Prepared as part of the National Water-Quality Assessment Program

Relations of Water Quality to Agricultural Chemical Use and Environmental Setting at Various Scales—Results from Selected Studies of the National Water-Quality Assessment Program

In 1991, the U.S. Geological Survey (USGS) began studies of 51 major river basins and aquifers across the United States as part of the National Water-Quality Assessment (NAWQA) Program to provide scientifically sound information for managing the Nation's water resources. The major goals of the NAWQA Program are to assess the status and long-term trends of the Nation's surface- and ground-water quality and to understand the natural and human factors that affect it (Gilliom and others, 1995).

In 2001, the NAWQA Program began a second decade of intensive water-quality assessments. The 42 study units for this second decade were selected to represent a wide range of important hydrologic environments and potential contaminant sources. These NAWQA studies continue to address the goals of the first decade of the assessments to determine how water-quality conditions are changing over time. In addition to local- and regional-scale studies, NAWQA began to analyze and synthesize water-quality status and trends at the principal aquifer and major river-basin scales.

This fact sheet summarizes results from four NAWQA studies that relate water quality to agricultural chemical use and environmental setting at these various scales:

- (A) Comparison of ground-water quality in northern and southern High Plains agricultural settings (principal aquifer scale);
- (B) Distribution patterns of pesticides and degradates in rain (local scale);
- (C) Occurrence of pesticides in shallow ground water underlying four agricultural areas (local and regional scales); and
- (D) Trends in nutrients and sediment over time in the Missouri River and its tributaries (major river-basin scale).

(A) High Plains Aquifer More Vulnerable in North than South to Nitrate and Pesticides

The High Plains aquifer underlies about 174,000 square miles in the central United States in parts of Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming. Ground water is the primary source for drinking water, irrigation, industry, and water supplies for animal production in the High Plains region. During 2003–04, an aquifer-scale study by Stanton and Fahlquist (2006) compared and contrasted the effects of different irrigated crop types and selected hydrogeologic factors on quality of recently recharged ground water in the southern and northern High Plains (fig. 1). This study was part of a larger, more comprehensive regional assessment of ground-water quality in the High Plains aquifer done by the NAWQA Program between 1999–2004 (McMahon and others, 2007).

Thirty water-quality monitoring wells were installed in the northern study area, an area covering about 10,000 square miles, and 30 wells were installed in the southern study

