PESTICIDES *in* U.S. Streams *and* Groundwater

A U.S. Geological Survey assessment shows widespread occurrence of pesticides, with concentrations in many streams at levels that may have effects on aquatic life and fish-eating wildlife.

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A 10-year study by the U.S. Geological Survey's (USGS's) National Water-Quality Assessment (NAWQA) Program provides a national-scale view of pesticide occurrence in streams and groundwater. The 1992–2001 study builds upon a preliminary analysis from NAWQA's first phase of studies during 1992–1996 (*1*, *2*). Pesticide data available from various studies prior to 1992 did not allow national assessment because of limited and variable geographic coverage (usually focusing on individual states or regions), sparse and inconsistent inclusion of pesticides in use, and variable sampling designs (*3–5*).

The expanded geographic coverage and improved data following 10 years of study (Figure 1) confirm and reinforce previously reported findings and enable more detailed analyses of each topic. This article summarizes selected findings from a comprehensive report (*6*), with a focus on the nature of pesticide occurrence and potential significance to human health and stream ecosystems. Information on study design and methods as well as additional analysis of geographic patterns and trends in relation to use and management practices are available in the full report (*6*).

Occurrence in streams and groundwater

Pesticide compounds were detected throughout much of the year in streams that have developed watersheds (>90% of the time, Figure 2). Developed watersheds are those dominated by agricultural, urban, or mixed land use (*6*). In addition, organochlorine compounds (such as DDT) were found in fish and bed-sediment from most streams in developed watersheds. Most of the organochlorine pesticides have not been used in the U.S. since before NAWQA studies began, but they continue to persist in the environment.

Pesticides were less common in groundwater than in streams, but occurred in >50% of wells that sampled shallow groundwater beneath agricultural and urban areas. One or more pesticide compounds were detected in 33% of the deeper wells that tap major aquifers used for water supply.

Streams are more vulnerable to pesticide contamination than groundwater and have more frequent occurrences of more compounds, as well as higher concentrations. Although groundwater is less vulnerable, it merits careful monitoring in agricultural and urban areas because contamination is difficult to reverse once it occurs.

DEX IMAGE

Assessing environmental significance

The frequent occurrence of pesticides raises the question: are concentrations high enough that they may have adverse effects on humans or aquatic ecosystems? The potential for adverse effects was evaluated by a screening-level assessment similar in concept to the U.S. EPA screening-level assessments (*7*). This provides a perspective on the extent and nature of potential effects and can be used to identify and prioritize needs for further investiga-

FIGURE 1

NAWQA study units

The NAWQA water-quality assessments followed a nationally consistent design in 51 major river basins and aquifer systems in the U.S., referred to as "study units", with 20 study units examined during 1992–1995, 16 during 1996–1998, and 15 during 1998–2001. Water samples were analyzed for 75 pesticides and 8 degradates, most of which are still in use, and bed sediment and fish tissue were analyzed for 32 organochlorine pesticide compounds (including 19 pesticides and 13 degradates and byproducts), most of which are no longer used in the U.S.

