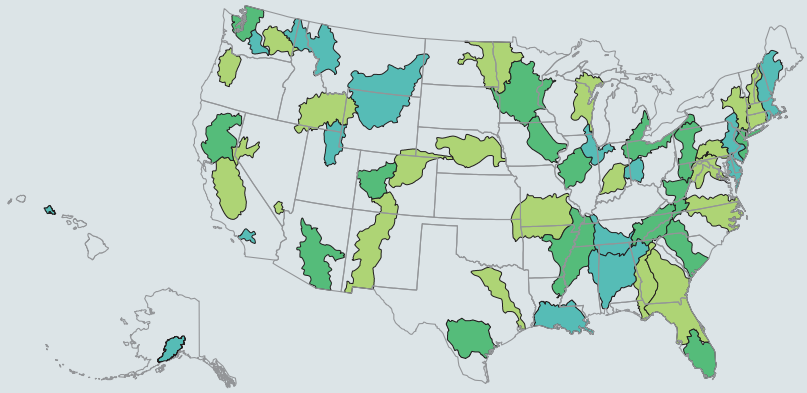
3 NAWQA's Approach to Pesticide Assessment

NAWQA's assessment of pesticides during 1992–2001 provides the most comprehensive analysis to date of pesticide occurrence in streams and ground water of the United States. The assessment followed a national study design in which the most important hydrologic systems were studied on a rotational schedule using nationally consistent sampling and analytical methods. This approach yields an understanding of water-quality conditions in a national context, while also supporting comparisons and assessments within and among individual watersheds, aquifers, and geographic regions. By systematically relating pesticide occurrence and transport to key factors that control contamination—such as pesticide use and properties, land use, hydrology, and other environmental features—NAWQA provides information needed for managing pesticides within the Nation's diverse land-use and environmental settings.



This chapter summarizes the primary features of the NAWQA study design, providing the context for understanding findings about pesticides in the Nation's streams and ground water.

Targeted Sampling Across the Nation's Diverse Land Uses and Environmental Settings

This report is based on results from NAWQA's first decade of water-quality assessments, which were completed on a rotational schedule from 1992 to 2001 in 51 major hydrologic systems across the country—referred to as Study Units—as well as the High Plains Regional Ground Water Study, using a nationally consistent study design (see p. iv–v). Assessments were conducted in 20 Study Units during 1992–1995; in 16 during 1996–1998; and in 15 Study Units during 1998–2001. Collectively, the 51 NAWQA Study Units and the High Plains Study cover a substantial portion of the Nation's land area; account for more than 70 percent of total water use and more than 50 percent of the population served by public water supplies and domestic wells; and are representative of the Nation's diverse landscapes, hydrologic systems, ecological resources, and land uses.

The primary objectives of the NAWQA pesticide assessment were to determine: (1) the occurrence and concentrations of pesticides in streams (ranging from small streams to large rivers) and ground water; (2) where and when pesticides occur in relation to factors that govern their sources and transport in the hydrologic system; (3) whether any pesticides may be present at concentrations that could affect human health, aquatic life, or fish-eating wildlife; and (4) how concentrations are changing over time.

To address these goals, NAWQA employed a targeted assessment focusing on studies of:

- streams and shallow ground water in specific, relatively homogeneous land-use and environmental settings to relate pesticide occurrence to individual types of nonpoint sources; and
- streams and major aquifers (regionally extensive aquifers that are important ground-water resources for water supply) in areas of mixed land uses to evaluate the integrated effects of multiple sources of pesticides on their occurrence and concentrations.

Details on the sampling design and analytical methods, as well as all data used in this report are available at: *http://ca.water.wr.usgs.gov/pnsp/pubs/circ1291/*.

For the targeted assessment by land use, streams and shallow ground water were sampled in agricultural and urban areas, and in undeveloped areas dominated by forest or rangeland. As described in more detail below and in the accompanying sidebar, streams and ground water were sampled most intensively in agricultural and urban areas because of the importance of assessing pesticide occurrence in areas where the compounds are used most intensively. The agricultural areas are diverse in climate, geography, and crop types, and span coastal, desert, and temperate environmental settings. They include, for example, areas dominated by production of corn and soybeans in the Midwest; wheat and other grains in the Great Plains; mixed row crops and poultry in the East; rangeland in the Southwest; rice in Louisiana; pineapple in Hawaii; and areas of grain, fruits and nuts, vegetables, and specialty crops in California and the Pacific Northwest. The areas sampled in urban settings were primarily residential, typically with low-to-medium population densities (300 to 5,600 people per square mile). Some commercial or industrial areas also were included, but point sources and extensive industrial and downtown urban areas generally were not assessed.