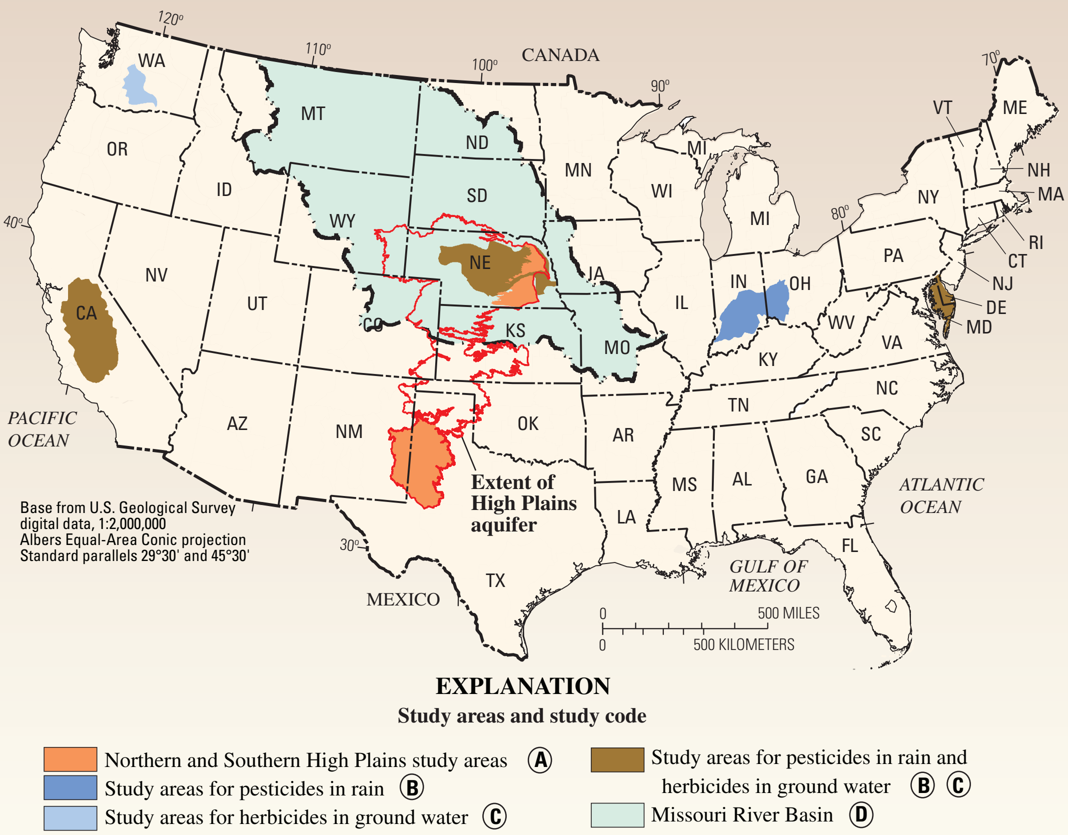

Figure 1. Location of the study areas for the four National Water-Quality Assessment (NAWQA) studies summarized in this fact sheet.

