

### Do NAWQA findings substantiate national concerns?

NAWQA findings indicate that streams and ground water in basins with significant agricultural or urban development, or with a mix of these land uses, almost always contain complex mixtures of nutrients and pesticides. Concentrations of nitrogen and phosphorus commonly exceed levels that can contribute to excessive plant growth in streams. For example, average annual concentrations of phosphorus in three-fourths of streams in urban and agricultural areas were greater than the U.S. Environmental Protection Agency (USEPA) desired goal for preventing nuisance plant growth in streams. Nitrate generally does not pose a health risk for residents whose drinking water comes from streams or from aquifers buried relatively deep beneath the land. Health risks increase in those aguifers located in geologic settings, such as in

sand, gravel, or karst (weathered carbonate rock), that enable rapid movement of water. The most prevalent nitrate contamination was detected in shallow ground water (less than 100 feet below land surface) beneath agricultural and urban areas. This finding raises potential concerns for human health, particularly in rural agricultural areas where shallow ground water is used for domestic water supply. Furthermore, high levels of nitrate in shallow ground water may serve as an early warning of possible future contamination of older underlying ground water, which is commonly a primary source for public water

At least one pesticide was found in almost every water and fish sample collected from streams and in more than one-half of shallow wells sampled in agricultural and urban areas. Moreover, individual pesticides seldom occurred alone. Almost every sample from streams and about onehalf of samples from wells with a detected pesticide contained two or more pesticides. Concentrations of individual pesticides in samples from wells and as annual averages in streams were almost always lower than current USEPA drinking-water standards and guidelines. Standards and guidelines have been established for 46 of the 83 pesticides and breakdown products measured in water. Effects of pesticides on aquatic life, however, are a concern based on U.S. and Canadian guidelines, which have been established for 28 of the pesticides measured. More than onehalf of agricultural and urban streams sampled had concentrations of at least one pesticide that exceeded a guideline for the protection of aquatic life.

Potential risks to humans and aquatic life implied by NAWQA pesticide findings can be only partially addressed by comparison to established standards and guidelines. Many pesticides and their breakdown

#### Nutrients and pesticides and their connection to land use

Relative levels of contamination are closely linked to land use and to the amounts and types of chemicals used in each setting. Thus, local and regional management of chemical use can go a long way toward improving water-quality conditions.

#### **RELATIVE LEVEL OF CONTAMINATION**

	Streams				Shallow Ground Water	
	Urban areas	Agricultural areas	Undeveloped areas		Urban areas	Agricultura areas
Nitrogen	Medium	Medium-High	Low	Nitrogen	Medium	High
Phosphorus	Medium-High	Medium-High	Low	Phosphorus	Low	Low
Herbicides	Medium	Low-High	No data	Herbicides	Medium	Medium-Hi
Currently used insecticides	Medium-High	Low-Medium	No data	Currently used insecticides	Low-Medium	Low-Mediu
Historically used insecticides	Medium-High	Low-High	Low	Historically used insecticides	Low-High	Low-High

products do not have standards or guidelines, and current standards and guidelines do not yet account for exposure to mixtures and seasonal pulses of high concentrations. In addition, potential effects on reproductive, nervous, and immune systems, as well as on chemically sensitive individuals, are not yet well understood. For example, some of the most frequently detected pesticides are suspected endocrine disrupters that have potential to affect reproduction or development of aquatic organisms or wildlife by interfering with natural hormones.

# Are seasonal and geographic patterns evident and important in determining protection strategies?

Land and chemical use are not the sole predictors of water quality. Concentrations of nutrients and pesticides vary considerably from season to season, as well as among watersheds with differing vulnerability to contamination. Natural features, such as geology and soils, and land-management practices, such as tile drainage and irrigation, can affect the movement of chemicals over land or to aquifers and can thereby exert local and regional controls on water quality. Understanding the national, regional, and local importance of land and chemical use, natural features, and management practices on water quality increases the effectiveness of policies designed to protect water resources in diverse settings.

Seasonal patterns in water quality of streams emerged in most basins. The patterns reflect many factors, but mainly the timing and amount of chemical use, the frequency and magnitude of runoff from rainstorms or snowmelt, and specific land-management practices, such as irrigation and tile drainage. Concentrations of nutrients and pesticides are highest during runoff following chemical applications. The seasonal nature of these factors dictate the timing of elevated concentrations in drinking-water sources and aquatic habitats.

Natural features and landmanagement practices make some areas more vulnerable to contamination than other areas, thus, concentrations of nutrients and pesticides can vary among seemingly similar land uses and types of chemical applications. Patterns are most evident on a local scale, but they also occur regionally where similar natural features, land use, and land-management practices extend over broad areas. For example, ground water underlying intensive agriculture in parts of the Upper Midwest is minimally contaminated where it is protected by relatively impermeable soils and glacial till that cover much of the region. Tile drains and ditches commonly provide quick pathways for nutrient and pesticide runoff to streams in this area. Another example is in the Southeast, where streams and ground water commonly contain relatively low concentrations of nitrogen, partly because soil and hydrologic characteristics in this region favor conversion to nitrogen gas. In contrast, relatively high nitrogen concentrations occur in streams and shallow ground water in the Central Valley of California and parts of the Northwest, Great Plains, and Mid-Atlantic regions because natural characteristics favor transport of nitrogen.