Table 3–1. Each stream sampled by NAWQA was classified according to the dominant land uses in its watershed. The land-use data set used for these classifications was an enhanced version of the USGS 1992 National Land Cover Data (NLCD), which classified land use for each 30-by-30-meter area of land in the conterminous United States. The original and enhanced versions of the NLCD are described, respectively, by Vogelmann and others (2001) and Nakagaki and Wolock (2005).

Land-use classification	Watershed land-use criteria
Agricultural	> 50 percent agricultural land and ≤ 5 percent urban land
Urban	> 25 percent urban land and ≤ 25 percent agricultural land
Undeveloped	≤ 5 percent urban land and ≤ 25 percent agricultural land
Mixed	All other combinations of urban, agricultural, and undeveloped land

NAWQA Stream Assessment in a National Context

Potential land-use influences on the quality of water sampled at NAWQA stream sites were characterized by determining the proportions of each major land use within each stream's contributing watershed. Table 3–1 lists the criteria used by NAWQA to classify each stream sampling site by its predominant land-use category. Streams classified as "mixed land use" drain mixtures of

Unique Features of the NAWQA Approach

Water-quality assessments by NAWQA, which is a single program among many local, State, and Federal programs, were not designed to address all of the Nation's water-resource information needs and issues. Listed below are several characteristics and limitations of the NAWQA approach that are important to consider when interpreting the findings on pesticides presented in this report.

- NAWQA assessments characterized the quality of the available, untreated water resources, and not the quality of drinking water (as would be done by monitoring water from water-treatment plants or from household taps). By focusing on the quality of streams and ground water in their present condition (ambient water quality), NAWQA complements many Federal, State, and local drinking-water monitoring programs.
- NAWQA assessments did not focus on specific sites with known water-quality problems or narrowly defined "issues of the day," but rather on the condition of the total resource, including streams and ground water in a wide range of hydrologic and land-use settings across the country.
- NAWQA assessments of pesticides focused primarily on non-point sources resulting from applications for pest management in agricultural, urban, and other land-use settings, although some sites—particularly those downstream from major metropolitan areas—also may be influenced by point sources, such as discharges from wastewater treatment plants.
- NAWQA assessments targeted specific land-use settings that are most extensive or important to water quality in a wide range of hydrologic and environmental settings across the Nation. This targeted approach gives priority to understanding the most critical factors influencing water quality. Extension of results to national analysis, however, requires careful definition of each type of water resource and environmental setting for which conclusions are drawn and the use of statistical models to extrapolate results to resources that have not been measured.
- USGS analytical methods were designed to measure concentrations as low as economically and technically feasible. Studies of contaminant occurrence and behavior benefit from the most information possible at all concentration levels, and such data help to identify emerging issues and to track changes in concentrations over time. By this approach, however, pesticides were commonly detected at concentrations far below Federal or State standards and guidelines for protecting water quality. Detections of pesticides do not necessarily indicate that there are appreciable risks to human health, aquatic life, or wildlife. The potential for such risks must be assessed by comparing measured concentrations with those that may cause adverse effects.
- USGS methods for analyzing pesticides in water measured concentrations in filtered water samples and, thus, may underestimate concentrations of compounds that have strong affinities for suspended particles. The potential for underestimation is greater for stream water compared with ground water because of the generally greater amounts of suspended particles present in stream water—which are removed by filtration along with any pesticides contained in or on the particles.
- Pesticide compounds analyzed in water by NAWQA included many of the most heavily used herbicides and insecticides, but they included only a fraction of all pesticides currently in use and few of their degradates. NAWQA findings provide insights about what to expect for pesticides and degradates that were not measured, but must be considered as only a partial assessment of currently used pesticides.
- Organochlorine pesticide compounds analyzed by NAWQA in bed sediment and fish tissue are predominantly related to pesticides that were no longer in use by 1990. Of the pesticide compounds measured in bed sediment and fish tissue, only dacthal, endosulfan, lindane, methoxychlor, and permethrin were used during all or part of the study period.

two or more land-use settings and do not meet the criteria described in table 3–1 for individual agricultural, urban, or undeveloped settings. Land-use classifications were adjusted for a small number of streams that have watersheds with substantial areas that did not contribute streamflow during the study period. Most streams that were classified as agricultural, urban, or undeveloped also commonly have small amounts of other land uses in their watersheds. For example, and of particular importance to findings for pesticides, many streams classified as undeveloped have some agricultural or urban activity in their watersheds.