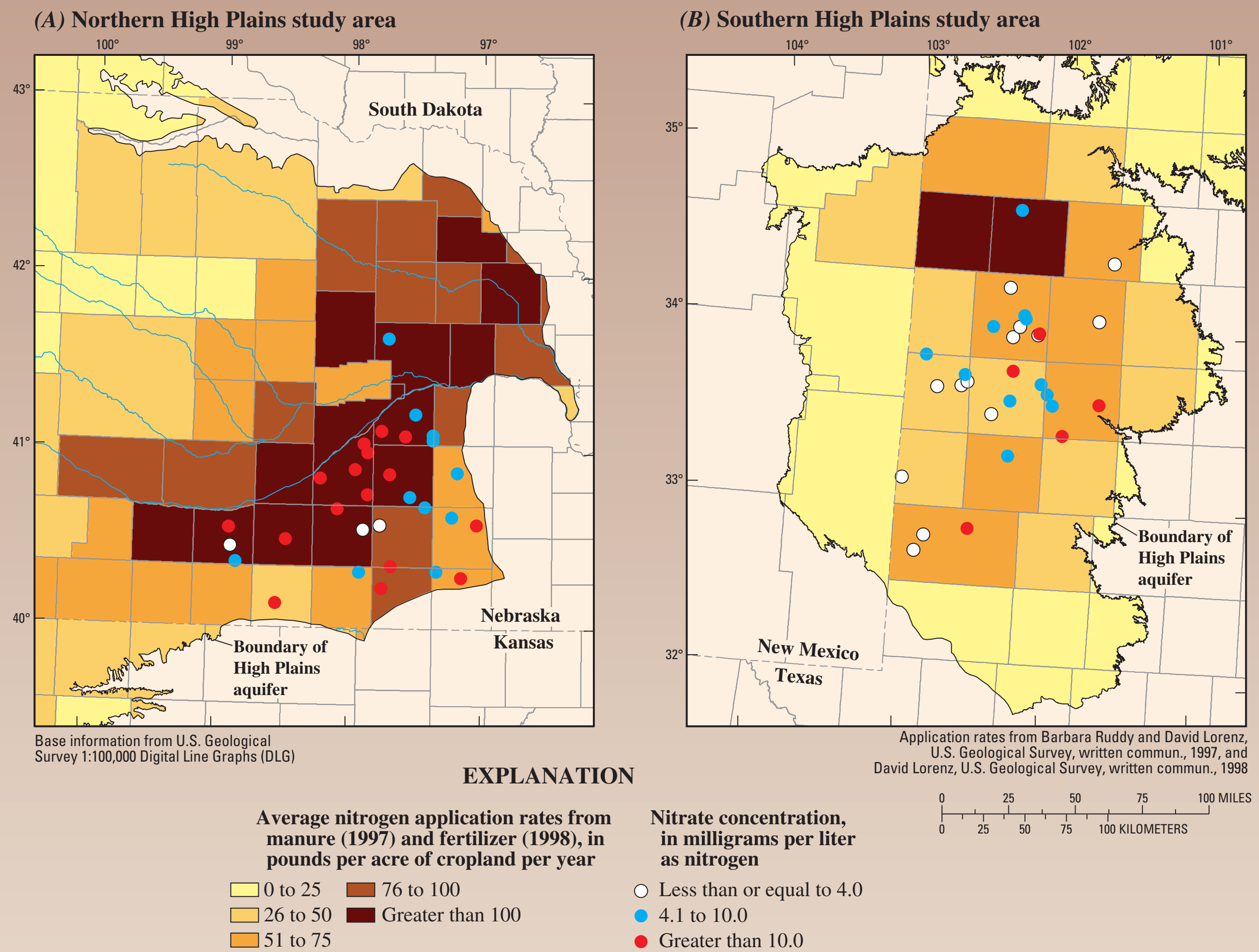

Figure 2. Most ground-water samples (27 of 30 samples) in the northern High Plains study area had a nitrate concentration greater than 4.0 milligrams per liter (or parts per million), indicating that nitrogen fertilizer had moved downward from agricultural fields and reached the aquifer. In the southern study area, about one-half of the water samples had a nitrate concentration large enough to indicate that nitrogen fertilizer had reached the aquifer.

area, an area covering about 29,000 square miles. Monitoring wells were installed in areas where irrigated agriculture was greater than 30 percent of the local land use. They were drilled such that the bottoms of the wells were about 20 feet below the measured water level.

Water levels measured in monitoring wells in the northern study area ranged from 35.1 to 164.4 feet below land surface, with a median of 84.6 feet. In the southern study area, water levels ranged from 78.8 to 195.2 feet below land surface, with a median of 153.2 feet. In addition, water samples collected from each of the 30 wells were analyzed for physical properties, concentrations of nitrogen and phosphorus compounds, nitrogen isotopes of nitrate, pesticides and pesticide degradates, dissolved solids, major ions, trace elements, dissolved organic carbon, and tritium.

The effect of irrigated agriculture on ground-water quality at the water table was more apparent in the northern study area. Samples collected there had larger nitrate concentrations and more detectable pesticide compounds than samples collected in the southern study area. The median nitrate concentration of northern-study-area samples (10.6 milligrams per liter or parts per million) was significantly larger than the median concentration in samples from the southern study area (4.1 milligrams per liter). At least one pesticide compound was detected in 22 northern samples (73 percent) and in 7 southern samples (23 percent).

Many factors in the northern study area were more favorable for movement of chemicals applied at the land surface into ground water than in the southern study area, including:

- Shallower depths to ground water;
- Greater precipitation;
- Less evaporation and plant respiration; and
- Greater ground-water recharge rates.

Also, pesticide application rates on cropland in the northern study area were about twice the rates of application to cropland in the southern study area, and nitrogen application rates near monitoring wells also were estimated to be greater in the northern study area (fig. 2).

The primary crops grown near sampled wells in the northern study area were corn and soybeans, whereas the primary crop in the southern study area was cotton. The types of pesticides detected in the two areas were related to the types of crops grown. Atrazine, alachlor, metolachlor, simazine, and degradates of those compounds were detected most frequently in ground-water samples collected from the northern study area. Except for simazine, these pesticides commonly are applied to corn or soybean fields and are on the list of top-10 pesticides applied in the northern study area. In the southern study area, deethylatrazine (a degradate of atrazine and propazine) was detected most often in ground-water samples. Although atrazine is not applied to cotton fields, it may have been applied previously in or near those same fields when sorghum was the dominant cash crop. Pesticides applied to cotton fields that were detected in ground water in the southern study area included fluometuron, malathion, and propazine, but these were at very low concentrations.