### Is water quality getting better or worse?

Water quality is constantly changing, from season to season and from year to year. Long-term trends are sometimes difficult to distinguish from short-term fluctuations. For many chemicals, it is too early to tell whether conditions are getting better or worse because historical data are insufficient or too inconsistent to measure trends. Despite these challenges, some trends are evident from monitoring of nutrients and pesticides. These trends show that changes in water quality over time frequently are controlled by factors similar to those that affect geographic variability, including natural features, chemical use, and management practices. For example, concentrations of the organochlorine insecticide DDT have decreased in sediment and fish since restrictions were imposed on its production and distribution in the 1970s.

Changes in concentrations of modern, short-lived pesticides also follow changes in use; these changes are often focused in specific regions and land-use areas. For example, increases in acetochlor and decreases in alachlor are evident in some streams in the Upper Midwest, where acetochlor partially replaced alachlor for control of weeds in corn and soybeans beginning in 1994. The changes in use are reflected quickly in stream quality, generally within 1 to 2 years. In contrast, ground water responds more slowly to changes in chemical use or land-management practices because of slower traveltimes. This response can be delayed by years or decades.

#### Water-quality patterns...

### Some of the highest levels of nitrogen occur in streams and ground water in agricultural areas

Applications of fertilizers, manure, and pesticides have degraded the quality of streams and shallow ground water in agricultural areas and have resulted in some of the highest concentrations of nitrogen measured in NAWQA studies. Concentrations of nitrogen in nearly half of the streams sampled in agricultural areas ranked among the highest of all streams measured in the first 20 Study Units. Concentrations of nitrate exceeded the USEPA drinking-water standard of 10 milligrams per liter (as nitrogen) in 15 percent of samples collected in shallow ground water beneath agricultural and urban land, signifying a possible concern in some rural areas where shallow aquifers are used for drinking-water supply.

#### Phosphorus is elevated, too

Compared to nitrogen, a smaller proportion of phosphorus (originating mostly from livestock wastes or fertilizers) was lost from watersheds to streams. The annual amounts of total phosphorus and total nitrogen measured in agricultural streams were equivalent to less than 20 percent of the phosphorus and less than 50 percent of the nitrogen that was applied annually to the land. This is consistent with the general tendency of phosphorus to attach to soil particles and move with runoff to surface water. Even with the lower losses from land for phosphorus than for nitrogen, however, phosphorus is more likely to reach concentrations that can cause excessive aquatic plant growth. Nitrogen concentrations are rarely low enough to limit aquatic plant growth in freshwater, whereas phosphorus concentrations can be low enough to limit such growth. Hence, excessive aquatic plant growth and eutrophication in freshwater generally result from elevated phosphorus concentrations (typically greater than 0.1 milligram per liter). In contrast, nitrogen is typically the limiting nutrient for aquatic plant growth in saltwater and coastal waters.

### Pesticides—primarily herbicides—are found frequently in agricultural streams and shallow ground water

Extensive herbicide use in agricultural areas (accounting for about 70 percent of total national use of pesticides) has resulted in widespread occurrence of herbicides in agricultural streams and shallow ground water. The highest rates of detection for the most heavily used herbicides—atrazine, metolachlor, alachlor, and cyanazine—were found in streams and shallow ground water in agricultural areas. Insecticides were frequently detected in some streams draining watersheds with high insecticide use but were less frequently detected in shallow ground water because most insecticides are applied at lower levels than herbicides and tend to sorb onto soil or degrade quickly after application.

Transport of a chemical compound in the environment depends on its mobility. Some compounds, such as nitrate and atrazine, readily dissolve and move with water in both streams and ground water. Many forms of phosphorus, however, attach to soil particles rather than dissolve; a large proportion of such compounds is transported to streams with eroded soil, particularly during times of high runoff from precipitation or irrigation. Ground water typically is not vulnerable to contamination by compounds that

attach to soils.

The transport of a chemical compound in the environment also depends on its persistence. Some pesticides are not readily broken down by microorganisms or other processes in the natural environment. For example, DDT and chlordane can persist in soil, water, sediment, and animal tissue for years and even decades. Other pesticides, such as carbaryl, are relatively unstable in water and break down to other compounds in days or weeks. Chemical compounds that persist for a long time are likely to be transported farther than compounds that are short-lived.

#### ...in agricultural areas

#### Health effects of pesticides are not adequately understood

Concentrations of individual pesticides generally were low compared to USEPA drinking-water standards and guidelines; pesticides exceeded standards or guidelines in less than 1 percent of sampled wells. This good news, however, is tempered by the current uncertainty in estimating risks of pesticide exposure. For example, most contamination occurred as pesticide mixtures, such as atrazine, metolachlor, and other pesticides, whereas most toxicity and exposure assessments are based on controlled experiments with a single contaminant. In addition, some breakdown products, for which there are no established standards or guidelines, may have effects similar to their parent pesticides. Finally, water-quality standards and guidelines have been established for only about one-half of the pesticides measured in NAWQA water samples.

#### Aquatic life may be at more risk than human health

Effects on aquatic organisms may be greater than on humans in many agricultural areas. Although there are no USEPA aquatic-life criteria for the major herbicides, Canadian guidelines were exceeded at 17 of the 40 agricultural streams studied, most commonly for atrazine or cyanazine. Also, currently used insecticides exceeded guidelines for aquatic life in at least one water sample from 18 of the 40 agricultural streams. The major organochlorine insecticides, such as DDT, dieldrin, and chlordane (which no longer are used but remain widely detected in sediment and fish in agricultural streams) exceeded recommended sediment-quality guidelines for protection of aquatic life at about 15 percent of agricultural sites.