Consistent with the sampling design, which was targeted by land use, the NAWQA pesticide findings discussed in this report generally are presented by land-use category. Aggregation of NAWQA findings for streams across all land-use categories would not accurately represent all streams in the conterminous United States (fig. 3–1), which were characterized by classifying the watersheds of all stream segments in the USEPA river reach file (Nolan and others, 2003) using NAWQA land-use criteria (table 3–1). For example, nearly 40 percent of the streams sampled by NAWQA were agricultural streams, whereas agricultural streams represent about 15 percent of all streams in the conterminous United States. Furthermore, as shown in figure 3–1, agricultural streams represent only about 10 percent of all streams with public water-supply intakes. There are 1,679 public water-supply intakes on streams across the Nation for which land use could be characterized. The NAWQA design also over-represented urban streams and under-represented undeveloped streams compared with the national occurrence of streams in these land-use settings (fig. 3–1).

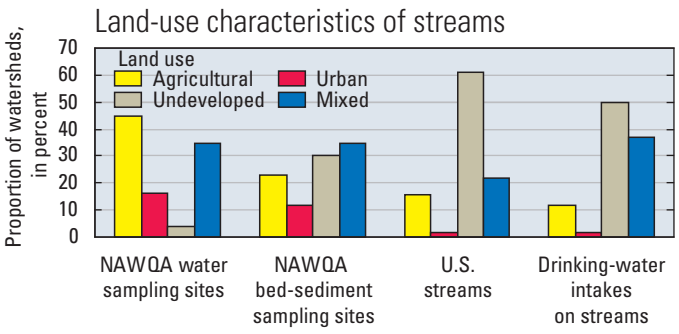


Figure 3–1. The NAWQA design for stream assessments placed greater emphasis on sampling streams that drain agricultural and urban watersheds (as defined in table 3–1), relative to those in undeveloped watersheds. Streams sampled by NAWQA included higher proportions of agricultural and urban streams—and lower proportions of undeveloped streams—compared with all streams in the conterminous United States and those with drinking-water intakes.

Even when grouped by land-use category, the watersheds of NAWQA sampling sites that were classified as agricultural and urban still tend to have higher proportions of agricultural and urban land than most streams nationwide in the same land-use groups, as well as streams with public water-supply intakes in the same land-use groups. For example, about 25 percent of agricultural streams sampled by NAWQA had watersheds with more than 90 percent agricultural land, compared with about 18 percent of all agricultural streams in the United States with more than 90 percent agricultural land. This indicates that NAWQA estimates of pesticide occurrence for agricultural and urban streams (for water and, to a lesser degree, bed sediment) are likely, as groups, to be high relative to those for other streams nationwide in these same land-use classes.

NAWQA Ground-Water Assessment in a National Context

NAWQA assessed pesticides in ground-water within specific land-use settings and in major aquifers with influences of a mixture of land uses. Land-use studies focused on shallow ground water primarily within agricultural and urban land-use settings, and to a lesser extent in undeveloped areas. Each of these studies involved the sampling of about 20 to 30 randomly located wells (using either existing or newly installed wells) within each targeted land-use area. Most of the wells selected or installed for the land-use studies sampled ground water from less than 20 feet below the water table, thus indicating as directly as possible the influence of each land use on shallow ground-water quality.

Major aquifer studies involved the sampling of about 20 to 30 domestic or public-supply wells that withdraw water from aquifers or aquifer systems that are major current or future sources of water supply. Wells that were sampled for these studies were randomly selected throughout the areas underlain by each major aquifer, without regard to land use. Thus, the ground water sampled for the major aquifer studies reflects the effects of a mixture of different land uses and ground-water ages on water quality, often including water that recharged long distances

from the sampled wells and in a variety of different land-use settings. The nature and extent of each major aquifer sampled for these studies is described in the summary report for the NAWQA Study Unit in which it occurs (see *http://water.usgs.gov/nawqa/*).

