix (fig. 3), or by direct flow down the well casing if the well became inundated (fig. 4). Because these flood waters are composites of water from the drainage basin at that point, the area of land that could affect the water quality in the aquifer is greatly increased, thereby increasing potential sources of herbicide contamination. No relation is apparent between changes in total herbicide concentration and the remaining three types of flooding effects (fig. 9).

Substantial changes in total herbicide concentration do appear to be related to other factors. Water from wells with a substantial increase in dissolved-oxygen concentration also generally had a substantial change (increase or decrease) in total herbicide concentration (fig. 10). A substantial increase in dissolved-oxygen concentration might indicate areas with increased recharge from stream flooding or intense rainfall. Increased recharge could decrease the time available for biotic processes that consume O_2 to occur and allow oxygenated water to travel farther along flow paths. Whether increased recharge causes increased or decreased total herbicide concentrations in unconsolidated aquifers depends on herbicide concentrations in the recharging waters. Factors

Table 2. Summary of previous (1991 and 1992) water-quality data by routine analytical methods for the 110 wells completed in the near-surface unconsolidated aquifers, upper Mississippi River Basin, sampled during 1993

[The compounds ametryn, prometryn, propazine, and terbutryn also were analyzed, but never detected above the 0.05-µg/L report limit. µg/L, micrograms per liter, - - -, no data or none available]

Chemical compound	Reporting limit (µg/L)	March–April 1991			July–August 1991			July–August 1992		
		Number of samples	Frequency of detection (percent)	Maximum concentration (µg/L)	Number of samples	Frequency of detection (percent)	Maximum concentration (µg/L)	Number of samples	Frequency of detection (percent)	Maximum concentration (µg/L)
Herbicides										
Alachlor	0.05	108	1.8	1.05	102	0	- - -	28	7.1	1.00
Atrazine	.05	108	21.3	1.08	102	31.4	1.01	28	32.1	1.03
Cyanazine	.05	108	.9	.21	102	2.0	.68	28	0	- - -
Deethylatrazine (DEA).	.05	108	17.6	1.41	102	31.4	2.32	28	32.1	1.79
Deisopropylatrazine (DIA).	.05	108	5.6	.59	102	13.7	1.17	28	17.8	.28
Ethanesulfonic acid (ESA).	.10	0	- - -	- - -	0	- - -	- - -	28	46.4	2.51
Metolachlor	.05	108	4.6	.90	102	4.9	.71	28	7.1	.76
Metribuzin	.05	108	0	- - -	102	2.0	.09	28	0	- - -
Prometon	.05	108	5.6	.31	102	6.9	.58	28	10.7	1.35
Simazine	.05	108	.9	.06	102	2.0	.10	28	3.6	.09
Inorganic nutrients (reporting limits and maximum concentrations in milligrams per liter)										
Ammonium	0.01	106	74.5	2.1	110	83.6	4.0	35	77.1	2.0
Nitrate	.05	109	72.5	23	110	74.5	25	35	88.6	27
Nitrite	.01	106	14.2	.12	110	40.9	.18	35	14.3	.04
Orthophosphate.	.01	106	49.1	.42	110	50.0	.43	35	77.1	.45
Volatile organics compounds (detections only)										
Chloroform	0.2	0	- - -	- - -	0	- - -	- - -	21	14.3	0.8
Tetrachloroethylene.	.2	0	- - -	- - -	0	- - -	- - -	21	4.8	.9

that could affect herbicide concentrations in recharging water are the amount of chemical application in the recharge area during 1993 and the quality of flood waters that might have inundated the recharge area.

An inverse relation was noted between the frequency of occurrence of wells with a substantial change in total herbicide concentration and classes (0–29 ft, 30–59 ft, 60–89 ft, 90 ft and greater) of well

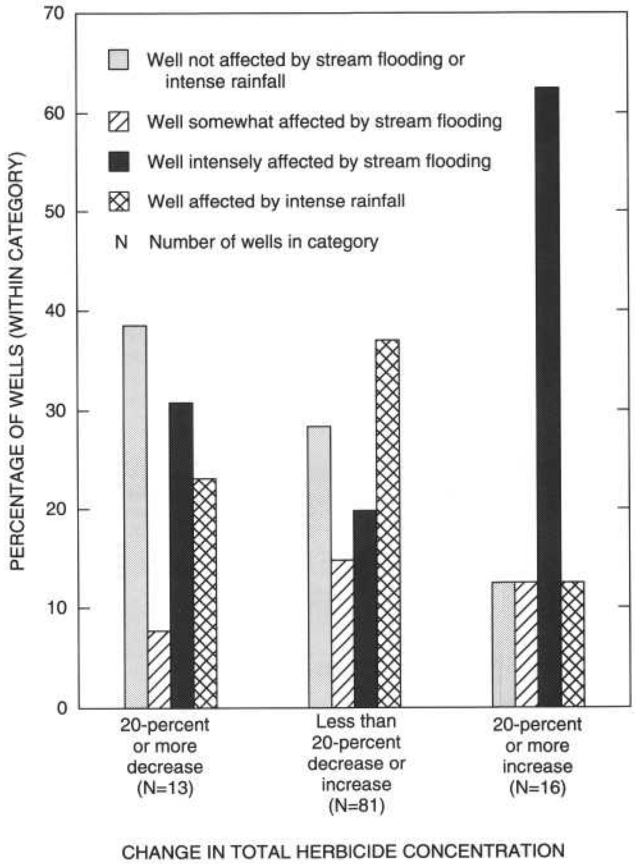

Figure 9. Relation between severity of 1993 flooding and change in total herbicide concentration in water samples collected during 1991 or 1992 and those collected for this study during 1993 from 110 wells completed in near-surface unconsolidated aquifers, upper Mississippi River Basin.