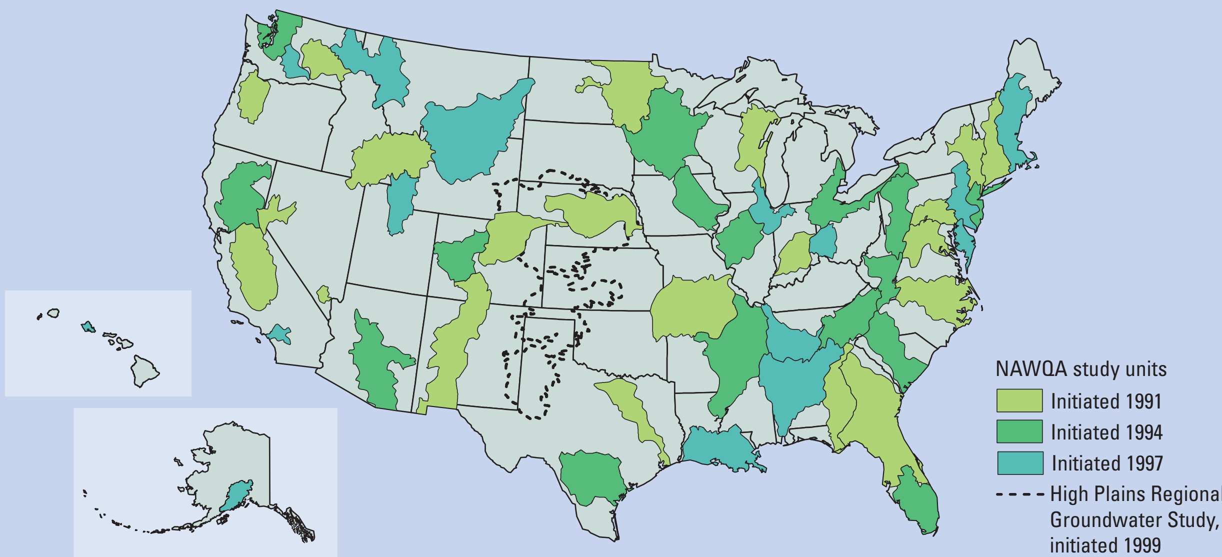
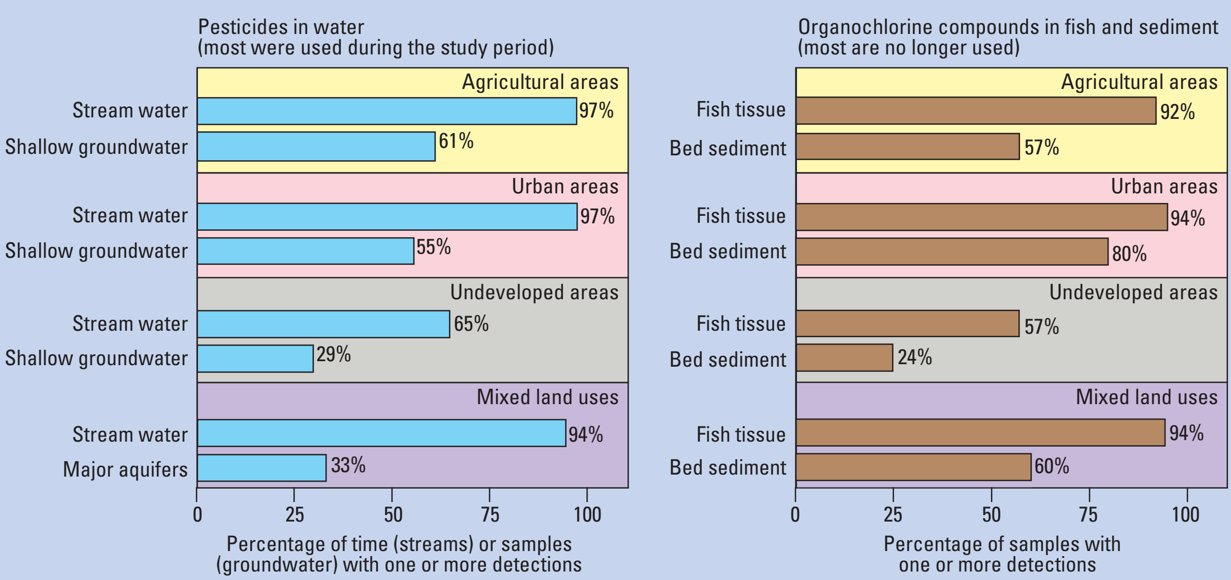


FIGURE 2

Occurrence of pesticides

Pesticide compounds are widespread in streams and groundwater, particularly in streams that have developed watersheds. All detections are included, regardless of concentration level.



tion. Concentrations of pesticides were compared with water-quality benchmarks derived from standards and guidelines established by EPA, toxicity values from EPA pesticide risk assessments, and selected guidelines from other sources (see pp 88–105 in Ref. 6). Most of the benchmarks are similar to "no-effect levels". Therefore, concentrations below the benchmark are expected to have a low likelihood of adverse effects and concentrations above the benchmark may have adverse effects, with increasing likelihood as concentrations increase.