NAWQA findings for ground water, as for streams, are grouped by land use in this report. NAWQA's targeted sampling design for ground water over-represented areas with urban and mixed land use, somewhat over-represented agricultural areas, and under-represented undeveloped areas when compared with the national distribution of these land-use settings by land area (fig. 3–2). Comparisons of land-use distributions for the NAWQA ground-water studies with those for the entire Nation were based on NAWQA land-use classifications (as defined in table 3–1) for every square kilometer in the conterminous United States. Although NAWQA agricultural and urban stream sites, as discussed above, tend to have greater proportions of agricultural and urban land in their watersheds than other streams in the same land-use groups, ground-water studies are not expected to have this tendency within these land-use groups because each well was selected by site-specific land-use criteria designed to meet the land-use objective for each study. Such site-specific control of land-use characteristics was not possible for streams because of the relatively large areas included in each watershed.

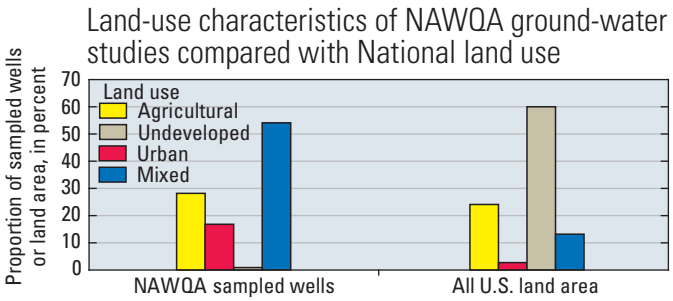


Figure 3–2. NAWQA's targeted sampling design for ground water emphasized areas with urban, mixed, and agricultural land use—and under-represented undeveloped areas—when compared with the national distribution of land uses. All wells sampled for major aquifer studies were classified as mixed land use for this graph.

Large streams and rivers required sampling from bridges, boats, or cableways.

Most wells sampled for major aquifer studies were existing water-supply wells.

Sampling Design

The NAWQA national assessment of pesticides is based on results from the analysis of more than 10,000 samples of water, bed sediment, and fish tissue from thousands of locations within the 51 NAWQA Study Units. Water-soluble pesticides, most of which were in use during the study period, were assessed in stream water and ground water. Organochlorine pesticides, which are no longer used in the United States, but remain persistent in the environment, were assessed in bed sediment and fish tissue—environmental media in which they accumulate.

Most wells sampled for agricultural and urban land-use studies were observation wells installed by NAWQA.

Stream Water

Water samples were collected at 186 stream sites for analysis of pesticides and degradates dissolved in water (fig. 3–3). The samples were collected from streams throughout the year, including high-flow and low-flow conditions. Sampling was most intensive during the time of highest pesticide use and runoff—generally weekly or twice monthly for a 4- to 9-month period. Most analyses in this report are based on 1 year of data for each site (generally representing the single most complete year of sampling) to give equal influence to each stream. Because of the rotational assessment approach, the most complete year of sampling for each stream ranged from 1993 to 2000, depending on the particular site.

Bed Sediment and Fish

Samples of bed sediment were collected at 1,052 sites (fig. 3–3) and fish-tissue samples were collected at 607 of the bed-sediment sites (plus 93 additional sites not shown on the map) for analysis of organochlorine pesticides and selected degradates and by-products. At each site, fine-grained surficial bed sediment (sieved to < 2 millimeters [mm]) was collected from multiple depositional areas within a stream reach on a single date—usually during low-flow conditions—and combined into a single composite sample for chemical analyses. For fish, multiple individuals of the same species were collected at a site, also on a single date, and whole fish were composited for chemical analyses of tissue.

Ground Water

Water samples were collected from 5,047 wells in 187 land-use and major aquifer studies for analysis of pesticides and degradates dissolved in water (fig. 3–3). For the land-use studies, most of the wells sampled were new or existing observation wells or domestic supply wells. The major aquifer studies focused almost exclusively on existing wells used either for domestic or public supply. Repeated sampling, such as that conducted at stream sites, was not included for ground water because of the comparatively slow rate of change in most ground-water systems, relative to streams. Data analyses were based on one sample per well.