#### Water-quality patterns...

### Insecticides typically were detected in urban areas, sometimes at high concentrations

Urban areas, covering less than 5 percent of land in the continental United States, traditionally have not been recognized as important contributors to pesticide contamination, especially when compared to agricultural land, which covers more than 50 percent of the United States. Findings in the first 20 Study Units, however, show a widespread occurrence of some insecticides commonly used around homes and gardens and in commercial and public areas. In fact, these insecticides occurred at higher frequencies, and usually at higher concentrations, in urban streams than in agricultural streams. Most common were diazinon, carbaryl, chlorpyrifos, and malathion. As in agricultural areas, insecticides were detected in ground water less frequently than in streams. Some herbicides—including atrazine, simazine, and prometon, which are used to control weeds in lawns and golf courses, and along roads and rights-of-way—also occurred frequently in samples collected from streams and shallow ground water in urban areas.

### Concentrations of insecticides in urban streams commonly exceeded guidelines for protection of aquatic life

Insecticides, which generally are more toxic to aquatic life than herbicides, frequently exceeded USEPA, Canadian, or International Joint Commission water-quality guidelines in urban streams. Almost every urban stream sampled had concentrations of insecticides that exceeded at least one guideline, and most had concentrations that exceeded a guideline in 10 to 40 percent of samples collected throughout the year.

### Urban streams had the highest frequencies of occurrence of DDT, chlordane, and dieldrin in fish and sediment, and the highest concentrations of chlordane and dieldrin

DDT is an insecticide that commonly was used in the United States until the early 1970s to control insects on cropland and lawns and mosquitoes in populated areas. Chlordane and aldrin (the parent compound that breaks down to dieldrin) were used widely until the late 1980s to control termites. Since the use of DDT was restricted, concentrations have decreased in sediment in urban areas, as indicated by sediment-core samples from urban reservoirs and lakes. Similar declines are not yet evident in concentrations of chlordane and dieldrin in sediment, most likely because of their continued use into the late 1980s. Despite downward trends in some areas, organochlorine insecticides commonly are found at elevated levels in bed sediment and fish in urban streams. Sediment-quality guidelines for protection of aquatic life were exceeded at nearly 40

#### ...in urban areas

percent of urban sites, and concentrations in whole fish exceeded guidelines for protection of wildlife at 20 percent of urban sites. Although most urban streams are not used for drinking water, the frequent occurrence of insecticides in water, sediment, and fish is a potential concern for recreational use and for fish consumption.

#### Complex mixtures of pesticides commonly occur in urban streams

Similar to agricultural pesticides, urban pesticides commonly occurred in mixtures. More than 10 percent of urban stream samples contained a mixture of the insecticides diazinon and chlorpyrifos, along with at least four herbicides. Two of the most common herbicides in these mixtures were simazine and prometon.

#### Concentrations of phosphorus were elevated in urban streams

Concentrations of total phosphorus in streams generally were higher in urban areas than in agricultural areas; concentrations commonly exceeded the USEPA desired goal (0.1 milligram per liter) to control excessive growth of algae and other nuisance plants in streams. Elevated concentrations of phosphorus are, in part, due to effluent from wastewater treatment plants, despite some long-term decreases in phosphorus resulting from improved treatment technology. The highest concentrations of total phosphorus were in streams in semiarid western and southwestern cities, where discharges from wastewater treatment plants may account for a significant proportion of streamflow. Concentrations of phosphorus also were high in urban areas in the East.

### Nitrogen levels have remained nearly unchanged in rivers downstream from wastewater treatment plants

Although NAWQA focused mostly on nonpoint sources of nutrients, sampling of some rivers downstream from wastewater treatment plants showed that total nitrogen levels have remained nearly stable since the 1970s. Improvements in wastewater treatment have kept pace with urban population growth in major metropolitan areas. However, wastewater treatment has resulted in changes in the forms of nitrogen in the water; specifically, nitrogen in the form of ammonia commonly is converted to nitrate during the treatment process. The conversion makes the discharge less toxic to fish, but it may not help to resolve problems with excessive growth of algae.



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#### Water quality patterns...

### Contamination of major aquifers is largely controlled by hydrology and land use

Concentrations of nutrients and pesticides in 33 major aquifers generally were lower than those in shallow ground water underlying agricultural and urban areas. Water that replenishes the major aquifers is derived from a variety of sources and land-use settings, and includes high-quality water from undeveloped lands. In addition, deeper aquifers generally are more protected than shallow ground water by relatively impermeable materials. Contaminants are most prevalent in major aquifers located in vulnerable geologic settings that allow rapid vertical movement of water from the shallow ground-water system. For example, in 4 of 33 major drinking-water aquifers sampled, the USEPA drinking-water standard for nitrate was exceeded in more than 15 percent of samples collected. All four aquifers are relatively shallow, in agricultural areas, and composed of sand and gravel that is vulnerable to contamination by land application of fertilizers. Water in one-third of wells sampled in major aquifers contained one or more pesticides, but only one well had a pesticide (atrazine) concentration that exceeded a drinking-water standard.

### Hydrology and land use also are major factors controlling nutrient and pesticide concentrations in major rivers

Concentrations of nutrients and pesticides in major rivers reflect the proportion of urban and agricultural land in the drainage basin. River basins with large proportions of agricultural and (or) urban land had concentrations of nutrients and pesticides that were similar to those in smaller agricultural and urban streams. The greatest variety of pesticides occurred in basins draining both agricultural and urban land. Concentrations of nutrients and pesticides were moderate in major rivers draining mixed land uses because of dilution by water from undeveloped areas. None of the major rivers exceeded drinking-water standards or guidelines, although the consistent presence of pesticide mixtures remains a concern. Guidelines for the protection of aquatic life were exceeded in water at 36 percent of river sites sampled for currently used pesticides. Sediment-quality guidelines were exceeded at 11 percent of sites for DDT and other historically used insecticides, whereas concentrations of these compounds in whole fish exceeded guidelines for the protection of fish-eating wildlife at 24 percent of sites.