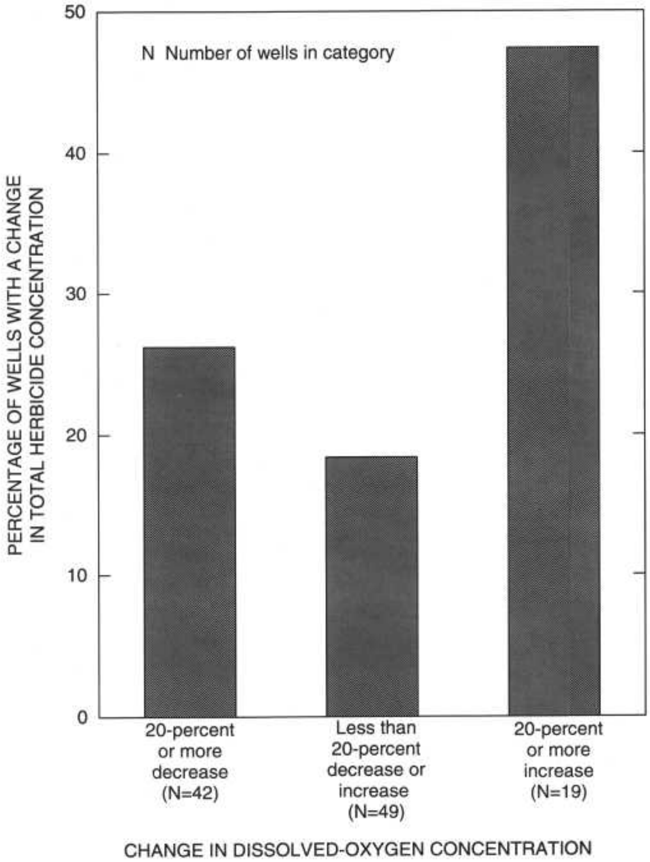

Figure 10. Relation between changes in dissolved-oxygen concentration and change in total herbicide concentration in water samples collected during 1991 or 1992 and those collected for this study during 1993 from 110 wells completed in near-surface unconsolidated aquifers, upper Mississippi River Basin.

depth (p = 0.018; Kruskal-Wallis test). As the well depths increased, changes (increase or decrease) in total herbicide concentration in the aquifer between the preflood and postflood samples were less (fig. 11). Because the age of the ground water in near-surface aquifers generally is older at greater depths (D.W. Kolpin and D.A. Goolsby, U.S. Geological Survey, unpub. data, 1994); water in shallow wells is more representative of recent recharge and more quickly reflects changes in water quality in response to the change in the quality of recharge than water at greater depth.

The percentage of land in corn and soybean production within a 400-m radius of a sampled well also was significantly (p = 0.019; Kruskal-Wallis test) related to changes in total herbicide concentration. As the amount of this land increased, the frequency of occurrence of wells with a substantial increase in total herbicide concentration also increased (fig. 12). This trend is likely source related. As percentage of land in corn and soybean production near the well increases, the corresponding increases in the amount and area of herbicide application increase the chances of herbicide transport to the aquifer.

About 83 percent of the samples from wells that had a substantial increase or decrease in total herbicide concentration also had a substantial increase or decrease in nitrate concentration. Only about 22 percent of the wells in which herbicides were detected, but had no substantial change in total herbicide concentration, had a substantial change in nitrate concentration. Changes in nitrate concentration may indicate environments where the potential for a change in the total herbicide concentration could also result.

Subregional spatial patterns in herbicide detections and concentrations were apparent for parts of the study area. The frequency of herbicide detection in samples from eight wells that are completed in the

the much shorter time to crop maturity, whereas others remained fallow for the entire 1993 growing season. This could have changed not only the timing of chemical application, but also the normal chemical-use patterns in many areas. More research is needed to determine if the increase in the frequency of herbicide detection in water from the Missouri River alluvium in 1993 is from increased recharge, changes in the timing of chemical application, or changes in chemical use.