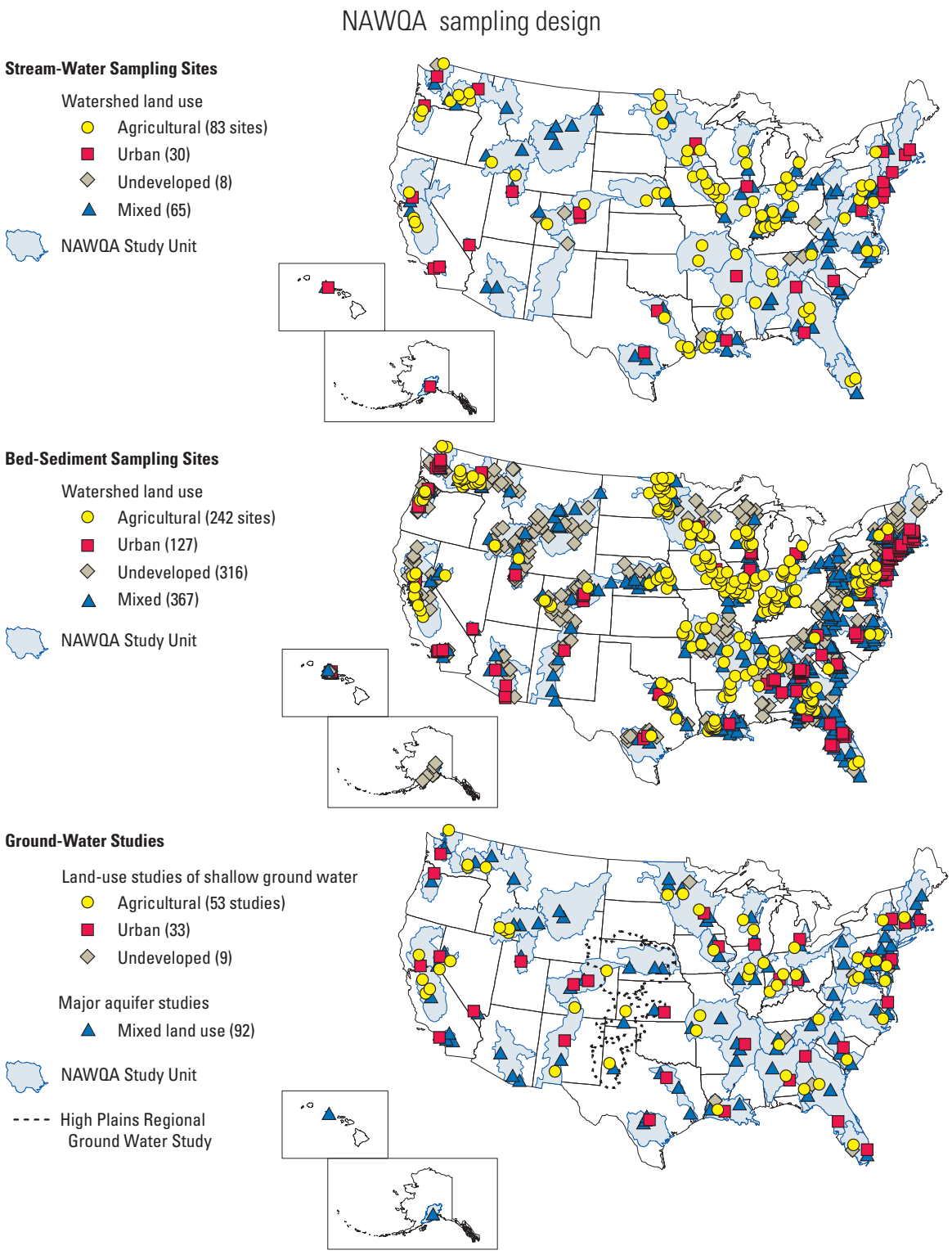


Figure 3–3. Stream sampling sites and ground-water studies in agricultural, urban, and undeveloped areas were distributed across the Nation's diverse environmental settings to evaluate the occurrence of pesticides within areas of specific land uses. Pesticides also were assessed in streams and major aquifers that represent the water-quality effects of mixed land uses and varied environmental settings.

