2 Pesticide Primer

Pesticides are used to control weeds, insects, and other pests in agricultural areas, urban areas, and a variety of other land-use settings. Once released into the environment, pesticides and their degradates can move through the hydrologic system to streams and ground water, where they may affect humans, aquatic life, or wildlife if concentrations occur at toxic levels. Many factors affect the transport and concentrations of pesticides in streams and ground water, including the intensity and distribution of their use; natural factors, such as climate and soil characteristics; and the physical and chemical properties of the pesticide compounds themselves.

This chapter provides a basic overview of the use of pesticides and the factors that control their transport and fate in streams and ground water, thus serving as a foundation for understanding the occurrence and significance of pesticides in the hydrologic system—topics that are examined in subsequent chapters.

Pesticides and Their Uses

A pesticide is any substance used to kill or control insects, weeds, fungi, rodents, bacteria, or other unwanted organisms. Pesticides provide a range of benefits, including increased food production and reduction of insect-borne disease, but their use also raises questions about possible adverse impacts on the environment, including potential effects on drinking-water sources and aquatic life.

All pesticide products contain one or more active ingredients, which are referred to as pesticides in this report. Most pesticide products also contain adjuvants, which are usually referred to as inert ingredients on product labels. Active ingredients specifically target the pest organism, whereas adjuvants are used to increase the effectiveness of the active ingredient. Adjuvants were not extensively assessed as part of NAWQA studies and are not addressed in this report, although some may have toxicological importance. As of 1997, about 900 pesticides were registered in the United States for use in more than 20,000 different pesticide products (Aspelin and Grube, 1999). New pesticides are introduced every year—for example, typically 10 to 20 new active ingredients were registered each year from 1967 to 1997 (Aspelin and Grube, 1999).

Trends in pesticide use

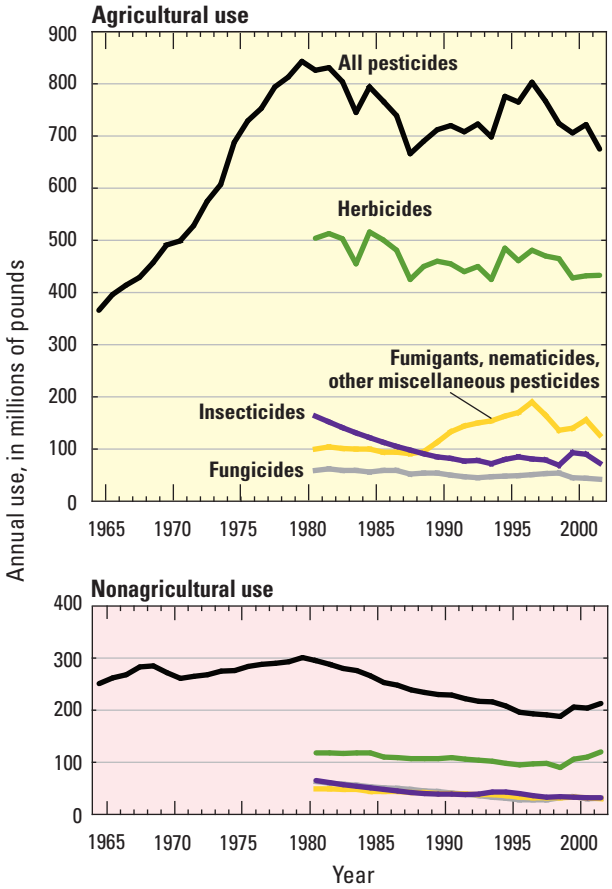

Figure 2–1. Total agricultural use of pesticides—more than half of which was accounted for by herbicides—increased from 1964 until about 1980 and then varied between about 700 and 800 million lb/yr until 2001. Nonagricultural use of pesticides, much of which occurs in urban settings, remained relatively steady from 1964 to 1979, gradually declined from 1979 to 1998, and then increased through 2001. (Data from Donaldson and others, 2002; and Kiely and others, 2004.)

Conventional pesticides include four major groups: herbicides, insecticides, fungicides, and a mixed group of fumigants, nematicides and other pesticides. An average of almost 1 billion pounds (lb) of conventional pesticides was used each year in the United States during the 1992–2001 study period (fig. 2–1). NAWQA studies focused primarily on herbicides and insecticides, as described further in Chapter 3. In addition to conventional pesticides, about 4 billion lb of other registered pesticides are used each year, including chlorine disinfectants, wood preservatives, and other specialty products. These other types of pesticides were not included in NAWQA assessments.

Pesticide names used in this report are the scientific names of the active ingredients, such as atrazine and diazinon—rather than product names—in order to minimize confusion among the vast array of products and their names. For example, a 1994 analysis identified a total of 7,340 different product names associated with 386 commonly used pesticides—an average of 19 different product names per pesticide (Milne, 1995).