B Most Pesticides in Rain Originated Locally

Pesticides can enter the atmosphere during and after application through volatilization or wind erosion (Bedos and others, 2002). Once airborne, a pesticide can remain in the gas phase, attach to particles, or undergo photochemical transformation reactions. Rainfall efficiently cleanses the atmosphere of these contaminants, and reintroduces a small, but significant, fraction of them back to the land surface and water bodies.

A local-scale study by Vogel and others (2008) measured the concentrations of a large number of pesticides and selected degradates in rain during two growing seasons (2003–04) at four locations across the United States. The three eastern and midwestern study locations (Maryland, Indiana, Nebraska) were dominated by corn and soybean row crops, whereas the western location (California) was dominated by almonds and vineyards with some corn and dairy. As an example, the concentrations of two acetanilide herbicides (alachlor and metolachlor) in weekly composite rain samples at the Nebraska study location are shown in figure 3.

The study tested for 42 parent pesticides and 40 degradates, representing a broad spectrum of pesticide classes, physical/chemical properties, use amounts, and application rates and methods. The mass of individual pesticides deposited by the rain at each site was calculated and compared to the mass of pesticides applied in the area at three different scales.

Generally, this study showed that some pesticides are capable of being transported in the atmosphere from outside the local area and gradually deposited by rain on the land surface over time. However, the largest percentage of pesticides in rain appeared to result from pesticides that were applied in the local area.

Degradation products of some herbicides [deethylatrazine (70-percent detection rate in Maryland)] and insecticides [chlorpyrifos oxygen analog (70-percent detection in California), malathion oxygen analog (25-percent detection rate in California, Indiana, and Nebraska), diazinon oxygen analog (76-percent detection rate in California), and 1-napthol (30-percent detection rate in California)] were found in rain in the areas where the parent compounds were used. Degradates of the acetanilide herbicides were found in less than 5 percent of all rain samples, even when the parent herbicide was detected, because the chemical properties of the compounds inhibit volatilization. The amount of pesticides deposited on the land from rainfall (assuming uniform distribution and concentration) was estimated to be less than 2 percent of that applied in all instances. Research on pesticides in rainfall began in 2007 and concluded in 2008 at two additional locations in Iowa and Mississippi as part of the Agricultural Chemical Transport topical study of the NAWQA Program (see URL *http://in.water.usgs.gov/NAWQA_ACT*).

C Occurrence of Herbicides and Degradates in Ground Water Reflects Degradation Rates and Hydrology

A study by Steele and others (2008) assessed the occurrence and fate of pesticides in ground water in relation to environmental and agricultural settings, depth to water, and age of ground water. From 2002 through 2004, 59 ground-water wells were installed in four different agricultural settings—California, Maryland, Nebraska, and Washington—to investigate agricultural chemicals in shallow ground water. At each local-scale study location, from 9 to 13 flow-path wells were installed in a transect along a conceptualized flow system starting in agricultural uplands and ending adjacent to a stream, and 1 to 5 additional areal wells were installed afield of the flow system to characterize regional variations. Altogether, there were 45 flow-path wells and 14 areal wells included in the study. Maximum depths to ground water were about 23 feet in California, 33 feet in Maryland, 69 feet in Nebraska, and 43 feet in Washington. Corn was grown at all locations. However, soybeans were grown at the Nebraska study location in 2003 and at the Maryland location in 2004.