Chemical Analyses

NAWQA chemical analyses encompassed the most complete range of pesticides ever measured in a single assessment, and included many of the Nation's most heavily used pesticides (Appendix 1). Most NAWQA water samples were analyzed for 75 pesticides and 8 pesticide degradates, which during the study period accounted for about 78 percent of the Nation's agricultural use of conventional pesticides, by weight of active ingredient (fig. 3–4). The analytical strategy resulted in relatively thorough coverage of the major herbicides and insecticides in use for agricultural purposes during the period of study, including 20 of the 25 most heavily used herbicides and 16 of the 25 most heavily used insecticides (fig. 3–5). All water samples were filtered prior to analysis. As a result, reported pesticide concentrations, particularly in stream water, may underestimate concentrations of some compounds that have

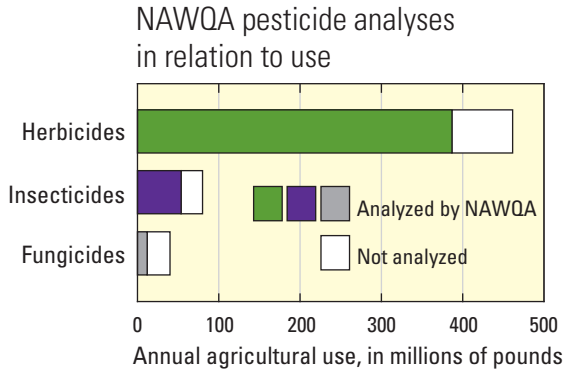


Figure 3–4. The NAWQA analytical strategy for water samples included 75 pesticides that accounted for about 78 percent of total national agricultural use during the study period, with relatively thorough coverage of the major herbicides and insecticides, but sparse coverage of fungicides, fumigants, and nematicides. (Use estimates are for 1997, as reported by Gianessi and Marcelli, 2000.)