Potential for human-health effects

Many of the wells sampled are used as sources of drinking water (domestic and public-supply wells), but human-health benchmarks were seldom exceeded in groundwater (Figure 3). One or more pesticides exceeded a benchmark in ~1% of the 2356 domestic and 364 public-supply wells that were sampled. The greatest proportion of wells exceeding a benchmark was for those tapping shallow groundwater beneath urban areas, including 1 public-supply well, 3 domestic wells, and 37 observation wells. Although observation wells are not used as sources of drinking water, they indicate pesticide occurrence in recently recharged groundwater, which may reach domestic or public-supply wells. Most pesticide occurrences in groundwater that exceeded a human-health benchmark were dieldrin, which was discontinued from use before the study began in 1992.

Although none of the NAWQA stream sites were located at drinking-water intakes, a perspective on

FIGURE 3

Comparison with human-health benchmarks

Concentrations of pesticides measured in streams (time-weighted annual means) and groundwater (single samples from wells) usually were lower than human-health benchmarks. Many of the wells sampled were sources of domestic or public water supplies during the study period, but none of the stream sites were located at drinking-water intakes.

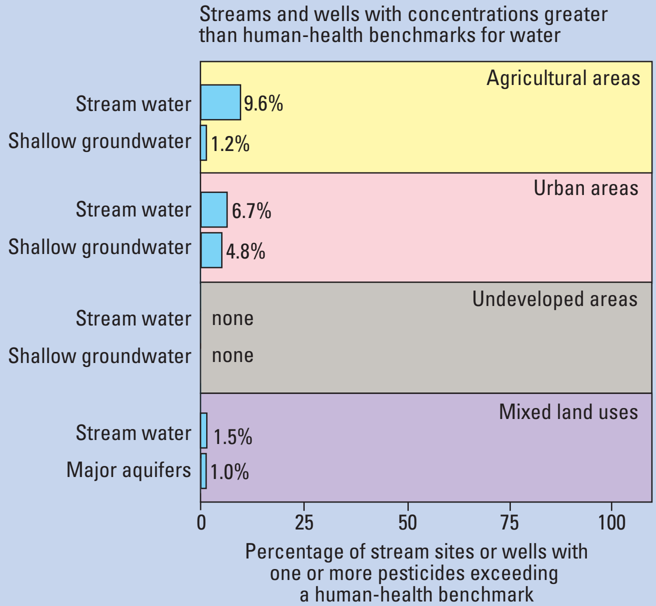
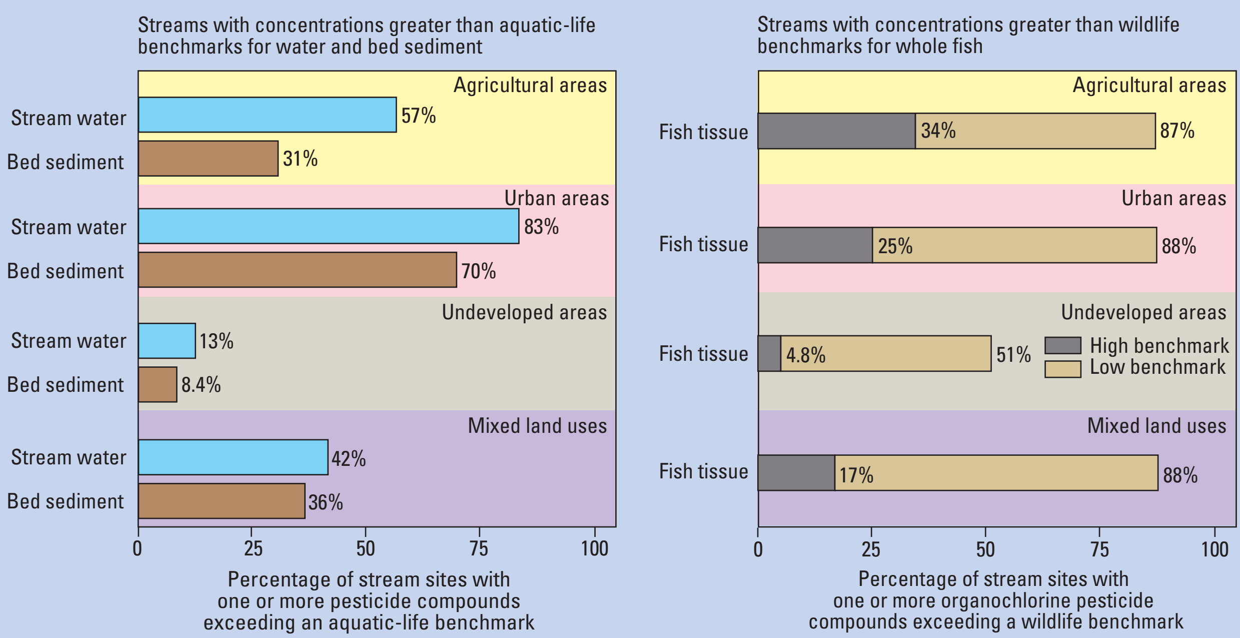
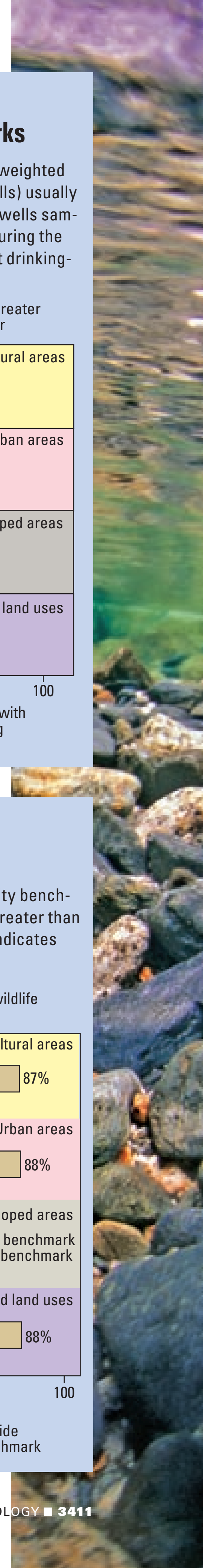