Increases in the frequency of herbicide detection were not found in other alluvial aquifers sam-

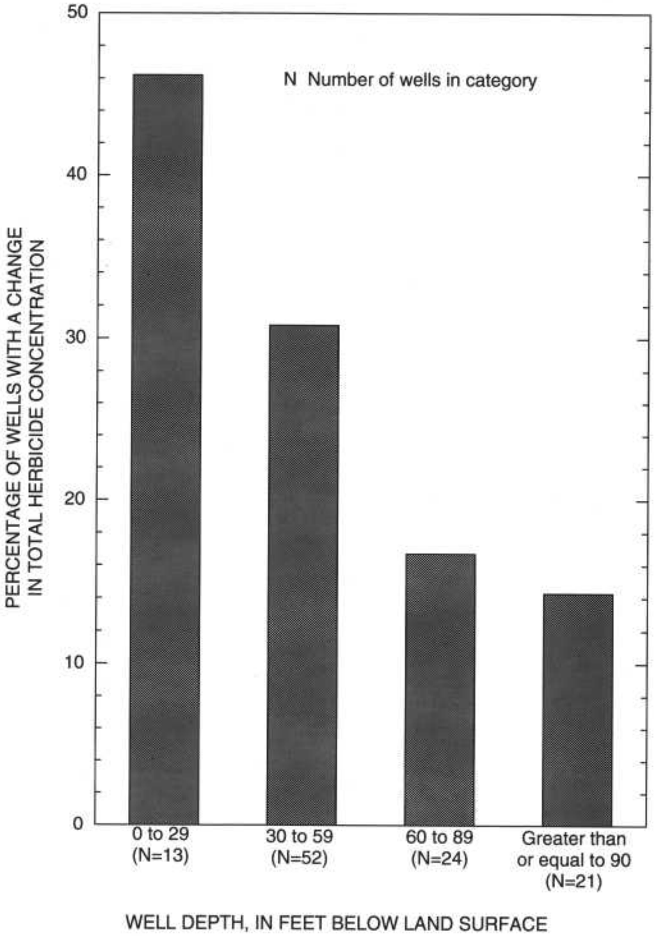

Figure 11. Relation between well depth below land surface and change in total herbicide concentration in water samples collected during 1991 or 1992 and those collected for this study during 1993 from 110 wells completed in near-surface unconsolidated aquifers, upper Mississippi River Basin.

Missouri River alluvium (fig. 13) increased from 12.5 percent in the previous studies to 50 percent in this study; triazine herbicides were not detected. The herbicides detected in these 8 wells during this study were alachlor (37.5 percent of samples), metribuzin (25 percent), and metolachlor (12.5 percent). These herbicides can be used on soybeans for weed control (alachlor and metolachlor can be used on corn and soybeans).

The cool, wet conditions that persisted during spring and early summer 1993 delayed or prevented the planting of corn in areas of the upper Mississippi River Basin. The number of acres planted in corn was greater than 2 million less than planned (U.S Department of Agriculture, 1993, 1994) in the nine States where the sampling for this study took place. Some of these fields that were intended to be planted with corn were instead planted with soybeans because of

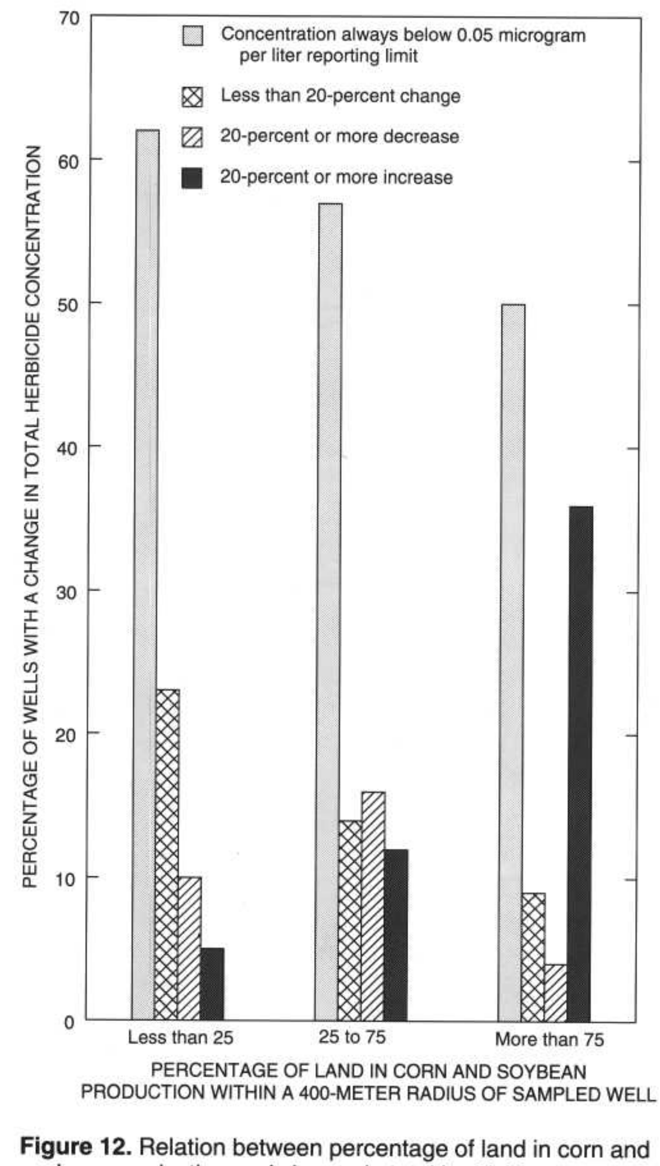

Figure 12. Relation between percentage of land in corn and soybean production and change in total herbicide concentration in water samples collected during 1991 or 1992 and those collected for this study during 1993 from 110 wells completed in near-surface unconsolidated aquifers, upper Mississippi River Basin.