#### Key factors include soils and slope of land

Key factors governing vulnerability of surface water to contamination include the type of soil and slope of the land, both of which help to control the amount and timing runoff. Streams in basins with poorly drained clayey soils, steep slopes, and sparse vegetation generally are most vulnerable to contamination.

Concentrations of nutrients and pesticides generally are higher and more prevalent in streams than in ground water; however, indications of emerging ground-water contamination are important because ground-water contamination is difficult to reverse. Ground-water flow rates are slow, and a contaminated aquifer can take years or even decades to recover.

#### ...in areas with mixed land use and a range of hydrologic and environmental settings

Tile drains and urban pavement also accelerate flow to streams. In contrast, shallow ground water is most vulnerable to contamination in well-drained areas with rapid infiltration and highly permeable subsurface materials. Crop-management practices, which commonly are designed to reduce or slow the movement of sediment, nutrients, and pesticides to streams, also can increase infiltration of water and contaminants into the ground.



INCREASING POTENTIAL for nitrogen and phosphorus to enter streams...¹

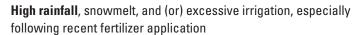
High rainfall, snowmelt, and (or) excessive irrigation, especially following recent fertilizer application

Steeply sloping areas with insufficient vegetation to slow runoff and sediment, or flat areas with artificial drains and ditches, which provide quick pathways for runoff to streams

Clayey and compacted soils underlain by poorly drained sediment and (or) nonporous bedrock, or extensive urban pavement, all of which create relatively impermeable surfaces for runoff



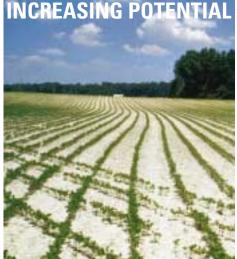
### INCREASING POTENTIAL for nitrate to enter ground water...



Well-drained and permeable soils that are underlain by sand and gravel or karst, which enable rapid downward movement of water

Areas where crop-management practices slow runoff and allow more time for water to infiltrate into the ground

Low organic matter content and high levels of dissolved oxygen, which can minimize chemical transformations of nitrate to other forms



<sup>&</sup>lt;sup>1</sup> These findings are based on general reviews of nutrient studies in agricultural and urban areas and do not necessarily indicate influences on specific forms of nitrogen or phosphorus.



The Missouri Department of Natural Resources, Division of Environmental Quality, has incorporated NAWQA stream-quality data into their database for statewide 305 (b) water-quality standards compliance monitoring. The Division will use these data to identify and prioritize problems, direct management, and assist in natural resource management, including the development of Total Maximum Daily Loads (TMDLs).

### Specific science-based considerations in this section are organized into four categories:

- Local and regional management strategies are needed to account for geographic patterns in land use, chemical use, and natural factors.
- Development of environmental policies must consider the entire hydrologic system and its complexities, including surface-water/ ground-water interactions and atmospheric contributions.
- Water-quality standards, guidelines, and monitoring programs should reflect environmental conditions, including seasonal variations and contaminant mixtures.
- Reliable predictive models are required to cost effectively estimate water-quality conditions that can not be directly measured for a wide range of possible circumstances.

### NAWQA FINDINGS on nutrients and pesticides suggest key science-based considerations for policies and strategies designed to restore and protect water quality.

Reductions of nutrient and (or) pesticide concentrations in streams and ground water clearly require management strategies that focus on reducing chemical use and subsequent transport in the hydrologic system. For these strategies to be effective, they should be developed with careful consideration of the patterns and complexities of contaminant occurrence, behavior, and influences on water quality. For example, concentrations of nutrients and pesticides vary from season to season, as well as among watersheds with differing vulnerability to contamination. These, and other patterns and complexities, frame four basic considerations that are critical for managing and protecting water resources in diverse settings across the Nation.

First, local and regional management strategies are needed to account for geographic patterns in land use, chemical use, and natural factors, which govern hydrologic behavior and vulnerability to contamination. Second, nutrients and pesticides are readily transported among surface water, ground water, and the atmosphere and, therefore, environmental policies that simultaneously address the entire hydrologic system are needed to protect water quality. Third, a top priority should be to reduce the uncertainty in estimates of the risks of pesticides and other contaminants to humans and aquatic life. This will require improved information on the nature of exposure and effects, and development of standards, guidelines, and monitoring programs that address the many complexities in contaminant occurrence. For example, neither current standards and guidelines nor associated monitoring programs, particularly with regard to pesticides, account for contamination that occurs as mixtures of various parent compounds and degradation products, or that is characterized by lengthy periods of low concentrations punctuated by brief, seasonal periods of higher concentrations. Finally, continued development of reliable predictive models is an essential element of cost-effective strategies to anticipate and manage nutrient and pesticide concentrations over a wide range of possible circumstances, over broad regions, and for the long term.

An understanding of these considerations will help water managers and policy makers in their implementation of environmental control and protection strategies, in investments in monitoring and science, and in the development of future environmental policies, standards, and guidelines. Such information should help guide answers to frequently asked questions, such as the following: How can we prioritize assessments and monitoring of nutrients and pesticides? What should we consider in the development of source-water protection programs and Total Maximum Daily Loads (TMDLs)? How often should we monitor nutrients and pesticides? Are certain times of year more critical than other times? How much and when does ground water contribute to streams?

### Local and regional management strategies are needed to account for geographic patterns in land use, chemical use, and natural factors.