Pesticides are released into the environment primarily through their application to agricultural lands, such as croplands and orchards, and for nonagricultural pest control, such as on lawns and gardens, commercial areas, and rights-of-way. In 2001, agriculture accounted for 76 percent of total national use, with the remaining 24 percent being applied for a wide range of nonagricultural purposes (Kiely and others, 2004).

The nature and extent of pesticide use for agriculture in the United States has continually changed over the past 40 years. Total use for agriculture steadily increased from 1964 to 1980—from less than 400 million to more than 800 million pounds per year (lb/yr)—and then varied between about 700 and 800 million lb/yr from 1980 to 2001 (fig. 2–1). From 1980 to 2001, the use of herbicides and fungicides decreased

slightly, insecticide use decreased by about half, and the combined use of fumigants, nematicides, and other pesticides increased.

By comparison, nonagricultural use of pesticides remained relatively constant from 1964 to 1979, in the range of 250–300 million lb/yr, and then gradually decreased to about 190 million lb/yr by 1998. From 1998 to 2001, nonagricultural use increased, driven primarily by increases in the amounts of herbicides, insecticides, and fungicides applied for home and garden pest control (Kiely and others, 2004).

Trends in the use of individual pesticides applied for agricultural or nonagricultural purposes commonly vary from these overall patterns, depending on factors such as market conditions, regulatory actions, and the introduction of new pesticides or approaches (for example, genetically engineered crops or organic agriculture). Selected trends are discussed in Chapter 8 as part of an evaluation of changes in pesticide occurrence in streams and ground water.

Most agricultural use of conventional pesticides is accounted for by fewer than 100 active ingredients. In 1997, for example, 25 herbicides accounted for approximately 92 percent of total herbicide use, 25 insecticides accounted for 91 percent of total insecticide use, 25 fungicides accounted for 99 percent of total fungicide use, and 20 pesticides accounted for 100 percent of total fumigant and nematicide use (Gianessi and Marcelli, 2000). The national use of a pesticide, however, does not necessarily indicate the importance of its use in a particular area. For example, some pesticides are used in small quantities nationally (ranking them outside the top pesticides by weight), but are used intensively or frequently in certain areas. Pesticide use within a particular agricultural area is determined by many factors, including the types of weeds, insects, and other pests of concern, the potency and application rates of specific pesticides, climate, regulatory limits, and cost. These factors are closely related to the types of crops and the extent of their production. For example, more than 50 percent of all agricultural pesticide use in the Nation (by weight) is for pest control on only three crops—corn, soybeans, and cotton. Applications to corn alone account for about 30 percent of total pesticide use in the United States (fig. 2–2). Estimates of pesticide use for agricultural purposes are available for more than 200 pesticides by crop and county for all States except Alaska and Hawaii (Thelin and Gianessi, 2000; see *http://ca.water.usgs.gov/pnsp/*).

Pesticides are used for nonagricultural purposes in urban and suburban areas to control weeds, insects, and other pests around homes and gardens, in parks and golf courses, along roads and other rights-of-way, and in commercial and industrial areas. Pesticides are also used for nonagricultural purposes in undeveloped and agricultural areas to control weeds, insects and other pests along fence rows and roadsides, in parks, and around rural residences. Nationally, total nonagricultural use is estimated to exceed the amount applied to any single crop except for corn (fig. 2–2). Data on nonagricultural use of pesticides, however, are much more limited than those for agricultural use. The only current published national data on nonagricultural use of specific pesticides are for 10 of the pesticides most commonly applied in each of two nonagricultural market sectors: (1) home and garden use by homeowners, and (2) use for industrial,

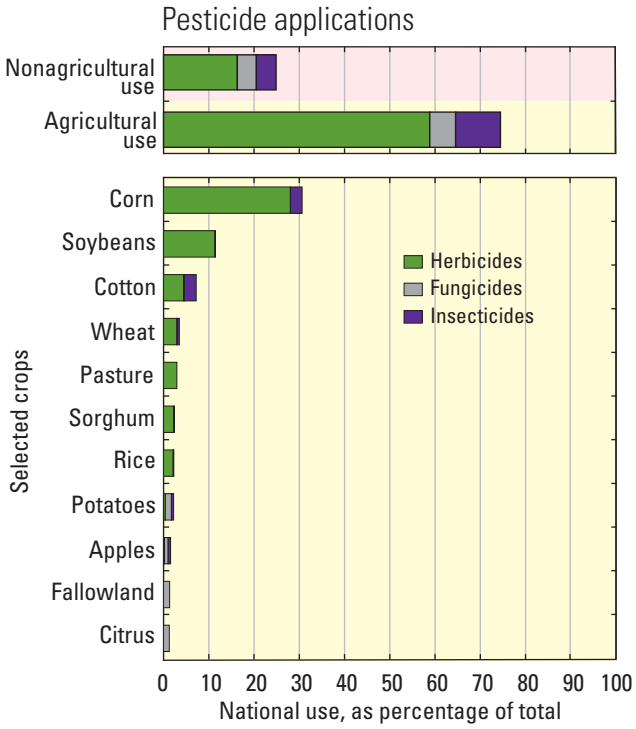

Figure 2–2. Agricultural use of pesticides in 2001 was about three times greater than nonagricultural use. However, nonagricultural uses, such as applications to control weeds and insects in urban and suburban areas, were second only to corn when compared with individual crops. (Pesticide use estimates for individual crops are for 1997 and are from Gianessi and Marcelli, 2000; use estimates for total agricultural and nonagricultural uses are for 2001 and are from Kiely and others, 2004.)

commercial, and government applications (Kiely and others, 2004).

