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Timothy J. Gish
USDA-ARS, timothy.gish@ars.usda.gov

Jared Williams
Brigham Young University - Idaho

John H. Prueger
USDA-ARS

William Kustas
USDA-ARS

Lynn G. McKee
USDA-ARS

See next page for additional authors

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Authors

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Pesticides generally include herbicides, insecticides, and fungicides and play an important role in maintaining worldwide food and fiber production by controlling weeds that compete for water and nutrients or by eliminating pests that reduce yields (Majewski and Capel, 1995). In the future, the role of pesticides and fertilizers in agriculture is likely to increase as marginal land is converted to agriculture to meet production needs (Helling, 1993). Furthermore, it has also been proposed that increasing food and fiber production by agriculture will be critical to maintaining political and social stability in many countries (Tilman et al., 2002). However, pesticides can be toxic to humans and other forms of life at low concentrations (Doull, 1989; Jin-Clark et al., 2002; Sparling et al., 2001; USEPA, 2008), so future research will have enhanced scientific, environmental, and regulatory significance (Jury and Flühler, 1992; Posner et al., 1995). To maintain productive and sustainable agricultural systems there is an immediate need to understand field-scale processes governing pesticide use and off-site movement.

Due to its size and diversity, agriculture is responsible for more than 75% of worldwide pesticide usage (Aspelin, 1994), resulting in more than 2.4 billion metric tonnes of pesticides applied to agricultural land during 2000 (USEPA Biological and Economic Analysis Division, 2004). Despite their global use, comprehensive pesticide field studies are rare, in part due to the complex interactions involving pesticide chemistry, soil properties, agricultural management practices, and local meteorological conditions (Table 12|1). Although detailed holistic studies on pesticides are rare, several national surveys have been conducted that shed light on pesticide fate and its potential human and environmental risks. One of the first national surveys was conducted by the USEPA (1990), which determined that more than 10% of community water system wells contained detectable amounts of at least one pesticide. From 1993 to 1995, the National Water-Quality Assessment program monitored 20 major basins in the United States and found pesticides in 54% of the 1034 sites sampled (Koplin et al., 1998). Furthermore, the U.S. Geological Survey observed that 97% of all streams sampled from agricultural and urban areas contain detectable concentrations of pesticides, while 65% of the streams in undeveloped areas contained observable levels of at least one pesticide (Gillion et al., 2006). In addition, Gillion et al. (2006)

T.J. Gish, USDA-ARS Hydrology and Remote Sensing Laboratory, Beltsville, MD 20705 (timothy.gish@ars.usda.gov); J. Williams, Department of Agribusiness, Plant and Animal Sciences, Brigham Young University-Idaho, Rexburg, ID; J.H. Prueger, USDA-ARS National Laboratory for Agriculture and the Environment, Ames, IA; W. Kustas, USDA-ARS Hydrology and Remote Sensing Laboratory, Beltsville, MD; L.G. McKee, USDA-ARS Hydrology and Remote Sensing Laboratory, Beltsville, MD; and A. Russ, Hydrology and Remote Sensing Laboratory, Beltsville, MD.

Table 12|1. Factors and processes increasing pesticide movement off-site.

Component	Property increasing loss
Pesticide characteristics	High vapor pressure High water solubility Large soil half-life ($T_{1/2}$) Low soil affinity (K_{oc} or K_d)
Soil and landscape properties	High soil water contents for surface broadcast applied herbicides Low soil water contents for incorporated fungicides Low organic matter content (K_{oc} or K_d) Sandy soil texture pH Bulk density (affects soil air space) High temperature (especially if soil is moist)
Agricultural practice	Application method (foliar spray > surface broadcast > incorporated) High application rates Plant residue (amount and type) Pesticide formulation (wettable powder > emulsions > micro-encapsulated)
Local-meteorological	Precipitation (relative to time of application) High wind velocity and turbulent flow conditions High solar radiation (R_N) High relative humidity (RH)

reported that more than one-half the shallow groundwater aquifers also contained measurable levels of pesticides. Clearly, pesticide occurrence in streams, groundwater aquifers, and community wells are well documented, although concentrations are typically low.