The Pennsylvania Department of Agriculture, in developing its State Pesticides and Ground-Water Strategy, has decided to prioritize ground-water areas for assessments of pesticides on the basis of NAWQA vulnerability concepts, pesticide analyses, and guality-assurance protocols.

NAWQA data and activities laid the framework for developing maps showing the vulnerability of ground water to contamination by the widely used herbicide atrazine (see, for example, p. 72). These maps are being used by the Idaho State Department of Agriculture to develop its State Pesticide Management Plan.

### Level of needed protection increases with increasing amounts of agricultural and urban land

Concentrations of nutrients and pesticides in streams and shallow ground water generally increase with increasing amounts of agricultural and urban land in a watershed. This relation results because chemical use increases and less water is available from undeveloped lands to dilute the chemicals originating from agricultural and urban lands. In Willamette Basin streams during high spring streamflow following fertilizer application, concentrations of nitrate increased proportionately (from less than 1 up to 10 milligrams per liter) with increasing drainage area in agriculture (from about 0 to nearly 100 percent). Concentrations of nutrients also were found to increase with the percentage of drainage areas in agriculture for watersheds in the Ozark Plateaus, Potomac River Basin, and Trinity River Basin. This relation is evident not only within small watersheds but also regionally where agricultural land and chemical use extend over broad areas. For example, intensive herbicide and fertilizer use in the Upper Midwest have resulted in some of the highest concentrations of atrazine collected in stream samples across the Nation. Management strategies that are successful in reducing use and transport of this herbicide could lead to regional improvements in water quality.



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The Washington State Department of Ecology recently has created a Ground Water Management Area (GWMA) to protect ground water from nitrate contamination. The GWMA covers Grant, Franklin, and Adams Counties, located in an intensive agricultural region of the Central Columbia Plateau.

### Shallow ground water used for domestic supply near agricultural settings requires special consideration

Shallow ground water (less than 100 feet below land surface) in or adjacent to agricultural land use requires special consideration, particularly in rural areas where it may be used for domestic supply. The proximity to land surface and the level of human activity increase the vulnerability of this resource to contamination. Homeowners usually are not aware of

potential risks because domestic wells



are not monitored regularly, as is required by the Safe Drinking Water Act for large public-supply wells. In addition, many homeowners in recently established residential areas that rely on domestic wells for drinking water are not aware that chemicals leached from previously farmed land can remain in the shallow ground water for decades as a result of its slow movement.

### Level of protection needed in major aquifers varies with vulnerability to contamination

Varied geologic settings result in differences in vulnerability to contamination in deep major aquifers. Recognition of this can help tailor and target the appropriate level of protection and monitoring to the major aquifers of most concern, as required in the Safe Drinking Water Act source-water and drinkingwater programs and in nutrient- and pesticide-management plans.

The most extensive environmental control strategies and monitoring should be considered in major aquifers in vulnerable geologic settings that allow rapid influx and vertical mixing of water from shallow ground-water systems. Such systems include sand and gravel aquifers or alluvial fans, particularly those that are heavily pumped for irrigation and public water supply, as well as karst settings that provide open conduits for relatively rapid downward movement of water. Equally important to consider are possible connections to deep parts of the aquifer through poorly constructed or improperly sealed wells that allow surface water to travel quickly down the outside of well casings.

In general, extensive environmental control strategies and monitoring are less critical for most deep aquifers when compared to shallow ground water in similar land-use settings. Water in major aquifers generally is buried and protected deep beneath the land surface. Frequent sampling is not needed because the quality of deep ground water in these aquifers is minimally affected



Concentrations of nitrate in major aquifers in the Lower Susquehanna River Basin are highest in agricultural areas in karst settings. In almost one-half of the samples, concentrations exceeded 10 milligrams per liter, the drinking-water standard for nitrate.

by seasonal events. Spatially intensive sampling generally is not needed because variations in water quality over short distances are small. Water in deep aquifers generally flows along deep and long paths that integrate water quality over large areas for extended periods, sometimes for centuries.

Even in relatively protected settings, major aquifers require some level of consideration to support long-term prevention from contamination. Ground water at all depths is part of an integrated system and can never fully escape future contamination as water moves downward from shallow systems. Future contamination in deep major aquifers could pose serious concerns because these aquifers commonly are used for public water supply and because restoration of the quality of this relatively inaccessible and slow-moving water would be costly and difficult.



Concentrations of nitrate in water from major aquifers in the Rio Grande Valley were less than 2 milligrams per liter, indicating that movement of shallow ground water into the deeper parts of the aquifer is minimal.

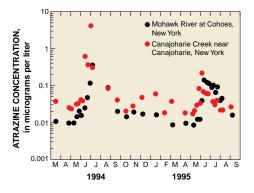
### Streams are more vulnerable to contamination than shallow ground water in areas that are extensively tile drained and ditched

Tile drains and ditches "short circuit" the ground-water system by intercepting soil water and shallow ground water and rapidly transporting it to streams. Tiling and ditching are commonly used to drain clayey glacial sediment in parts of the Midwest and organic, clayey Coastal Plain sediment in the Southeast. Streams in these areas can have elevated concentrations of agricultural chemicals because of outflow from drains and ditches. Seepage into the ground is minimized, resulting in lower concentrations of chemicals in ground water. An awareness of these conditions can help tailor the appropriate level of management and protection to streams in these areas.



### Small streams are more vulnerable to rapid and intense contamination than are larger rivers

Hydrologic and basin characteristics, including size of the basin and amount of streamflow, affect the timing of and magnitude of exposure to contaminants in the environment. Small streams respond quickly to rainfall or irrigation and, therefore, pulses of contaminants reach higher concentrations and rise and fall more quickly than in larger rivers. In contrast, larger rivers generally have more moderate levels of contaminants, but for longer durations. Recognition of these differences can help target the appropriate timing and degree of management and protection for different types of streams.