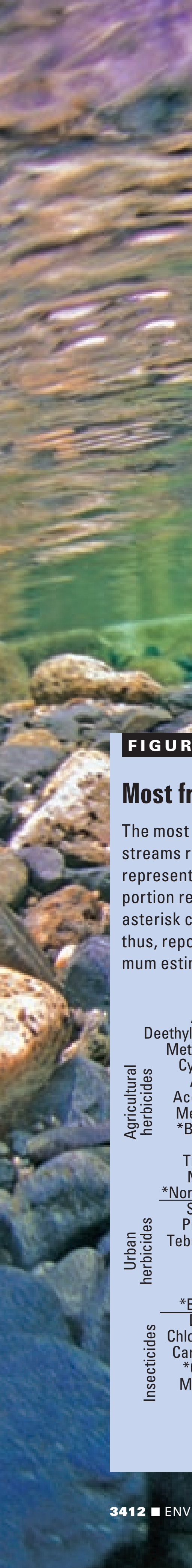
FIGURE 4

Comparison with benchmarks for aquatic life and wildlife

Concentrations of pesticide compounds measured in stream water and bed sediment frequently exceeded water-quality benchmarks for aquatic life. In addition, concentrations of organochlorine compounds measured in whole-fish tissue were greater than benchmarks for fish-eating wildlife at many sites. However, the range of results for low- and high-benchmark values indicates relatively high uncertainty.







the potential significance of pesticides to drinking-water sources was obtained by comparing the land-use settings of 1679 public-water-supply intakes on streams throughout the U.S. with the land-use settings of NAWQA streams. About 87% of drinking-water intakes on streams have undeveloped or mixed-land-use watersheds. No NAWQA streams with undeveloped watersheds and only one stream with a mixed-land-use watershed had an annual time-weighted mean concentration greater than a human-health benchmark. This indicates a low probability of benchmark exceedances for most water-supply intakes on streams.