In addition to total use, the intensity of pesticide applications—expressed as the amount applied per unit of land area (such as pounds per acre)—also is an important consideration in assessing possible effects on water quality. For example, land devoted to corn production constitutes only about 8 percent of the total national area of agricultural and urban land uses, and yet pesticide applications to corn account for 30 percent of total national use. In contrast, pasture lands constitute about 50 percent of the total national area of agricultural and urban land, but account for only 4 percent of the total pesticide use. Collectively, urban areas across the Nation cover about the same area of land as corn (about 8 percent of the total agricultural and urban land area) and account for much of the 24 percent of total pesticide use that is attributed to nonagricultural purposes (Kiely and others, 2004). Estimates from the early 1990s indicate that the intensities of applications of herbicides to turf grass at sod farms, golf courses, and residences—and of applications of fungicides to turf at golf courses—are greater than the intensities of applications to most crops (Barbash and Resek, 1996). Available information indicates a relatively high intensity of nonagricultural use in urban areas.

The specific pesticides applied in a particular area differ by land use, crop type, and targeted pests. For example, during the 1992–2001 study period, certain pesticides, such as 2,4-D, diuron, diazinon, and chlorpyrifos, were more intensively used in urban and suburban areas across the Nation than in most agricultural settings. The types of crops largely determine which pesticides are applied in agricultural areas, resulting in distinct geographic patterns of use (fig. 2–3). The use of each pesticide during 1997 was estimated by combining the 1997 state-level use data reported by Gianessi and Marcelli (2000), with county crop acreages from the 1997 Census of Agriculture (U.S. Department of Agriculture, 1999), using methods described by Thelin and Gianessi (2000). Use intensity was mapped for agricultural land using land-cover data from the early 1990s (Vogelmann and others, 2001) as described by Nakagaki and Wolock (2005). For example, molinate is used only on rice, which is grown primarily in the lower Mississippi River Valley and in parts of Louisiana, Texas, and California. Diazinon, atrazine, and diuron also have their own unique patterns of application. Considering the combined use of all pesticides, the overall intensity of pesticide application for agriculture is greatest in the croplands of the Corn Belt, the Mississippi River Valley, Florida, the coastal plain of the Southeast and Mid-Atlantic states, and irrigated areas of the West.

Although the amounts and intensities of pesticide applications largely define the sources of pesticides to the environment in a particular location, the potential of a pesticide to affect water quality is also influenced by its sources and pathways in the hydrologic system, its chemical and physical properties (which determine mobility and persistence), and its toxicity to humans, aquatic life, and wildlife. A basic background on the influences of sources, transport pathways, and pesticide properties on the behavior of pesticides in hydrologic systems—and some of the potential implications for water quality—is summarized below and these factors are further explored in Chapters 4 and 5. The potential effects of pesticides on humans, aquatic life, and wildlife are examined in Chapter 6.