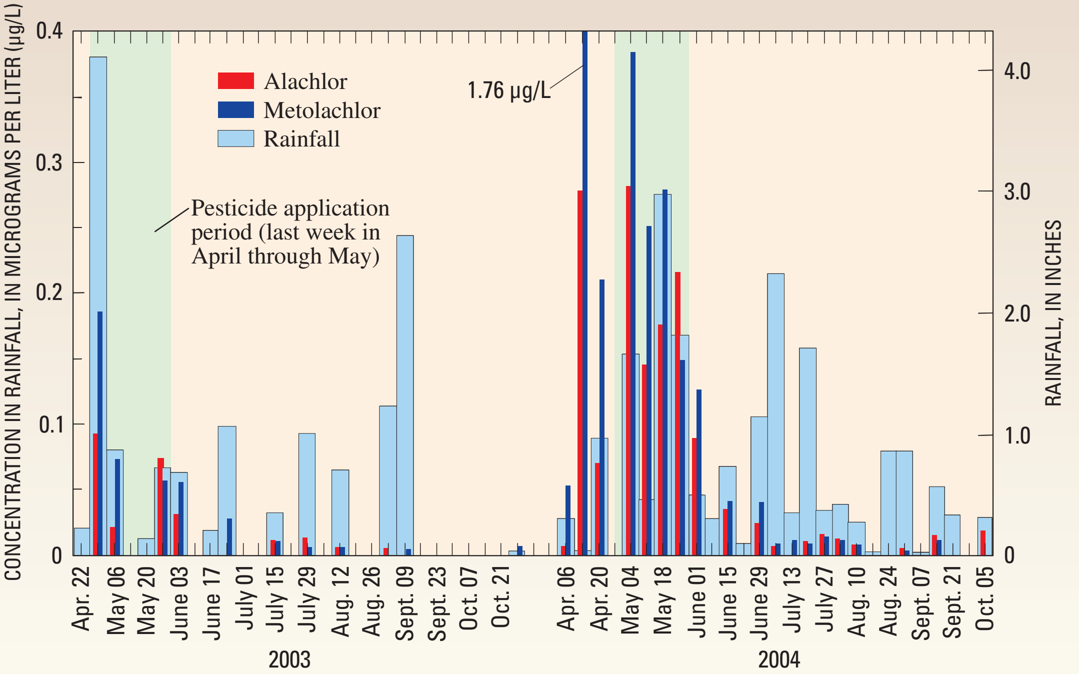

Figure 3. Alachlor and metolachlor concentrations in weekly composite rain samples and weekly rainfall amounts at the rainfall study location in Nebraska during the 2003–04 growing seasons, demonstrating the typical seasonality and magnitude of pesticide concentrations in rainfall.

The California and Washington study locations comprised mixed agricultural settings of orchards, vineyards, and fields of alfalfa and corn. These two western study locations featured extensive use of irrigation to support the crops.

During 2004, water samples from 59 monitoring wells were analyzed for major ions, nutrients, and pesticide concentrations. Pesticides were present in ground-water samples from all four agricultural study locations but were predominantly of two classes—triazines (atrazine and simazine) and acetanilides (acetochlor, alachlor, and metolachlor) (table 1). None of the analytes that are subject to drinking-water standards were found at concentrations in this study that exceeded those standards. Of the 7 pesticide compounds detected in more than 10 ground-water samples from all study locations combined, 4 of the 5 most frequently detected compounds were degradates of parent pesticides.

Pesticides used (2003–04) or recently used on corn fields at the four study locations were detected in ground-water samples. Atrazine (maximum concentration 1.1 µg/L, micrograms per liter) and its degradate, deethylatrazine (maximum concentration 1.0 µg/L), typically were detected together. Atrazine concentrations were largest in samples of young ground water from shallow depths at the Maryland study location and decreased in samples of older ground water (approximate date of ground-water recharge before 1980) (fig. 4). In contrast, excluding Maryland, degradates of alachlor and metolachlor (maximum concentrations of 0.9 and 0.1 µg/L, respectively) primarily were detected without the parent product. Atrazine can biodegrade in soils, but in samples collected for this study, both the parent compound and deethylatrazine were detected in shallow and deep wells. Therefore, degradation rates for atrazine were generally slower than transport rates. The proportion of metolachlor in ground water was far less than for its degradates, of which metolachlor ethanesulfonic acid (ESA) was predominant. In all, once in the ground-water system, metolachlor appeared to degrade quicker than atrazine.