Concentrations of atrazine were 10 times higher and increased more rapidly in Canajoharie Creek than in the Mohawk River following Summer 1994 storms in the Hudson River Basin. The Mohawk River receives water not only from Canajoharie Creek but also from other tributaries draining a mix of land uses.



Development of environmental policies must consider the entire hydrologic system and its complexities, including surface-water/ground-water interactions and atmospheric contributions.

#### Effects of contaminants on the aquatic environment depend on surface-water flow

Contaminants and their potential effects on the environment vary throughout the year and largely depend on the amount of water flowing in a stream. Frequent monitoring is needed to characterize variations in contaminants, such as those that occur between low and high flows. Measurements of streamflow during these different conditions, in combination with water-quality samples, are needed to fully assess the amounts of contaminants transported by a stream throughout the year to a receiving body, such as an estuary. This information, particularly over the long term, is critical for developing TMDLs for streams and for assessing the potential effects of contaminants on the health and aquatic life of receiving waters.

### Ground water can be a major nonpoint contributor of nutrients and pesticides to streams

Historically, ground water has been overlooked as a major nonpoint contributor of contaminants to streams and coastal waters. Ground-water issues for water managers, however, continue to grow in importance in many parts of the Nation. For example, more than one-half of the water and nutrients that enter Chesapeake Bay first travel through the ground-water system. (3) Consideration of ground-water contributions is needed in water-resource programs, such as State programs designed to establish TMDLs in streams. Exclusion of ground water may prevent a full accounting of all available sources and may limit the effectiveness that TMDLs could have in future stream restoration and protection. Consideration of ground water also may be needed to ultimately reach Clean Water Act goals for fishable, swimmable, and drinkable waters.

The significance of ground water varies with local differences in geology and soils. Ground-water contributions to streams are most significant in geologic settings that allow rapid exchange between ground- and surface-water systems. Areas underlain by karst or by permeable and well-drained sediment can undergo relatively rapid, even seasonal, exchanges of water and contaminants. As seen in agricultural areas of the Platte River Valley in Central Nebraska, high concentrations of contaminants in streams commonly seep into shallow ground water following spring applications when river flows are high. In contrast, contaminants in aquifers can flow into adjoining streams during periods of low streamflow, such as noted in the Suwannee River in Florida.



Measurements of streamflow, in combination with water-quality samples, are needed to fully assess the amount of material transported by a stream to receiving bodies, such as estuarine or coastal waters.

In some areas, concentrations of contaminants may decrease as water is exchanged between streams and aquifers. For example, nitrate concentrations in about one-half of wells sampled near the South Platte River in Colorado exceeded the drinking-water standard. Ground water contributes a substantial amount of flow to the river in this area, but concentrations in the river were much lower than in the ground water because bacteria removed the nitrate as the ground water passed through the organic-rich streambed sediment.



During low-flow conditions, when inflow to a 33-mile reach of the Suwannee River, Florida, is entirely from springs and other ground water, the daily load of nitrate transported in this reach nearly doubled.

### Atmospheric contributions can be significant, too

The atmosphere can be a major source of nitrogen and pesticides. More than 3 million tons of nitrogen are deposited in the United States each year from the atmosphere, derived either naturally from chemical reactions or from the combustion of fossil fuels, such as coal and gasoline. The highest contributions of nitrogen from the atmosphere occur in a broad band from the Upper Midwest through the Northeast. Recent studies have shown that as much as 25 percent of the nitrogen entering Chesapeake Bay comes from the atmosphere. (4)

Nearly every pesticide that has been investigated has been detected in air, rain, snow, or fog throughout the country at different times of year. Annual average concentrations in air and rain are generally low, although elevated concentrations can occur during periods of high use, usually in spring and summer months. Several instances have been recorded in which concentrations in rain have exceeded drinking-water standards for atrazine, alachlor, and 2,4-D.<sup>(5)</sup> Atmospheric contributions are most likely to affect stream quality during periods when direct precipitation and surface runoff are the major sources of streamflow.

The atmosphere is an important part of the hydrologic cycle that can transport nutrients and pesticides from their point of application and deposit them outside the area or basin of interest. Consideration of atmospheric contributions is critical for effective management of water resources. Because atmospheric transport can cross State boundaries, full implementation of watershed-management strategies may require State and (or) regional involvement.

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Water-quality standards, guidelines, and monitoring programs should reflect environmental conditions, including seasonal variations and contaminant mixtures.

### Pesticide breakdown products and contaminant mixtures present new challenges for understanding health and environmental effects of pesticides

Pesticides break down to other compounds over time in the natural environment. Little is known about the occurrence of breakdown products, or their possible health and environmental effects. Frequent detections of some breakdown products, however, indicate the need for their consideration in the development of water-quality standards and monitoring strategies. For example, the herbicide atrazine commonly breaks down to DEA (deethylatrazine) and other products, both in streams and ground water; atrazine and DEA were detected together in more than 25 percent of ground-water samples in the first 20 Study Units. Water samples without detectable parent compounds, seemingly indicating no contamination, may merely reflect chemical transformations to other compounds. In fact, studies have shown that the parent compounds metolachlor, dacthal, alachlor, and cyanazine are often less commonly found in ground-water samples than their breakdown products. (6,34)

Mixtures of contaminants also require special consideration in assessing possible health and environmental effects, and thus in developing and improving water-quality standards. More than one-half of all stream samples contained five or more pesticides, and nearly one-quarter of ground-water samples contained two or more. These mixtures of pesticide parent compounds also occur with breakdown products and other contaminants, such as nitrate. Continued research is needed to help reduce the current uncertainty in estimating risks from commonly occurring mixtures. As improved information is accumulated, the occurrence of contaminant mixtures should be considered when developing water-quality standards and monitoring requirements.