Pesticide concentrations exceeding a human-health benchmark are more likely for streams with agricultural or urban watersheds, which account for ~12% and 1%, respectively, of public water-supply intakes on streams. Annual mean concentrations exceeded 1 or more human-health benchmarks in 8 of 83 agricultural streams sampled by NAWQA, and in 2 of 30 urban streams.

Overall, the screening-level assessment indicates that the individual pesticides measured by NAWQA, and which have human-health benchmarks, have a low potential to affect humans from long-term consumption of most drinking-water sources. Limitations of the assessment—including no consideration of mixtures, incomplete coverage of pesticides and degradates, and the lack of water-quality benchmarks for some of the compounds that were measured and detected—prevent drawing broader conclusions.

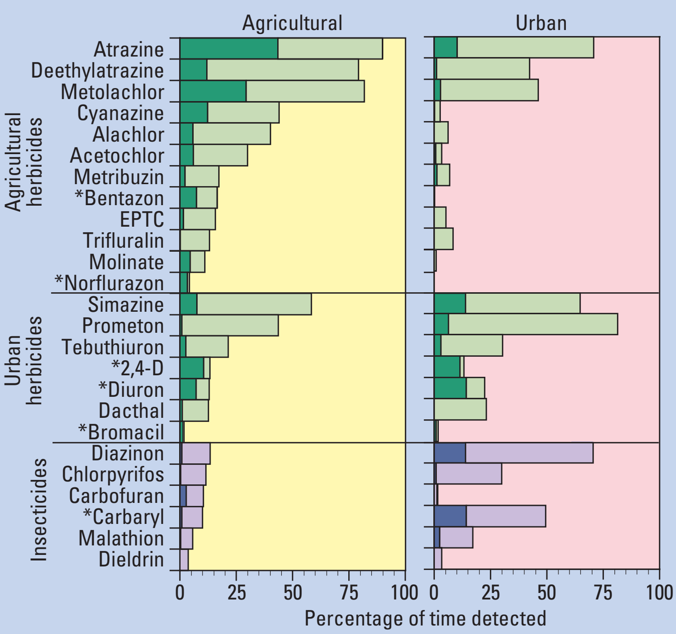
Overview of findings

- Pesticides were frequently present in streams and, to a lesser extent, groundwater, particularly in areas with substantial agricultural and/or urban land use.
- The geographic and seasonal distribution of pesticide occurrence follows patterns in land use and pesticide use.
- Individual pesticides were seldom found at concentrations that exceeded water-quality benchmarks for human health.
- Pesticides occurred in many streams at concentrations that exceeded water-quality benchmarks for aquatic life or fish-eating wildlife.
- Pesticide compounds with the potential to adversely affect aquatic ecosystems include currently used pesticides as well as organochlorine compounds from historic use of pesticides that were banned years ago.
- Pesticides usually occurred as mixtures of multiple pesticide compounds, rather than individually, potentially leading to underestimation of toxicity when assessments are based on individual compounds.

FIGURE 5

Most frequently detected pesticides

The most frequently detected pesticides in agricultural and urban streams reflect their predominant uses. The full length of each bar represents all detections, regardless of concentration, and the dark portion represents detections ≥0.1 µg/L. Pesticides marked with an asterisk could not be detected reliably at concentrations <0.1 µg/L; thus, reported frequencies for these pesticides <0.1 µg/L are minimum estimates.