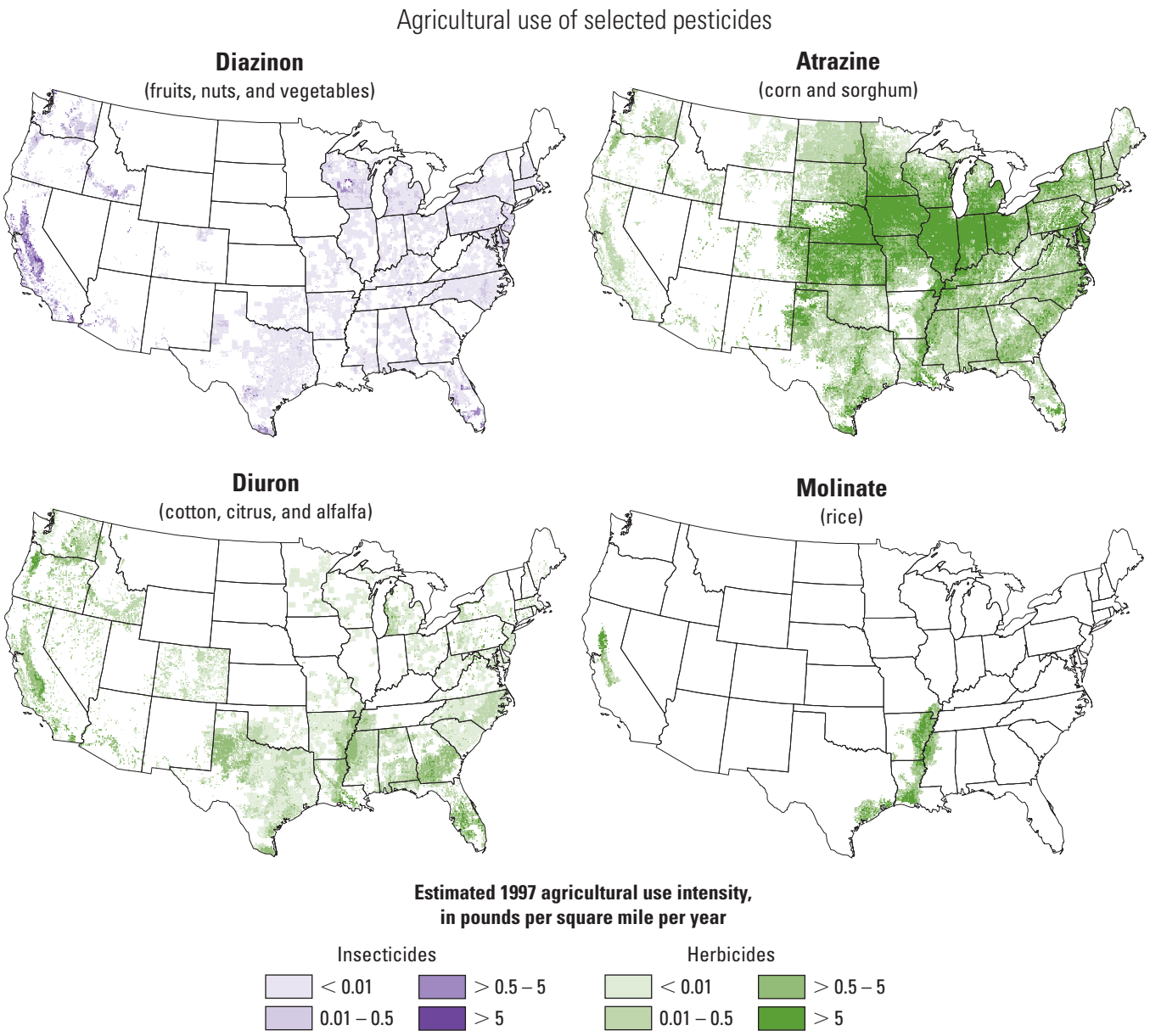

Figure 2–3. The geographic distribution of the use of each pesticide follows the distributions of crops and pests for which it is applied. Examples for the 1997 agricultural use of the insecticide diazinon and the herbicides atrazine, diuron, and molinate show four distinctly different geographic patterns of use. (Use intensity for 1997 was mapped for agricultural land using methods described on p. 24.)

Sources and Pathways in the Hydrologic System

Pesticides, like most other water contaminants, enter the hydrologic system from point sources, which are associated with specific points of release, and from nonpoint sources, which are diffuse and widely dispersed. Nonpoint sources are the dominant sources of pesticides found in streams and ground water (fig. 2–4). Nonpoint sources include runoff to streams from agricultural and urban land, seepage to ground water in areas where pesticides are used, and deposition of pesticides from the atmosphere. Potential point sources of pesticides include pesticide manufacturing plants, mixing-and-loading facilities, spills, wastewater recharge facilities (wells or basins), waste disposal sites, and sewage treatment plants. Once pesticides and their degradates (new compounds formed by the transformation of a pesticide by chemical or biological reactions) reach the atmosphere, streams, or ground water, they move through the hydrologic system with air, water, or particles, depending on the chemical and physical properties of the compounds.

Atmosphere

The atmosphere is an important part of the hydrologic system in which pesticides can be transported substantial distances from where they are applied (for example, Goolsby and others, 1997; Cromwell and Thurman, 2000). In fact, atmospheric transport can be global and is thought to be responsible for the detection of long-lived organochlorine pesticides such as chlordane, DDT, and dieldrin in remote areas of Scandinavia and the Arctic—locations where these pesticides probably were never used (Majewski and Capel, 1995; Nowell and others, 1999; Hermanson and others, 2005).

Pesticides can be transported from the atmosphere to streams and ground water with precipitation or the deposition of particles. For example, studies in the Upper Tennessee River Basin showed that atrazine and metolachlor