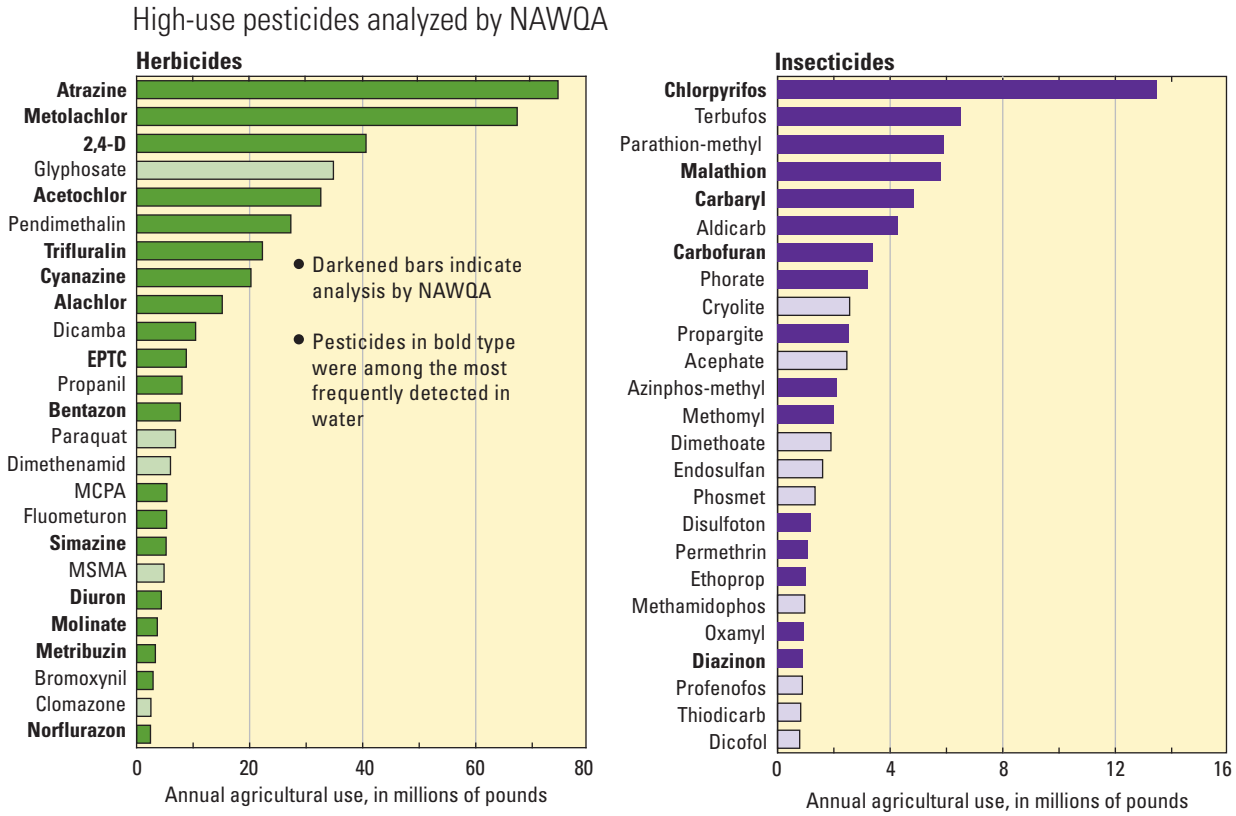


Figure 3–5. The NAWQA analytical strategy for water samples included 20 of the 25 most heavily used herbicides and 16 of the 25 most heavily used insecticides during the study period. More than half of these 36 high-use pesticides included in NAWQA analyses (dark bars) were among those most frequently detected in water (bold type), as described in Chapter 4. Some high-use pesticides, such as glyphosate, were omitted because no suitable analytical method was available, or because of budget constraints. (Use estimates are for 1997, as reported by Gianessi and Marcelli, 2000.)

strong affinities for suspended particles because of removal by filtration.

Historically used organochlorine insecticides (such as DDT) and selected degradates and by-products were analyzed in bed sediment and fish tissue—environmental media in which they continue to persist long after the uses of the parent compounds were discontinued in the United States. Bed-sediment and fish-tissue samples were analyzed for up to 32 pesticide compounds, consisting of 19 parent pesticides and 13 degradates and by-products. Results for organochlorines are sometimes described for pesticide groups (such as "total DDT") because all compounds in the group are derived either from common parent pesticides (for example, the isomers p,p′-DDD and p,p′-DDE are degradates of p,p′-DDT), or from indistinguishable pesticide products (for example, dieldrin may originate from application of dieldrin or or as a degradate of aldrin). Pesticide groups are identified and defined in Appendix 1B. Together, the organochlorine pesticides examined by NAWQA account for more than 90 percent of the Nation's historical use (by weight) of organochlorine pesticides in agriculture.

Some pesticides and degradates were assessed only in selected study areas or for limited periods of time. For example, several degradates of alachlor and metolachlor were measured at selected sites in different parts of the Nation, including streams draining parts of the Great and Little Miami River Basins, where use of the parent pesticides was high. Some pesticides were included in newly developed analytical methods late in the study period and were examined only in selected high-use areas, as was the case for fipronil in the Acadian–Pontchartrain Drainages. These and other pesticides with limited data are described for selected case studies in this report, but are not included in the national analysis.

Pesticides Not Assessed

Many potentially important pesticides and degradates were not assessed because of limited analytical methods or budget constraints. For example, glyphosate, the pesticide that ranked fourth among the top 10 herbicides used in 1997, was not routinely analyzed because its chemical structure and properties require analytical methods that are different from NAWQA methods, which were designed to cost-effectively measure large suites of compounds simultaneously. As a result, a separate method was developed for glyphosate and it was added as an analyte in selected studies late in the study period. Similarly, cryolite—an inorganic insecticide used on grapes and that ranked ninth among the top 10 insecticides used in 1997—was also not routinely analyzed in NAWQA samples. Of all the fungicides used, only chlorothalonil (ranked highest in use among fungicides) was included, and there were no nationally consistent analyses of any fumigants or nematicides. Other pesticide compounds that were not assessed by NAWQA include other inorganic pesticides (such as sulfur and copper), oil, biological pesticides, and numerous pesticide degradates, manufacturing by-products, and adjuvants.

Although NAWQA included the broadest and most complete range of pesticides measured in a single national assessment, it still must be considered selective. Consequently, NAWQA results should be expected to underestimate the overall occurrence of pesticides and degradates in many of the hydrologic systems that were studied.