Potential for effects on aquatic life and fish-eating wildlife

The potential for pesticides to adversely affect aquatic life and fish-eating wildlife is greater and more widespread than for humans. Concentrations were higher than water-quality benchmarks for aquatic life and fish-eating wildlife in more than half of the agricultural and urban streams (Figure 4). Of the 178 streams with developed watersheds, 56% had one or more pesticides in water that exceeded at least one aquatic-life benchmark. Most urban streams (83%) had benchmark exceedances—mainly by the insecticides diazinon, chlorpyrifos, and malathion. Although benchmark exceedances for these compounds declined during and after the study period (benchmarks were exceeded in 95% of urban streams sampled during 1993–1997 and in 64% during 1998–2000), their uses are being replaced by other insecticides that were not measured by NAWQA. More than half of agricultural streams (57%) had benchmark exceedances—most frequently by chlorpyrifos, azinphos-methyl, atrazine, *p,p′*-DDE, and alachlor. As the use of alachlor declined through the study period, benchmark exceedances also declined, with no exceedances during the last 3 years of study.

Aquatic-life benchmarks for organochlorine compounds in bed sediment also were frequently exceeded, particularly in urban areas. Most compounds that exceeded benchmarks for sediment were derived from organochlorine pesticides, such as DDT, chlordane, aldrin, and dieldrin, which have not been used since before the study began. Concentrations of organochlorine compounds in fish indicate a wide range of potential for effects on fish-eating wildlife. A lack of consensus on toxicity values for some organochlorine compounds, particularly DDT, results in high uncertainty in benchmarks for fish-eating wildlife.

Management of the potential effects of pesticides on aquatic life and wildlife is complicated by the combined presence of currently used pesticides and degradates, together with organochlorine pesticide compounds derived from pesticides that were largely banned prior to 1990.

Frequently detected pesticides and patterns of occurrence

The specific pesticides detected most frequently were, not surprisingly, among those that were used most heavily during the study or in the past. Their occurrence correlates with patterns in land use and use intensity, with additional influences—especially for groundwater—by natural factors and management practices.

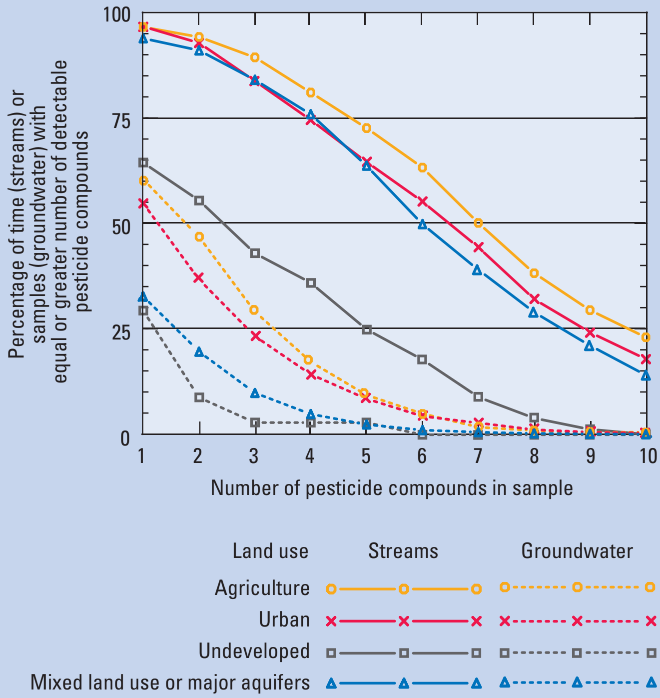
Herbicides used mainly for agriculture (atrazine, metolachlor, cyanazine, alachlor, and acetochlor) were detected most often and at the highest concentrations in streams in agricultural areas where their use was greatest, particularly in the Corn Belt. Five herbicides commonly used in urban areas (simazine, prometon, tebuthiuron, 2,4-D, and diuron) and three insecticides (diazinon, chlorpyrifos, and carbaryl) were most frequently detected in urban streams (Figure 5). Pesticide levels in stream water followed strong seasonal patterns, usually characterized by lengthy periods of low concentrations punctuated by seasonal pulses of much higher concentrations.