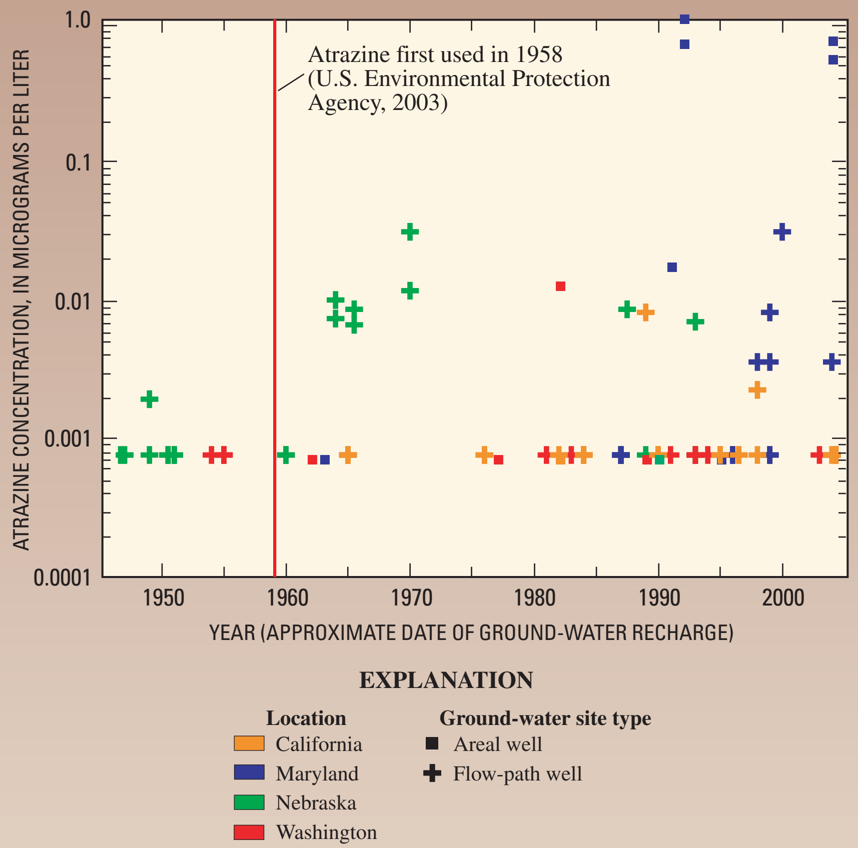

Figure 4. In part because atrazine degrades slower in ground water than in the soil, atrazine most likely entered the ground-water system rapidly at the Nebraska study location, which helped the chemical to persist in Nebraska ground water for more than 40 years.

Table 1. Relation of selected pesticide degradates to their parent pesticides.

Parent pesticide	Degradate
Triazines	
Atrazine	Deethylatrazine
Acetanilides	
Alachlor	Ethanesulfonic acid (ESA)
	Oxanilic acid (OXA)
	Sufinylacetic acid (SAA)
Metolachlor	ESA
	OXA
Other	
Carbaryl	1-napthol
Chlorpyrifos	Oxygen analog
Diazinon	Oxygen analog
Malathion	Oxygen analog

In ground-water samples from California, Nebraska, and Washington, metolachlor ESA was also the predominant metolachlor degradate and generally constituted more than 50 percent of the metolachlor product found in the samples. In the Maryland samples, measurable concentrations of metolachlor were detected with two of its degradates—ESA and oxanilic acid (OXA). Metolachlor OXA was found less frequently and usually occurred at smaller concentrations than metolachlor ESA.

The differences in relative amounts of metolachlor degradates were related to age of the ground water and depth of the samples. Similar to atrazine, metolachlor ESA concentrations were largest (maximum concentration 9.8 µg/L) in samples from shallow, younger ground water from Maryland and decreased in samples of deeper, older ground water from California and Nebraska. Initial degradation of the acetanilide herbicides seems to favor the production of the OXA degradate form; however, the relative fraction of initial pesticide mass occurring as ESA increases over time.

The Washington study location had by far the smallest concentrations of pesticides in ground water, as indicated by the median sum of analyzed pesticides, and that location also was the only one where the ground-water system was recharged primarily by irrigation-canal leakage of imported river water, which has the effect of diluting pesticide concentrations in the ground water (Capel and others, 2008). In Maryland, where the median sum of pesticide concentrations in ground water was more than 300 times larger than in Washington, hydrology again was important. Plentiful precipitation and sandy soils characterize the Maryland study area. Storm-water detention ponds are common, and they promote focused recharge to the shallow aquifer (Capel and others, 2008). Understanding the differences in hydrology among the four study locations was key to interpreting the chemical transport rates that, in tandem with degradation rates, helped explain why pesticide parent compounds were found in ground water at some locations, whereas only degradates were found at others. The results of this study imply that improvements in ground-water quality are possible through a more hydrologically informed, integrated management of the agricultural and hydrologic systems.