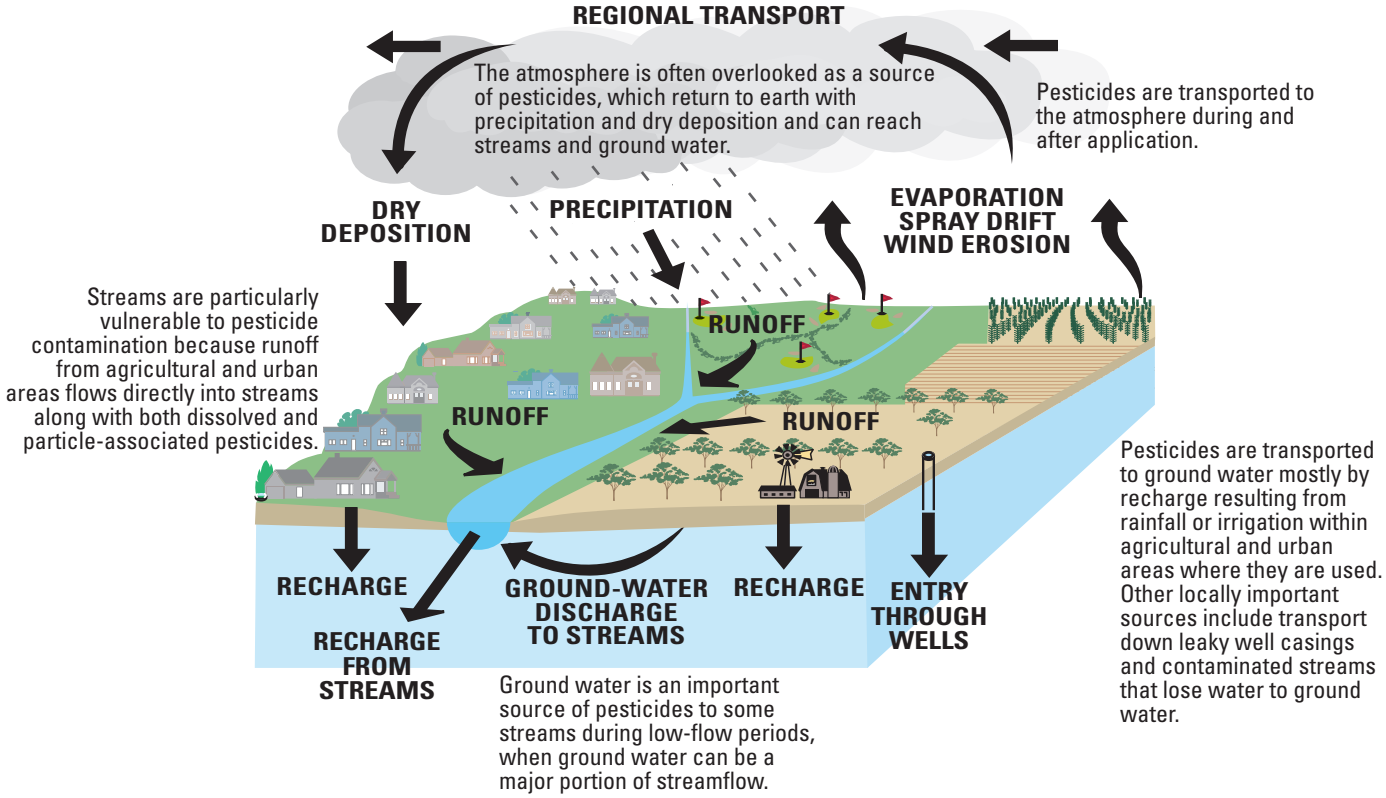

Figure 2–4. Pesticides are transported to streams and ground water primarily by runoff and recharge. Nonpoint sources of pesticides originating from areas where they were applied—rather than point sources such as wastewater discharges—are the most widespread causes of pesticide occurrence in streams and ground water. (Modified from Majewski and Capel, 1995.)

were frequently detected in Clear Creek in the Obed National Wild and Scenic River watershed (fig. 2–5). Seasonal patterns of occurrence of these two compounds matched those in nearby agricultural streams, indicating an atmospheric source from agricultural areas (Hampson and others, 2000). Similarly, metolachlor, EPTC, and atrazine were detected in rainwater within the Minneapolis–St. Paul metropolitan area—where they had not been applied—also indicating that these pesticides had been transported from nearby agricultural areas (Andrews and others, 1998; Capel and others, 1998). All three pesticides were found in rainwater at concentrations that were usually higher than those measured in the ground water of the Minneapolis–St. Paul study area; thus, atmospheric inputs alone could have accounted for most of their occurrence in the ground water.

Streams

Pesticides are transported from land into streams primarily by runoff or drainage resulting from rainfall or irrigation. These event-generated inflows to streams can occur by surface runoff, shallow subsurface flow, or flow through drainage ditches and subsurface tile-drain systems. Some compounds, such as atrazine, readily dissolve in and move with water. Other compounds, such as chlorpyrifos, more strongly associate with soil particles and organic matter and are transported primarily with eroded soil, particularly during times of high runoff from precipitation or irrigation.

Transport to streams is controlled, in large part, by the timing of precipitation and associated runoff and drainage relative to pesticide applications (Leonard, 1990). For example, figure 2–6 shows elevated concentrations of atrazine in the White River during runoff events that occurred soon after spring applications in May and June, but lower concentrations in response to runoff events of comparable or greater magnitude at other times of the year when use was lower, such as in April or August. The phenomenon of high herbicide concentrations in spring runoff has been extensively documented, especially in the Midwest (for example, Thurman and others, 1991).