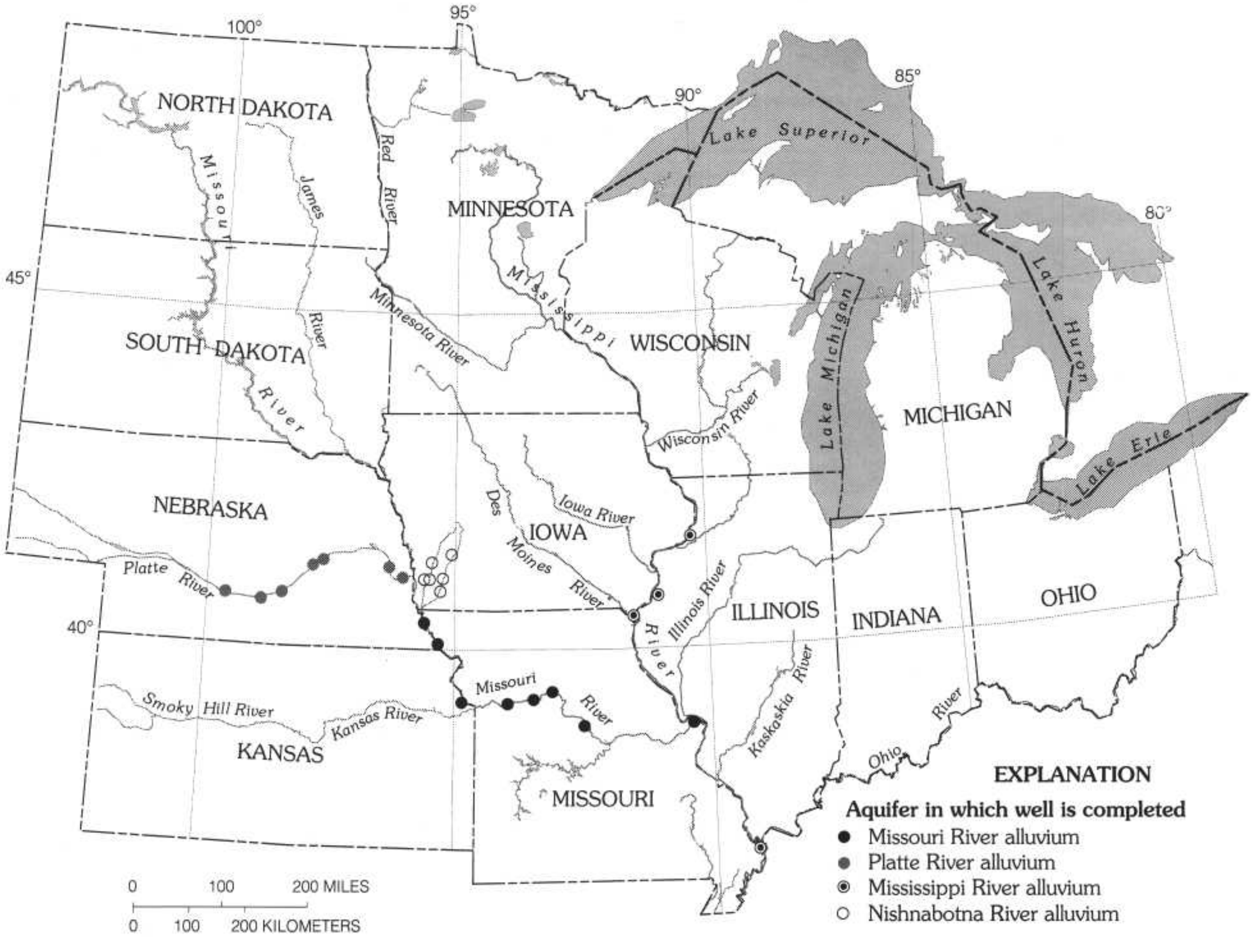

Figure 13. Location of wells completed in selected alluvial aquifers.

pled. Herbicides were detected in all seven wells completed in the Platte River alluvium (fig. 13) in the samples collected for previous studies and this study. Herbicides were detected in one of four wells in the Mississippi River alluvium in the samples collected for previous studies and this study. Water in this well had a substantial increase in total herbicide concentration. The six wells completed in the Nishnabotna River alluvium (includes the East and the West Nishnabotna Rivers in southwestern Iowa) were similar to those in the Mississippi River alluvium in that the frequency of herbicide detection (33 percent) did not change and the total herbicide concentration increased in the two wells that contained herbicides.

Nutrients

The results of the nutrient analyses for samples from the 110 wells sampled are summarized in table 3. The most frequently detected nutrient was ammonium followed by orthophosphate, nitrate, and nitrite. Although nitrate was the third most frequently detected nutrient, it had the highest median concentration (0.82 mg/L). Water from 33.6 percent of the wells contained nitrate concentrations that were equal to or greater than 3.0 mg/L; this level has been suggested as a division between natural and anthropogenic sources of nitrate (Madison and Brunett, 1985, p. 93). Nitrate concentrations exceeded the MCL of 10.0 mg/L (U.S. Environmental Protection Agency, 1992) in 10 percent of the samples. The nutrient results from preflood water-quality samples collected for the same 110 wells are summarized in table 2.