D Few Upward Trends for Streamflow, Nitrogen, and Sediment in Missouri River Basin

Data collected by the U.S. Geological Survey provide insight into how water-quality conditions have changed over time in the Missouri River and selected tributaries and how natural features and human activities have contributed to those changes (Sprague and others, 2007).

Nutrients and suspended sediment were tested for trends for the period from 1993 through 2003 using both flow-adjusted and non-flow-adjusted techniques. “Flow adjusted” means streamflow trends are removed to allow more direct assessment of the effect of management practices. Streamflow trended downward at about three-fourths of the 34 monitoring sites in the Missouri River Basin where trends were tested for 1993–2003 (fig. 5A). During 1993–97, streamflow of many Missouri River Basin streams was above average; however, this wet period was followed by widespread drought conditions in the basin from 2000–2003, as indicated by reduced snowpack levels, below normal regional rainfall averages, and elevated drought indices. In contrast, streamflow trends were positive during 1993–2003 for two streams, but streamflow in one of these is regulated by an upstream reservoir.

The other upward trend was for the spring-fed Dismal River that drains an area of the Nebraska Sand Hills. There the upward trend in streamflow continued a pattern that began about 1980 and, though the cause is uncertain, it parallels trends in nearby Sand Hills streams (Zelt, 2008) and water-table observation wells. Ground-water levels had begun rising in Tryon well during 1991, whereas at Hecla well, water levels generally had been rising since 1982, but showed a steeper rise beginning in 1993 (U.S. Geological Survey, 2008). Through 2003 the seasonal high water table had not demonstrated drought effects, but typically it takes longer for drought effects to be seen in ground water than in surface runoff.