Once applied to soil a portion of the pesticide will be adsorbed to soil particles, while the remaining pesticide mass will be associated with the liquid and/or vapor phases. The degree to which a pesticide is partitioned between adsorbed, liquid, and vapor phases strongly influences its subsequent dispersal into the environment (Cousins et al., 1999; Jury et al., 1983; Taylor and Spencer, 1990). Pesticide partitioning between these three phases is primarily a function of pesticide chemistry, pesticide formulation, soil properties, and local metrological conditions. For example, pesticides with high vapor pressure are more likely to favor the vapor phase while those with a high affinity for the soil matrix will favor adsorption to soil particles. Because pesticides exist in all three phases, there are several loss pathways that can simultaneously interact to influence water quality and the environment. As a result, methods for monitoring pesticide behavior at the field scale are expensive and difficult to interpret due to process interactions that are a function of scale, as well as soil properties that vary spatially and temporally (Fig. 12|1). Thus, although scientists have quantified the impact of various factors on pesticide movement in controlled environments, monitoring and interpreting field-scale pesticide behavior is more ambiguous. During application, pesticide emissions can occur as spray drift in concentrated droplets or as pesticide attached to dust particles (Symons, 1977; Majewski and Capel, 1995). Pesticide loss from drift and volatilization can be transported through the boundary layer of the atmosphere to forested areas and deposited directly into streams via tree wash-off (personal communication, 2010, Dr. Clifford Rice, USDA-ARS Beltsville, MD). Once on the soil surface, pesticides degrade in situ or move away from the targeted area by leaching into groundwater, runoff into adjacent streams, and/or volatilization into the atmosphere. The rate at which pesticides are lost from these three loss pathways is influenced by a number of small-scale factors like soil moisture content, organic matter content, soil hydraulic properties, as well as large-scale influences such as wind speed profiles, agricultural management practices, timing of rainfall events relative to application, and field slope. As a result, to reduce risks associated with pesticide use all major loss pathways must be evaluated so as to avoid simply shifting pesticides and their metabolites from one part of the environment to another.

Although field studies monitoring all possible loss pathways are essentially nonexistent, specific aspects of pesticide movement have been rigorously studied. Among the major loss pathways, pesticide runoff has been the most intensively studied. Results show that in general annual runoff losses are less than 3% of that applied,

with the largest portion of this loss occurring near the time of application (Haith and Rossi, 2003). Enhanced pesticide runoff relative to leaching from tile-drained fields supports the hypothesis that pesticide runoff is more detrimental to the environment than pesticide leaching (LaFleur et al., 1975; Muir and Baker, 1976; Ng et al., 1995). Unfortunately, field-scale pesticide leaching losses in non-tile-drained fields is difficult to quantify due to soil heterogeneity, but it is thought that leaching losses due to preferential flow are probably <<5% of that applied. The third loss pathway, volatilization, is a major environmental concern, with as much as 90% of some pesticides applied being lost to the atmosphere (Taylor and Spencer, 1990). Unfortunately, efforts to determine the impact of field-scale variables like management and climate on pesticide volatilization are still in their infancy.

In this chapter, the primary principles and factors governing pesticide movement at the field scale will be discussed. Pesticide movement will be evaluated by examining how pesticides are partitioned between runoff, groundwater leaching, and volatilization processes.

Surface Runoff

Pesticide surface runoff is a concern in many watersheds since intensive agriculture may be adjacent to sensitive ecosystems (Capel et al., 2008). Although rainfall timing, intensity, and duration are the most critical factors governing pesticide runoff, the rate of application, pesticide formulation, management practice, and landscape features are also important (Caro, 1976; Wauchope, 1978; Hall et al., 1983; Felsot et al., 1990; Domagalski et al., 2008). Typically, pesticide losses from a single rainfall event are small—less than 1 to 2% of that applied. In rare situations, such

Fig. 12|1. Properties and processing influencing pesticide movement and their relative scales of observation.

as when a major rainfall event follows the application of a wettable powder formulation on a sloped field, as much as 15% of the pesticide applied can be lost through runoff (Baker, 1980; Haith and Rossi, 2003). Regardless of the pesticide mass lost from runoff, detrimental impacts decrease with increasing distance from the application site due to dilution from other runoff sites, streams, rivers, and lakes.