When the nutrient analyses from this study (postflood) were compared statistically with those of samples collected from the same wells in either summer 1991 or 1992 (preflood), ammonium ($p = 0.028$; one-tailed Wilcoxon signed-rank test) and orthophos-

Table 3. Summary of 1993 nutrient data for the 110 wells completed in the near-surface unconsolidated aquifers, upper Mississippi River Basin, sampled for this study

[mg/L, milligrams per liter; - - -, no data or none available]

Chemical compound	Frequency of detection (percent)	Reporting limit (mg/L)	Maximum concentration (mg/L)	Maximum contaminant level[1] (mg/L)	Health advisory level[1] (mg/L)
Ammonium (dissolved as nitrogen)	93.6	0.01	4.2	- - -	- - -
Nitrite (dissolved as nitrogen).	9.1	.01	.06	- - -	- - -
Nitrate (dissolved as nitrogen)	72.7	.05	21	10	- - -
Orthophosphate (dissolved as phosphorus) . . .	77.3	.01	.48	- - -	- - -

[1]U.S Environmental Protection Agency (1992).

phate ($p < 0.001$; one-tailed Wilcoxon signed-rank test) concentrations were found to be significantly higher in the postflood samples. Nitrite ($p = < 0.001$; one-tailed Wilcoxon signed-rank test) concentrations were found to be significantly lower in the postflood samples. However, 78 percent of the increases in ammonium concentration, 88 percent of the increases in orthophosphate concentration, and 97 percent of the decreases in nitrite concentrations were less than or equal to 0.05 mg/L. These low-level changes could occur randomly as a function of laboratory holding times or similar variations. Nitrate ($p = 0.471$; one-tailed Wilcoxon signed-rank test) concentrations were not found to be significantly different between the preflood and postflood samples.

Nitrate

To determine possible temporal differences in nitrate concentration, analyses from the postflood samples were compared with the preflood nitrate analyses at each well. In most cases, these were the water samples collected during summer 1991, but water samples collected during summer 1992 were used where available. A 20-percent difference in concentration between the preflood and postflood samples was the threshold to define a substantial change in nitrate. This threshold was selected because an examination of preflood quality-assurance results (Kolpin and others, 1994) indicated that differences of greater than 20 percent should be greater than that caused by analytical error. By using this threshold, 19 wells were determined not to have a nitrate concentration above reporting limits, 29 had no substantial change, 31 had a substantial decrease, and 31 had a substantial increase in nitrate concentration. When the data were separated according to the severity of flooding effects, the number of samples from wells in which the nitrate concentrations increased or decreased from the preflood sample remained almost equal for each category (fig. 14).

Because information was not available on nitrate concentrations in the water that recharged the aquifers, an increase or decrease in nitrate concentration could not be determined for any given well. The increased mass transport of nitrate into the Mississippi River and its large tributaries during 1993 flood (Goolsby and others, 1993) may indicate the expected effects on ground-water quality, but these surface-water-quality results might not be representative of ground-water quality within the unconsolidated aquifers sampled for this study. Factors that could affect nitrate concentrations in water that recharged the aquifers include the amount of fertilizer applied in the recharge area during 1993 and the quality of any flood waters that inundated the recharge area. Thus, possible increased recharge as a result of flooding could cause an increase or decrease in nitrate concentration in ground water depending on these factors. Another complicating factor is the much greater and more variable response times of ground water to the possible water-quality effects from the 1993 flood than surface water. Ground water moves slowly compared with surface water. The rate of ground-water movement can vary greatly

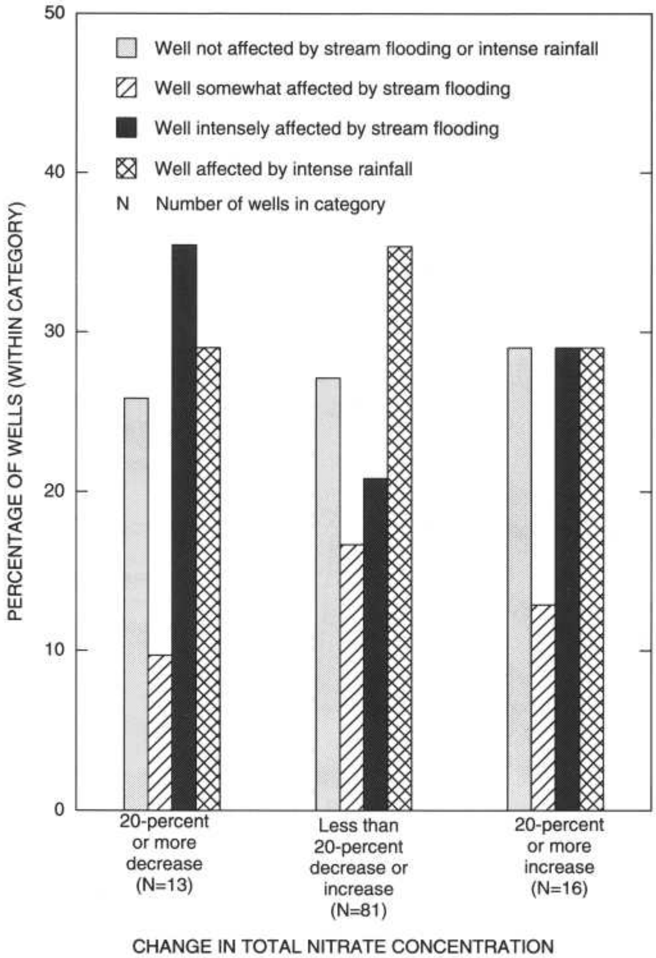

Figure 14. Relation of categories of flooding to changes in nitrate concentration between the samples collected during 1991 or 1992 and those collected for this study during 1993 from 110 wells completed in near-surface unconsolidated aquifers, upper Mississippi River Basin.

depending on the materials through which the water passes, the hydraulic conductivity of the unsaturated zone, and the distance from the land surface to the saturated zone. Thus, more time might pass before effects of the flood on the quality of water in near-surface unconsolidated aquifers become apparent.