# Karen Riva-Murray

The New York State Department of Environmental Conservation is applying NAWQA pesticide information and monitoring protocols in its statewide pesticide monitoring. The NAWQA data represent a broader array of analyses and lower detection limits than data previously available. The collaborative effort was sparked by public concerns over pesticides in New York State waters and their possible relation to the incidence of breast cancer.

### Some widely detected pesticides are not recognized in drinking-water monitoring requirements

New pesticides are introduced each year. It is often difficult to predict their behavior in the environment from laboratory experiments and to establish the appropriate level of monitoring needed to measure their occurrence. Designing appropriate monitoring programs for pesticides will, therefore, continue to be a dynamic process, continually evolving as new information is collected.

As an example, several pesticides that currently are not recognized on the USEPA Contaminant Candidate List were detected frequently in the first 20

Study Units. The USEPA is working with the USGS to target several of these pesticides for occurrence monitoring and guidance, including health advisories, as required by the Safe Drinking Water Act. Pesticides that were commonly detected in NAWQA analyses in the first 20 Study Units but that are not currently on the contaminant list are the herbicides 2,4-D and tebuthiuron and the insecticides carbaryl, malathion, and chlorpyrifos. Although not as frequently detected in the first 20 Study Units, the herbicide acetochlor, a probable human carcinogen approved for use in 1994, also is not on the list.

### Seasonal patterns dictate the timing of high concentrations in drinking-water supplies and aquatic habitats

The vulnerability to contamination of streams and ground water can differ seasonally. Increased monitoring and special management of water-supply sources may be needed during high-flow conditions and periods of agricultural chemical applications. The temporary use of ground-water sources of supply—if they have been developed and are available—might be considered as an alternative to surface-water sources to decrease the potential for not meeting drinking-water standards or aquatic-life criteria during such periods.

Concentrations of nutrients and some pesticides in streams draining agricultural areas commonly are higher during spring and summer months than during the rest of the year. Chemicals generally are transported shortly after application during high-flow conditions that result from spring rains, snowmelt, and (or) irrigation. Heavy irrigation runoff, which commonly carries high concentrations of nutrients and pesticides, is of special concern in the western part of the Nation (such as in the Trinity River Basin, San Joaquin-Tulare Basins, Rio Grande Valley, and Central Columbia Plateau) because such runoff can account for the majority of streamflow.

In other parts of the Nation, patterns can be different. For example, concentrations of diazinon in streams in the San Joaquin-Tulare Basins are high during winter because of high rainfall and use of dormant sprays on orchards. Differences in patterns also result from local water-management practices, including the timing of reservoir storage and water use. Seasonal patterns must be characterized and understood for each watershed because they dictate the timing of the highest concentrations in drinking-water supplies and aquatic habitats.



Surface runoff in agricultural areas can carry eroded sediment and attached chemicals, such as DDT, to streams during periods of heavy irrigation and (or) precipitation.

#### Monitoring during storms is needed to track peak inputs of contaminants to streams

Excessive amounts of contaminants can enter streams during storms and can have overriding effects on the quality of streams and the respective receiving bodies, such as estuarine or coastal waters. High flows in the Susquehanna, Potomac, and James Rivers during January 1996, for example, carried nearly one-half of the phosphorus and one-quarter of the nitrogen that typically is transported to the Chesapeake Bay in an average year. Fortunately, this flood occurred in winter, a time when grasses and many living organisms were dormant and when farmland, rich in nutrients, was frozen. Effects, such as increased algal growth and low levels of dissolved oxygen from subsequent algal decay, could have been much greater if the flood had occurred in spring or summer. Without monitoring information during major hydrologic events, a full accounting of nutrients and pesticides transported by streams is incomplete, and a full understanding of the effects of these contaminants on the health and living resources of receiving waters, such as the Chesapeake Bay, is restricted.



Major events affecting streams used for drinking-water purposes may require intensified monitoring during peak fertilizer- and pesticide-application periods. As an example, the Potomac River at Washington, D.C., carried an estimated 3,300 pounds of the herbicide atrazine and 3.3 million pounds of nitrogen in 5 days during a flood in June 1996. On two consecutive days following the storm, atrazine was measured at concentrations greater than the drinking-water standard of 3 micrograms per liter.

#### Considerations in monitoring the effectiveness of conservation buffers

Conservation buffers are small areas or strips of vegetation designed to mitigate the movement of sediment, nutrients, and pesticides within and from farm fields. They are supported by the U.S. Department of Agriculture (USDA) Farm Bill

and many conservation programs, such as the Conservation Reserve Program, Environmental Quality Incentives Program, and the Stewardship Incentives Program. The USDA goal is to help landowners install 2 million miles of conservation buffers by the year 2002.<sup>(8)</sup>

There are two considerations in monitoring the effectiveness of conservation buffers. The first consideration relates to tracking ground-water quality. In some areas, slowing the transport of runoff to streams by use of conservation buffers can increase infiltration of water and contaminants into the ground. As shown by the USGS in the Delmarva Peninsula, a pilot NAWQA study initiated in the mid-1980s, the transport and fate of these contaminants in the ground is variable, depending on soil and aquifer composition, topography, and rates and pathways of ground-water flow. (9) Monitoring of ground-water quality might, therefore, be beneficial to fully assess potential effects of conservation strategies.