Pesticide in surface runoff occurs through two mechanisms that occur simultaneously: (i) erosion of pesticide adsorbed to sediment and (ii) dissolution of the pesticide into the runoff water. Pesticide *concentrations* in runoff sediment can be several times higher than that observed in the water phase; however, the greatest pesticide *mass* lost in runoff is from the water phase, as runoff water volumes are typically much greater than sediment mass losses (Wauchope, 1978).

Rainfall and Pesticide Runoff

The primary factors governing pesticide runoff losses are the intensity, duration, and timing of the rainfall events relative to application. To account for the interaction
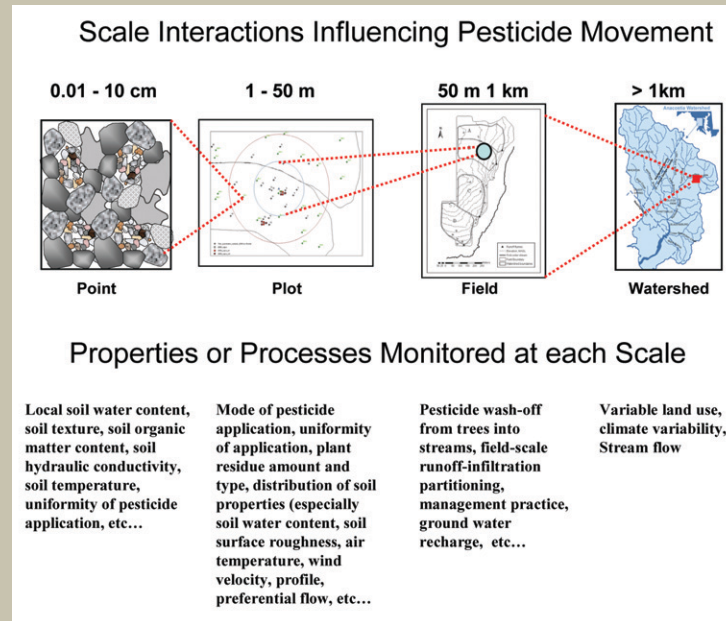
between rainfall intensity, duration, and timing, three types of pesticide runoff events have been proposed: minor, critical, and catastrophic (Wauchope, 1978). Minor runoff events are a product of rain events that produce small amounts of runoff shortly after pesticide application (generally within 1–2 d). These minor events typically have high concentrations of pesticide in a relatively small amount of surface runoff and account for pesticide losses <1% of that applied (Wauchope, 1978). However, the high concentration of pesticides in these minor runoff events can significantly affect streams, rivers, and watershed ecosystems. The second type, a critical runoff event occurs within 2 wk of pesticide application and has at least 50% of the rainfall exiting the field through surface runoff. The amount of pesticide lost in a critical event is also dependent on pesticide soil persistence, adsorption affinity, formulation, and landscape features (Shipitalo et al., 2000; Ma et al., 2004). Pesticide runoff losses can be significant with a critical runoff event even if the pesticide has a high affinity for the soil matrix since sediment loss is common with such events. As a result, critical runoff events typically produce the bulk of the pesticide runoff loss from agricultural fields and account for 1 to 2% of the applied pesticide (Ma et al., 2004). The third type, catastrophic runoff events are rare and differ from a critical runoff event by the high intensity of the rainfall occurring shortly after pesticide application (Wauchope, 1978; Schulz et al., 1998). For example, catastrophic runoff events are typically caused by severe thunderstorms that produce large amounts of rainfall within 3 days of the pesticide application and can account for more than 5% of the pesticide applied. Although a *higher percentage* of the pesticide applied is lost in a catastrophic event, the *concentration* of pesticide in the water phase exiting the field is relatively low because of dilution. Occurrences of catastrophic runoff events are rare, because timing of a major storm and application of pesticide must coincide, and farmers typically try to avoid such situations. Although, rainfall is recognized as the principle factor governing pesticide runoff, pesticide soil persistence, formulation, method of application, and landscape features interact with rainfall to influence pesticide runoff losses.