Wells that had a substantial increase in dissolved-oxygen concentration had a greater frequency of substantial increases in nitrate concentration (53 percent) than those that had either no substantial change (26 percent) or a substantial decrease (19 percent) in dissolved-oxygen concentration. As was discussed above, an increase in the dissolved-oxygen concentration may indicate areas with increased recharge from either extensive stream flooding or intense rainfall.

Wells that had a substantial decrease in nitrate concentration had significantly higher water levels ($p = 0.011$; median water level = 3.6 m below land surface) than those that had either no change (median water level = 6.1 m) or a substantial increase (median water level = 6.7 m) in nitrate concentration. One possible cause for these decreases in nitrate is denitrification, which takes place under anaerobic conditions in the presence of labile organic carbon and denitrifying bacteria. Previous research has found that denitrification tends to occur in aquifers that have a shallow water table (Starr and Gillham, 1993). The dissolved-oxygen concentrations detected indicate the possibility of suitable conditions for denitrification. For example, water from wells that had a substantial decrease in nitrate concentration also had a smaller median dissolved-oxygen concentration (0.5 mg/L) than those that had either no change (0.96 mg/L) or a substantial increase (1.83 mg/L) in nitrate concentration.

A map of the temporal differences in nitrate concentration show possible subregional spatial patterns (fig. 15). Water in a cluster of wells in central Illinois generally had a substantial increase in nitrate concentration, and another cluster in western Iowa, western Minnesota, and southeastern South Dakota generally had a substantial decrease in nitrate concentration.

Volatile Organic Compounds

The postflood results of the analyses for volatile organic compounds from the samples collected from the 110 wells are summarized in table 4. During this study, 15 volatile organic compounds were detected. Only 1,2-dichloroethane and benzene concentrations in one sample exceeded the USEPA MCL for treated drinking water. The three most frequently detected compounds, in decreasing order, were chloroform, dichlorobromomethane, and chlorodibromomethane. A possible source of these compounds is the chlorination treatment of raw water to obtain drinking water (Howard, 1990). These compounds were detected in eight wells, of which four were public-supply wells, three were domestic wells, and one was an industrial well. In this study, water samples were collected to be representative of the aquifer; thus, samples should have been obtained before any water-treatment processes. However, of these public-supply wells, two had no access points to sample water before treatment and required chlorinators to be turned off 24 hours before sampling, and one was flushed and disinfected before sampling to reduce potential bacterial contamination as a result of recent floodwater inundation.