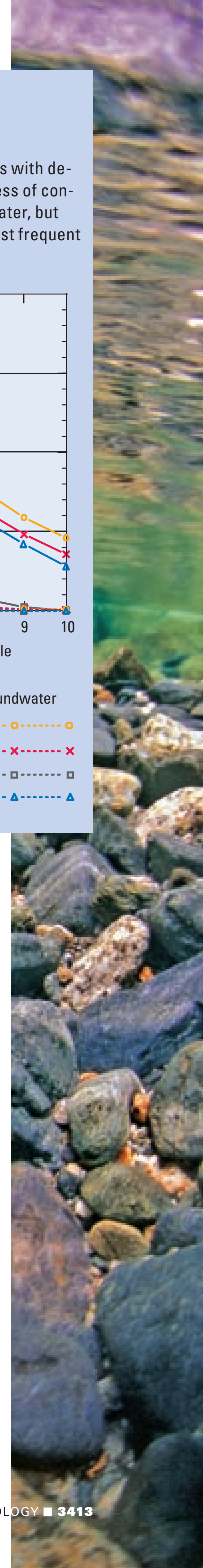
Pesticide detections in groundwater followed similar patterns in relation to land use, but at much lower frequencies of detection than in streams. Groundwater was most vulnerable to contamination in areas with highly permeable soil and aquifer materials and where subsurface drainage systems are absent and, thus, do not divert recharge to surface water. Understanding these patterns of pesticide occurrence and the factors that influence them enables anticipation and prioritization of the pesticides most likely to affect water quality in each land-use setting.

FIGURE 6

Frequency of pesticide mixtures in water

Mixtures of pesticide compounds are prevalent in streams with developed watersheds (all detections are included, regardless of concentration level). Mixtures are less prevalent in groundwater, but shallow wells in agricultural and urban areas have the most frequent occurrences.





Priorities for filling information gaps

• Improve tracking of pesticide use in agricultural and nonagricultural areas, including amounts, locations, and timing. Reliable information on use is key to efficient and cost-effective water-quality monitoring and assessment, including development of predictive models.

• Add assessments of new pesticides and others not yet studied. Regular updates to water-quality assessments are needed to keep findings relevant to present-day use patterns.

• Improve assessment of pesticide degradates. Although major degradates are considered as part of registration studies, environmental occurrence and potential adverse effects are not adequately understood.

• Evaluate potential effects of mixtures on humans and aquatic life. Mixtures are the most common mode of occurrence, but toxicity has not been assessed for many compounds and has been assessed only for a small proportion of specific combinations.

• Evaluate the effects of management practices on concentrations and transport of pesticides. Relatively little information exists on the effects of common management practices such as drainage, buffer strips, and tillage practices on pesticide transport to streams and groundwater.

• Improve methods for prediction of pesticide levels. There will never be enough resources to measure all the places, times, and compounds for which information is needed; thus, predictive tools are essential.

• Sustain and expand long-term monitoring for trends. Pesticide use is constantly changing over time, including phaseouts of some products and introductions of new ones, making long-term monitoring critical for up-to-date water-quality assessment and evaluation of trends.

Mixtures of pesticides

Pesticides occurred as mixtures of multiple pesticide compounds much more often than individually. Streams with developed watersheds contained ≥2 pesticide compounds >90% of the time, and ≥10 compounds ~20% of the time (Figure 6). Although mixtures were less common in groundwater, 47% of the shallow wells in agricultural areas, and 37% of shallow wells in urban areas, contained ≥2 compounds. The herbicides atrazine (and its degradate, deethylatrazine), simazine, and prometon were common in mixtures found in streams and groundwater in agricultural areas. The insecticides diazinon, chlorpyrifos, carbaryl, and malathion were common in mixtures found in urban streams. The frequent occurrence of pesticide mixtures, particularly in streams, implies that the total combined toxicity of pesticides in aquatic ecosystems may often be greater than that of any single pesticide that is present.

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