The second consideration relates to time of year and its implications on tracking stream quality. The effectiveness of conservation buffers on stream quality is likely to be most evident when streamflow is dominated by runoff from rainfall, snowmelt, and (or) irrigation following chemical applications. Their effectiveness is likely to be less evident during low-flow conditions, when most of the streamflow is from ground-water discharge.



Vegetation along waterways can help slow surface runoff and movement of nutrients, pesticides, and sediment within and from farm fields and can improve stream quality.

### Long-term monitoring may be needed to evaluate the effectiveness of crop-management practices

Long-term monitoring may be needed to evaluate the effectiveness of some environmental control strategies, such as crop-management practices, because of the slow rate of ground-water flow and the time lag between adoption of practices and improvement of water quality. As demonstrated in the San Joaquin-Tulare Basins, shallow ground water below farmland will improve first, sometimes in several years or less. Decades may pass, however, before water quality improves in deeper aquifers.

A time lag between adoption of crop-management practices and improvement of water quality also can occur for streams. Because ground water containing elevated concentrations of nutrients and pesticides can discharge to surface water, enhancement of stream quality also could lag changes in agricultural practices by years or decades.

### Consistent and systematic information is needed over the long term to measure local, regional, and national trends

For many chemicals, it is too early to assess trends because historical data are insufficient or inconsistent. Some trends have emerged, however, from monitoring nutrients and pesticides; they show that changes in water quality over time are controlled largely by soils, geology, and other natural features, and by changes in chemical use and management practices. For example, concentrations of phosphorus and ammonia have decreased in rivers downstream from wastewater treatment plants since the 1970s because of improved treatment technology. Concentrations of organochlorine insecticides have been reduced in sediment and fish since restrictions on production and distribution of these pesticides in the 1970s and 1980s.

Changes in concentrations of modern, short-lived pesticides follow changes in use and tend to be focused in specific regions and land-use areas. For example, increases in acetochlor and decreases in alachlor are evident in some streams in the Upper Midwest, where acetochlor began replacing alachlor for control of weeds in corn and soybeans in 1994. The changes in use are reflected in stream quality relatively quickly, generally within 1 to 2 years.

In contrast, ground-water quality responds more slowly to changes in chemical use or adoption of land-management practices, typically lagging by several years and even decades. Local variations in natural features, such as soil types and amounts of recharge, can result in variable rates of ground-water flow, which thereby affect long-term responses to land-management practices. For example, concentrations of nitrate decreased significantly (from about 18 milligrams per liter in the mid-1980s to less than 2 milligrams per liter in the mid-1990s) in ground water underlying parts of the Central Platte Natural Resources District, Nebraska, after implementation of fertilizer management strategies. Yet, despite implementation of the strategies, the response has been delayed in other parts of the District because of differences in local features controlling ground-water flow. Specifically, concentrations of nitrate remained greater than two times the USEPA drinking-water standard in nearly one-fourth of wells in one area sampled by the District in the mid-1990s.

Systematic and consistent monitoring over the long term is essential at local, State, and national levels. Such monitoring will help water managers and policy makers to evaluate how well local and regional environmental controls are working and to choose the most cost-effective resource strategies for the future.



Progress in water-quality improvement, especially in ground water, may not be evident for years after farmers change their land-management practices because of slow ground-water movement.



# Reliable predictive models are required to cost effectively estimate water-quality conditions that can not be directly measured for a wide range of possible circumstances.

Effective strategies for managing nutrients and pesticides, as well as related water-quality issues, require far more information than we can afford to directly measure for the full range of places and times that are important. Moreover, many management problems, ranging from deciding how much to spend on a management strategy to approving a pesticide for use, are inherently related to predicting potential effects on water quality. Models and other methods can be useful for predicting water-quality conditions over a wide range of possible circumstances and are essential for improving water-quality management over broad regions.

NAWQA findings are beginning to play an important role in model development and validation, and an increased emphasis of explanatory and predictive modeling is planned for the second cycle of investigation in each Study Unit. Early examples are the estimation of ground-water vulnerability to atrazine contamination in the Upper Snake River Basin (p. 72) and to nitrate contamination in the Puget Sound Basin (see sidebar). In addition, ground-water vulnerability to nitrate contamination also was assessed at the national scale (p. 51). Although not directly predicting an outcome, these analyses use correlations to rank the likelihood and risk of contamination.

One of the most important roles that NAWQA can fulfill in working with water-management agencies is to provide systematic, high-quality data that can be used to develop and test predictive models for hydrologic systems throughout the Nation. The USEPA, for example, is using NAWQA pesticide data to test the reliability of models now being used to predict possible pesticide occurrence in streams and reservoirs. Water-quality models have been in use for many years, but their utility depends on their reliability for representing actual conditions. Without demonstrated reliability based on comparisons to measured conditions, confidence in a model is difficult to attain, and the usefulness of the model in decision making, especially in controversial situations, is limited.

As NAWQA studies progress from an emphasis on assessing and documenting water-quality conditions and cause-and-effect factors (during the first cycle of investigation) to an emphasis on a more detailed understanding of the most critical processes controlling water quality (during the second cycle), the development of predictive models will continue to grow and play a more vital role in both analysis and water-management applications.

#### Predicting ground-water vulnerability to nitrate contamination

A statistical model was created to predict the vulnerability of ground water to nitrate contamination from human activities in urban and agricultural areas in the Puget Sound Basin, Washington. [10] Factors that were used to predict the risk of contamination were well depth, surficial geology, and the percentage of agricultural and urban land use within a 2-mile radius of the well. Results from risk models provide managers with tools for guiding future land-use development, assessing potential health risks associated with nitrate, and designing cost-effective monitoring programs.