Pesticides also enter streams with inflowing ground water—which can be a continuous source of pesticides and degradates throughout the year in some areas (Squillace and others, 1993). For example, during baseflow conditions on the Delmarva Peninsula, Shedlock and others (1999) measured pesticide concentrations in streams that were similar to those found in nearby wells. Baseflow conditions occur during periods of minimal precipitation, when streamflow is dominated by ground-water discharge. Similarly, in Waikele Stream, which drains a watershed with mixed land use on the Island of Oahu, Hawaii, concentrations of the herbicides bromacil, atrazine, and diuron were highest during baseflow conditions (Anthony and others, 2004).

Once in a stream, a pesticide may transform, be taken up by aquatic organisms, attach

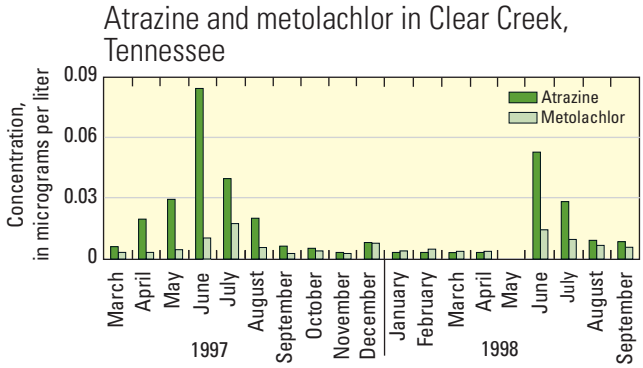

Figure 2–5. Atrazine and metolachlor were frequently detected in Clear Creek in the Obed National Wild and Scenic River watershed (Upper Tennessee River Basin). The seasonal patterns in concentrations followed those of applications in nearby agricultural areas, suggesting atmospheric transport (Hampson and others, 2000).

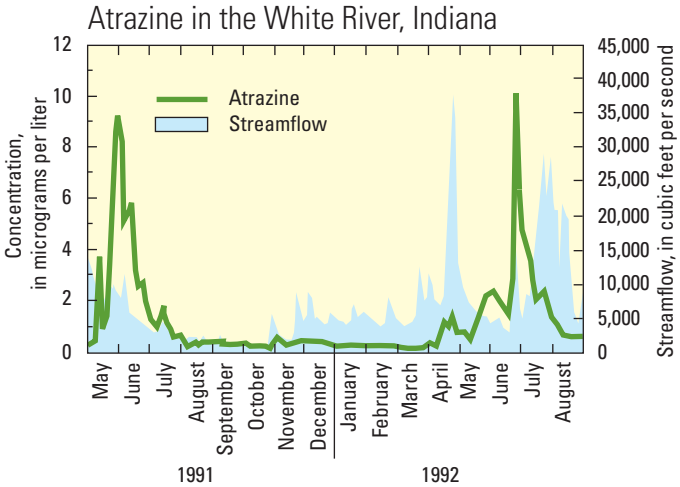

Figure 2–6. Atrazine concentrations in the White River (White River Basin) rose rapidly and peaked during the first runoff events that occurred soon after spring applications of atrazine in May and June. High runoff and streamflow either before or substantially after the high-use period typically did not result in similarly high concentrations (Carter and others, 1995).

to suspended particles and be deposited in bed sediment, or volatilize to the atmosphere—all resulting in losses of the parent compound from stream water. Model calculations by Capel and others (2001) for 39 high-use pesticides indicated that transformations are the dominant cause of pesticide losses from streams, accounting for most of the predicted losses for 27 of the 39 compounds, compared with 4 pesticides lost mostly by volatilization, and 8 pesticides lost by multiple processes.

Ground Water

Pesticides reach ground water primarily in water that infiltrates the soil and passes through the underlying unsaturated zone to the water table. As with streams, most pesticide transport to ground water is driven by rainfall or irrigation when one or both result in ground-water recharge. Ground-water transport is different from transport in streams because only dissolved forms of pesticides and their degradates move substantial distances with ground water. Particle-bound compounds are largely retained by soil and aquifer materials. In addition, transport of pesticide compounds to and within ground water is much less predictable than transport in streams because the flow of ground water is considerably slower and more complex than the flow of stream water.

Pesticides and their degradates can move readily to ground water through mobile zones, such as cracks, worm holes, or permeable sediments, but a portion of pesticide compounds is retained in immobile zones within the subsurface where flow is minimal. Pesticide compounds that are retained in immobile zones can be released gradually to ground water by diffusion and subsequent leaching, sometimes long after application. Much as a soap-filled sponge must be repeatedly rinsed and wrung before all of the soap is removed, the soil acts as a reservoir from which pesticides and their degradates continue to leach after application. As a result, pesticides may be found in ground water much sooner than expected after application (because of rapid movement through mobile zones), as well as for extended periods afterward (because of gradual release from immobile zones).