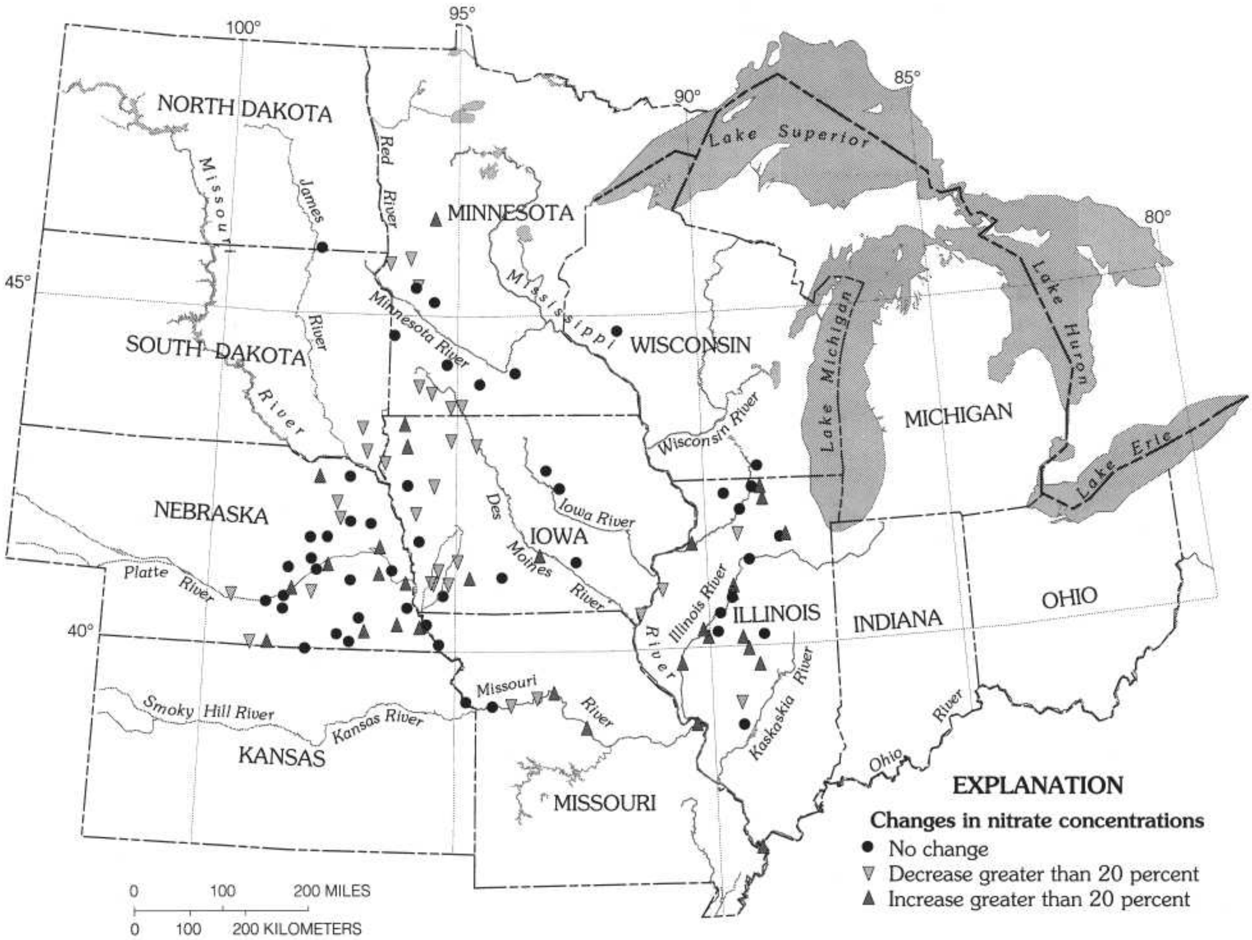

Figure 15. Changes in nitrate concentration between the samples collected during 1991 or 1992 and those collected for this study during 1993 from 110 wells completed in near-surface unconsolidated aquifers, upper Mississippi River Basin.

The few wells in this study with available background data on volatile organic compounds make identification of temporal differences tenuous. Whether the subset of wells with background data are representative of the entire population of wells sampled for this study cannot be determined; however, the frequency of volatile organic compound detection was almost identical between the samples collected during 1992 and this study. Volatile organic compounds were detected in water from 14.3 percent (3 of 21) of the wells sampled during summer 1992 and 14.5 percent (16 of 110) of those sampled for this study. None of the wells that were sampled during 1992 had concentrations that exceeded 1.0 μg/L, whereas 62.5 percent (10 of 16) of the samples from the wells in which volatile organic compounds were detected had concentrations that exceeded 1.0 μg/L for this study.

The difference ($p = 0.5446$; Kruskal-Wallis test) was not significant in the frequency of volatile organic compound detection when the data were separated according to the severity of flooding effects. Only 1 of 12 samples from wells inundated by flood waters had a volatile organic compound detection. Land use, however, may be a more important factor in determining the frequency of volatile organic compound detection. Significantly higher amounts of urban-residential ($p = 0.037$) and industrial ($p = 0.011$) land use were within a 30-m radius of the wells in which volatile organic compounds were detected compared to those in which volatile organic compounds were not detected.

SUMMARY

Water samples were collected during September and October 1993 from 110 wells to determine the immediate effects the 1993 flood had on the

Table 4. Summary of 1993 volatile organic compound data for the 110 wells completed in the near-surface unconsolidated aquifers, upper Mississippi River Basin, sampled for this study

[µg/L, micrograms per liter; - - -, no data or none available]

Chemical compound	Frequency of detection (percent)	Reporting limit (µg/L)	Maximum concentration (µg/L)	Maximum contaminant level[1] (µg/L)	Health advisory level[1] (µg/L)
1,1,1,2-Tetrachloroethane	0	0.2	- - -	- - -	70
1,1,1-Trichloroethane	2.7	.2	1.3	200	200
1,1,2,2-Tetrachloroethane	0	.2	- - -	- - -	- - -
1,1,2-Trichloroethane	0	.2	- - -	5	3
1,1-Dichloroethane	2.7	.2	.4	- - -	- - -
1,1-Dichloroethylene	0	.2	- - -	7	7
1,1-Dichloropropene	0	.2	- - -	- - -	- - -
1,2,3-Trichlorobenzene	0	.2	- - -	- - -	- - -
1,2,3-Trichloropropane	.9	.2	2.3	- - -	40
1,2,4-Trichlorobenzene	0	.2	- - -	70	70
1,2,4-Trimethylbenzene	0	.2	- - -	- - -	- - -
1,2-Chlorotoluene	0	.2	- - -	- - -	100
1,2-Dibromoethane	0	.2	- - -	- - -	- - -
1,2-Dichlorobenzene	0	.2	- - -	600	600
1,2-Dichloroethane	2.7	.2	6.9	5	- - -
1,2-Dichloropropane	0	.2	- - -	5	- - -
1,2-Transdichloroethene	0	.2	- - -	100	100
1,3,5-Trimethylbenzene	0	.2	- - -	- - -	- - -
1,3-Dichlorobenzene	0	.2	- - -	600	600
1,3-Dichloropropane	0	.2	- - -	- - -	- - -
1,4-Chlorotoluene	0	.2	- - -	- - -	100
1,4-Dichlorobenzene	0	.2	- - -	75	75
2,2-Dichloropropane	0	.2	- - -	- - -	- - -
2-Chloroethylvinylether	0	1	- - -	- - -	- - -
Acrolein	0	20	- - -	- - -	- - -
Acrylonitrile	0	20	- - -	- - -	- - -
Benzene	2.7	.2	78	5	- - -
Bromobenzene	0	.2	- - -	- - -	- - -