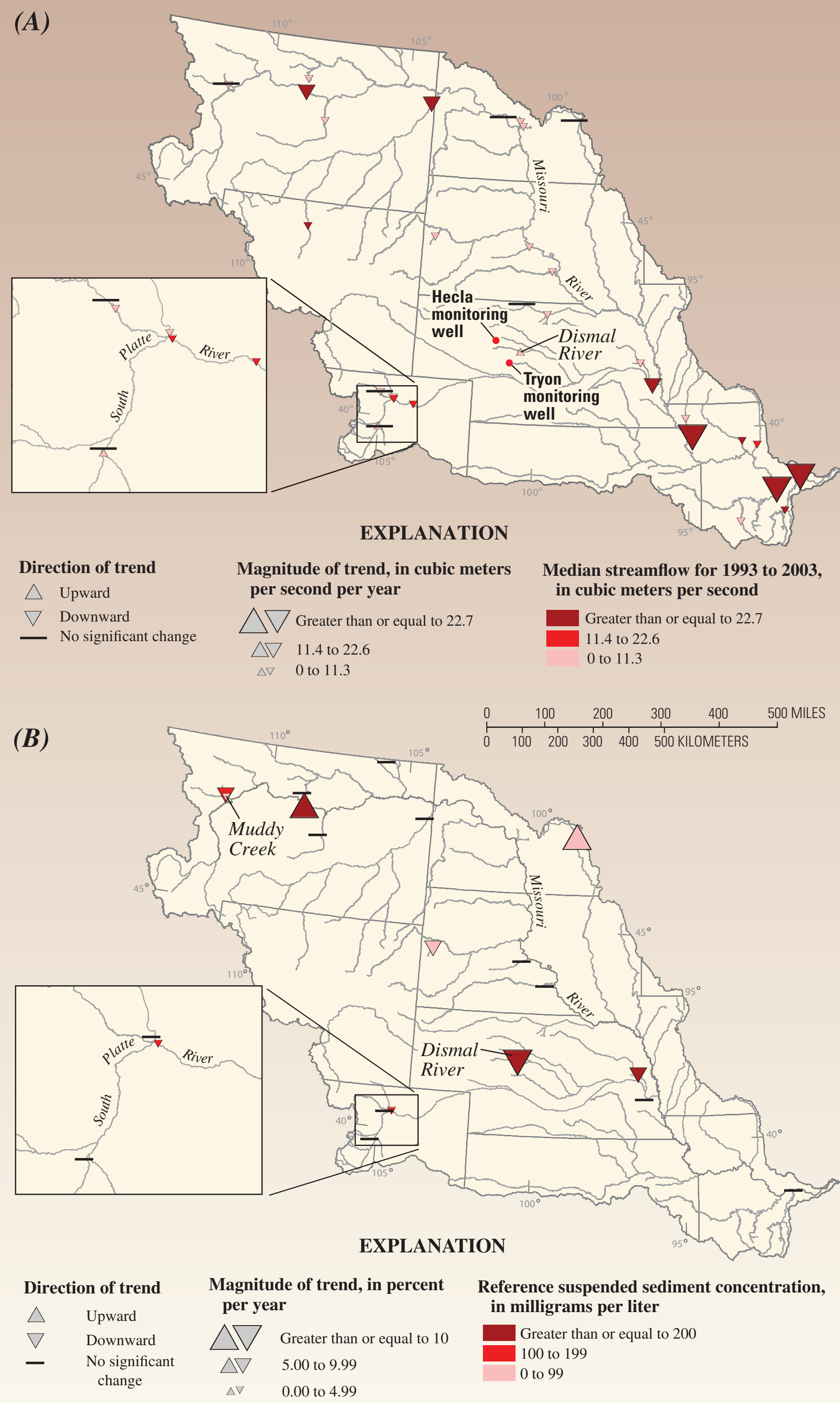

Figure 5. Location of *(A)* trend-assessment sites, trends in streamflow from 1993 to 2003, and *(B)* flow-adjusted trends in concentrations of suspended sediment from 1993 to 2003 at selected locations in the Missouri River Basin (modified from Sprague and others, 2007). (Reference concentration describes central tendency in the concentration data for site.)

At about one-half of the 19 monitoring sites where flow-adjusted trends in concentrations of both inorganic nitrogen species were tested, trends indicated a beneficial effect from management practices. No strong relations between any of the nitrogen trends and changes in nutrient sources or landscape characteristics were identified.

Although there were no upward trends in inorganic nitrogen from 1993 to 2003, there were upward flow-adjusted trends in total phosphorus concentrations at nearly one-half of the monitoring sites. At these sites, pollution-control strategies were not contributing to measurable decreases in total phosphorus concentrations, and indeed there was likely an increase in phosphorus loading on the land surface. This indicates that in some areas of the Missouri River Basin, overall concentrations of total phosphorus would have been higher without the decrease in streamflow and the associated decrease in surface runoff during the study period (1993–2003).

At 6 of 18 sites where trends were tested, management practices contributed to decreases in flow-adjusted suspended-sediment concentrations (fig. 5B), but at the majority of sites, there were no measurable effects from pollution-control strategies. Flow-adjusted trends in suspended-sediment concentration were significantly downward and greater than 8 percent per year for only two tested sampling sites during 1993–2003. The sediment load of Muddy Creek in Montana has decreased through improved irrigation efficiency that has decreased irrigation return flows, combined with bank stabilization (Browning and others, 2005). Moreover, in Muddy Creek the relation between flow and sediment was not consistent with time, primarily because of differences in sediment-transport responses to high flows related to irrigation operations rather than precipitation events (Browning and others, 2005). Dismal River had the largest downward flow-adjusted trend in suspended sediment during 1993–2003 and, because land use in its drainage is essentially 100 percent rangeland, the downward trend may reflect improvements in vegetative cover resulting from either wetter climate or improved range-management practices during the period.

In some parts of the Missouri River Basin, nutrient and suspended-sediment concentrations may have been larger without the decrease in streamflow and storm runoff that occurred during the study period. Without additional steps to minimize surface runoff or nutrient loading on the land, it is possible that concentrations will increase when streamflow and runoff increase again.

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