Pesticides generally are detected most frequently in ground water where the permeability of the soil and the hydraulic conductivity of the aquifer are highest, allowing relatively rapid transport. Deep aquifers usually have less pesticide contamination than shallow ground water because: (1) it takes a long time—decades or more, in many cases—for water to move from the land surface to deep ground water (resulting in long residence times for ground water and any solutes it may contain); (2) long travel distances increase the likelihood that pesticides will transform or attach to aquifer materials; (3) protective, low-permeability deposits (which inhibit flow and transport) may be present between the land surface and deep aquifers; and (4) the mixing of water from complex flow paths over long distances and time periods tends to result in a mixture of land-use influences on the quality of deep ground waters, commonly including contributions from areas of undeveloped land.

Influence of Pesticide Properties on Environmental Behavior

The occurrence and transport of pesticides in the environment are strongly influenced by the chemical and physical properties that affect their persistence and partitioning. Persistence refers to the tendency of a compound to remain in its original chemical form in the environment. Partitioning is the process by which pesticides become distributed among different environmental media, such as water, sediment, biota, and air, generally resulting in higher concentrations in some media than in others.

Pesticides with high persistence remain in their original chemical form in the environment for long periods, whereas those with low persistence rapidly transform following their release. Transformations proceed at widely varying rates, depending on the structure of the compound and environmental conditions (Barbash, 2004). As a result, the persistence of a pesticide—which is commonly expressed in terms of a half-life for transformation (the amount of time that it takes for half of the compound to transform)—can vary from hours to decades. Some transformations of pesticides in the hydrologic system result in degradates whose chemical properties, toxicities, and ultimate fate are not well known, although much information on the properties of major degradates has begun to emerge in recent years as part of pesticide registration studies in the United States and Europe (Sinclair and Boxall, 2003). Generally, persistent pesticides or degradates may be transported for long distances or accumulate in soils, sediment, or biota. In some cases—as with several of the historically used organochlorine pesticides—both long-distance transport and accumulation have been observed.

The tendency of a pesticide or degradate to partition into water, sediment, or other media determines where it is most likely to be detected in the environment, and how it is transported through the hydrologic system. Two of the parameters used most often to describe the partitioning of a compound among environmental media are (1) the Henry's law constant (K_H), which describes partitioning between air and water, and (2) the soil organic carbon-water partition coefficient (K_{oc}), which describes partitioning between water and the organic matter in soil or sediment. Values of K_H and K_{oc} for the pesticides and degradates that were detected most frequently in NAWQA studies are provided in Appendix 2. These values were compiled from a variety of sources, including the U.S. Environmental Protection Agency (USEPA) and the U.S. Department of Agriculture (USDA). A pesticide with a high K_H is volatile and thus, primarily tends to reside in and be transported by air. As a result, such compounds are rarely retained for long in streams or soil, but if they reach ground water, these compounds may remain for substantial periods of time because there is comparatively little exposure to the atmosphere. A pesticide with a high K_{oc} has a greater tendency to accumulate in soil or sediment than to remain dissolved in water. Because they associate more strongly with organic matter than with water, pesticides with high K_{oc} values are sometimes referred to as hydrophobic. Compounds with low K_{oc} values (which therefore tend to favor water over organic matter) are described as hydrophilic. As a result of their affinity for organic matter, the more persistent hydrophobic pesticides are likely to accumulate not only in soils and sediments, but also in fish, birds, mammals, and other biota (Nowell and others, 1999).

Understanding the factors that affect the persistence of a pesticide and its occurrence in different environmental media is key to evaluating and anticipating its potential effects on water quality. For example, atrazine, which moves readily with water and is relatively persistent, reached streams in 10 times greater proportions than EPTC, which is less persistent, more volatile, and, unlike atrazine, usually incorporated into the soil when applied. Nationally, an average of about 1 percent of the atrazine applied to the land in watersheds of sampled streams reached its associated stream outlet, as opposed to only about 0.1 percent for EPTC (fig. 2–7) (Larson and others, 1999; Capel and others, 2001). Similarly, NAWQA data from agricultural areas across the Nation indicate that pesticides with

Pesticides with high K_{OC} values attach to sediment particles and are transported during runoff events when suspended-sediment concentrations are high.

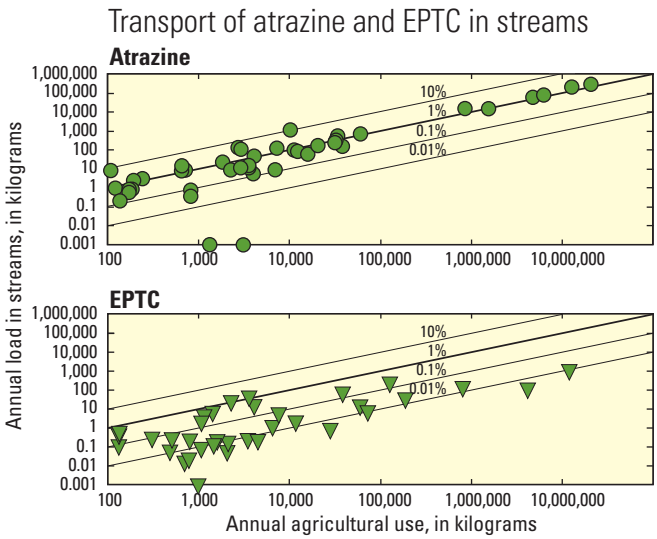

Figure 2–7. The annual transport of atrazine in streams was typically equivalent to about 1 percent of the amount applied in a particular watershed (percentages are shown by diagonal lines), whereas annual transport of EPTC in streams, which is less persistent and more volatile than atrazine, was less than 0.1 percent of annual use for more than half of the sites (Larson and others, 1999).