Table 4. Summary of 1993 volatile organic compound data for the 110 wells completed in the near-surface unconsolidated aquifers, upper Mississippi River Basin, sampled for this study—Continued

Chemical compound	Frequency of detection (percent)	Reporting limit (µg/L)	Maximum concentration (µg/L)	Maximum contaminant level[1] (µg/L)	Health advisory level[1] (µg/L)
Bromochloromethane	0	.2	---	---	90
Bromoform	.9	0.2	1.7	100	---
Carbontetrachloride	0	.2	---	5	---
Chlorobenzene	0	.2	---	---	---
Chlorodibromomethane	2.7	.2	5.7	100	60
Chloroethane	0	.2	---	---	---
Chloroform	6.4	.2	51	100	---
Cis-1,2-dichloroethene	0	.2	---	---	---
Cis-1,3-dichloropropene	0	.2	---	---	---
Dibromochloropropane	0	1	---	.2	---
Dibromomethane	0	.2	---	---	---
Dichlorobromomethane	4.5	.2	25	100	---
Dichlorodifluoromethane	0	.2	---	---	1,000
Trichlorotrifluoroethane	0	.5	---	---	---
Ethylbenzene	.9	.2	.9	700	700
Hexachlorobutadiene	0	.2	---	---	1
Isopropylbenzene	0	.2	---	---	---
Methylbromide	0	.2	---	---	
Methylchloride	0	.2	---	---	---
Methylene chloride	.9	.2	.4	---	---
Methyltertbutylether	0	1	---	---	---
N-Butylbenzene	0	.2	---	---	---
N-propylbenzene	0	.2	---	---	---
Naphthalene	0	.2	---	---	20
P-isopropyltoluene	0	.2	---	---	---
Sec-butylbenzene	0	.2	---	---	---
Styrene	0	.2	---	100	100
Tert-butylbenzene	0	.2	---	---	---
Tetrachloroethylene	.9	.2	.6	5	---
Toluene	2.7	.2	12	1,000	1,000

Table 4. Summary of 1993 volatile organic compound data for the 110 wells completed in the near-surface unconsolidated aquifers, upper Mississippi River Basin, sampled for this study—Continued

Chemical compound	Frequency of detection (percent)	Reporting limit (μg/L)	Maximum concentration (μg/L)	Maximum contaminant level[1] (μg/L)	Health advisory level[1] (μg/L)
Trans-1,3-dichloropropene	0	.2	---	---	---
Trichloroethylene	.9	0.2	0.4	5	---
Trichlorofluoromethane	0	.2	---	---	2,000
Vinyl chloride	0	.2	---	2	---
Xylenes	.9	.2	5.3	10,000	10,000

[1]U.S Environmental Protection Agency (1992).

occurrence, concentration, and transport of agricultural chemicals and volatile organic compounds in near-surface unconsolidated aquifers of the upper Mississippi River Basin. Of the 110 wells sampled, 30 were reported to be unaffected by flooding or intense rainfall, 15 were somewhat affected by nearby stream flooding (flood waters nearby, but not in the immediate vicinity of the well), 30 were severely affected by stream flooding (12 of which were inundated at least to the base of the well), and 35 were affected not by stream flooding, but by standing water from rainfall. Results from these samples were compared with those obtained from the same wells that were sampled during 1991 or 1992. There was no statistically significant difference in either the frequency of herbicide detection or total herbicide concentration between the previous samples and those collected for this study. However, water from about 63 percent of the wells that had at least a 20-percent increase in total herbicide concentration also were severely affected by stream flooding. No direct relation was determined between the historic flooding and intense rainfall during 1993 for either the nitrate or the volatile organic compound concentrations. However, the substantial increases in dissolved-oxygen concentration in some wells may indicate areas of increased recharge. The extensive stream flooding and intense rainfall is one possible explanation for such an increase. Water from wells that had at least a 20-percent increase in dissolved-oxygen concentration had the greatest likelihood of substantial increases or decreases in total herbicide concentration and substantial increases in nitrate concentration. Water in shallow wells more quickly reflect changes in water quality in response to changes in recharge.

The frequency of herbicide detection increased from 12.5 percent in previous samples to 50 percent in those collected from this study for the eight wells that were completed in the Missouri River alluvium. The herbicides detected in samples from these wells were alachlor, metribuzin, and metolachlor, all of which are used to control weeds in soybeans. The 1993 flood could have caused this increase in the frequency of herbicide detection by increasing the chemical transport to ground water, changing the normal timing of chemical application, and changing the normal patterns in crop types and chemical use.

These results document only the immediate effects the 1993 rainfall and stream flooding had on ground-water quality of near-surface unconsolidated aquifers. Because ground-water moves much more slowly than surface runoff, additional data will be required to determine if the 1993 flood has long-term effects on ground-water quality.

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