greater persistence in soil are more likely to be detected in shallow ground water than compounds that are less persistent (Barbash and others, 1999). For example, within areas of relatively equal use, atrazine (soil half-life of 146 days) was detected in shallow ground water much more frequently than the less persistent metolachlor (soil half-life of 26 days) (fig. 2–8).

The effects of chemical and physical properties on the environmental behavior of pesticides were also illustrated by the differences between hydrophobic and hydrophilic pesticides in their transport within streams of the Yakima River Basin. Hydrophobic pesticides ($K_{oc} \geq 300$ milliliters per gram, mL/g) were found to be most readily transported in basins dominated by rill irrigation—a management practice that involves distributing large volumes of water across the land surface, and which often causes soil erosion (fig. 2–9). In contrast, annual loads of hydrophilic pesticides ($K_{oc} < 300$ mL/g) were not affected by the extent of rill irrigation because the compounds are, for the most part, transported in the water rather than in suspended sediment (Fuhrer and others, 2004).

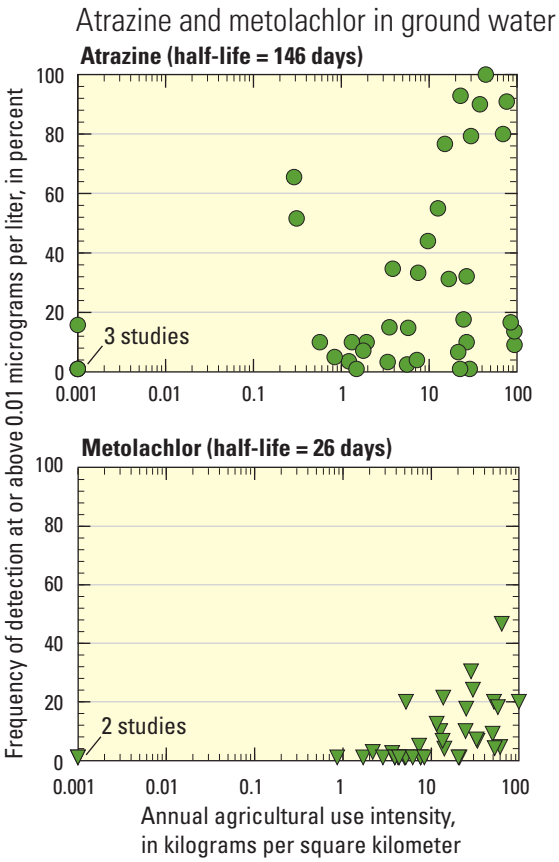

Figure 2–8. Frequencies of detection in shallow ground water beneath agricultural areas were usually greater for atrazine than for metolachlor given equivalent annual use rates, in part because of the greater persistence of atrazine in soil (Barbash and others, 1999).

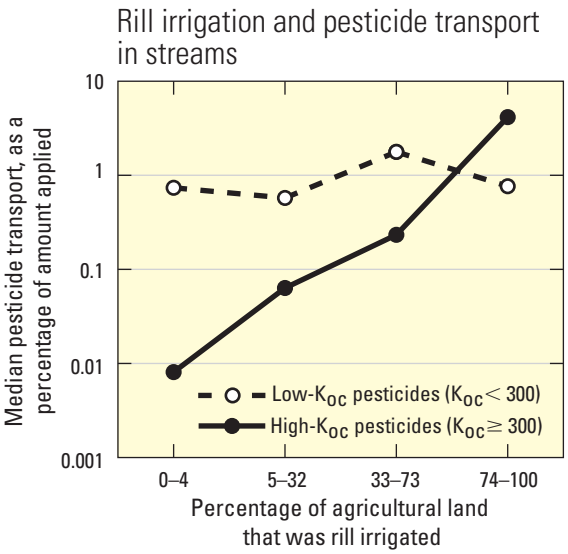

Figure 2–9. In the Yakima River Basin, transport of pesticides with high K_{oc} values (high affinity for soil particles) was greater in streams draining larger proportions of farmland that was rill irrigated, a practice that results in soil erosion. In contrast, the amount of rill irrigation had little effect on low-K_{oc} pesticides, which have lower affinities for soil particles and are not as affected by soil erosion. (modified from Fuhrer and others, 2004.)