The major factors influencing pesticide soil persistence include application method (Hall et al., 1983), adsorption affinity (Jenks et al., 1998; Spark and Swift, 2002), leaching potential (Webb et al., 2008), formulation and volatilization potential (Gish et al., 1994), and degradation processes (Kearney et al., 1969; Gan et al., 2005). Pesticide degradation is typically quantified as a half-life ($T_{1/2}$), which represents the time taken for one-half of the pesticide to degrade. Where pesticide persistence is high ($T_{1/2} > 2$ wk) concentrations in the second and third runoff events may actually be higher than in the first runoff event (Caro et al., 1972; Gan et al., 2005). In addition, pesticides that persist in soil for long periods are more likely to be adsorbed to soil particles. A persistent pesticide poses an environmental threat to neighboring ecosystems through sediment loss, especially if critical or catastrophic runoff events occur. Pesticide application methods such as soil incorporation can reduce runoff, leaching, and volatilization losses even though soil persistence may increase (Caro et al., 1974). For example, soil incorporation can reduce pesticide runoff losses from 1/4 to 1/20 of the surface-applied pesticide loss (Baker and Laflen, 1979). Foliar applications should be avoided if possible because they tend to exhibit a short pesticide persistence and are easily washed off and transported off-site in runoff water before being adsorbed to the soil (Wauchope, 1978; Gevao et al., 2000). Applying pesticides as an encapsulated formulation can also increase soil persistence as this practice reduces pesticide susceptible to groundwater leaching by preferential flow (Gish et al., 1994). Multiple applications of a pesticide may result in metabolic pathways being established which increase biological degradation rates and reduces soil persistence (Kearney et al., 1969). Since persistent pesticides pose a greater environmental risk, most long-term persisting pesticides, such as DDT and other organochlorine pesticides, have been banned.

Pesticide formulation can also influence pesticide runoff losses. For example, wettable powder formulations have the highest runoff potential, with losses generally ranging from 2 to 5% of that applied (Wauchope, 1978). Since wettable powder formulations subjected to critical and catastrophic runoff events can result in pesticide runoff losses exceeding 5% of that applied, they should be

avoided. Pesticides applied as an emulsion have the next highest potential for runoff, with typical losses of about 1% of that applied. Water-soluble pesticides have a much greater potential of being lost in water runoff, whereas, non-water-soluble pesticide often have an affinity for soil particles and will most likely be lost in the sediment portion of runoff. An example of the influence of formulation on pesticide runoff is observed with ester- and amine salt–based herbicides (Barnett et al., 1967; Caro, 1976). The amine salt, which is water soluble, rapidly dissolves in water and can be leached into the soil or moved by the water phase of a runoff event. Ester herbicides are relatively insoluble, but are readily adsorbed to soil particles and are primarily lost through the erosion of sediment. All other pesticide formulations (e.g., pelleted and micro-encapsulated) exhibit runoff losses less than 0.5% of that applied, except when a critical or catastrophic event occurs (Wauchope, 1978).

Landscape attributes interact with the type of runoff event, pesticide chemistry, and formulation to influence runoff losses. All other conditions being equal, pesticide runoff losses increase with increasing slope (Hall et al., 1983; Felsot et al., 1990). For example, pesticide runoff from a 3% slope can be as high as 2% of that applied, while slopes of 10 to 15% may result in pesticide runoff losses exceeding 5% of that applied (Wauchope, 1978). Furthermore, relative to other pesticide formulations, wettable powders will be more susceptible to runoff as slopes become steeper and as critical and catastrophic runoff events occur.

Soil properties that influence pesticide runoff losses include soil organic matter (Jenks et al., 1998; Spark and Swift, 2002), pH (Weber et al., 1972; Jenks et al., 1998), soil compaction (Baker and Laflen, 1979), soil moisture content (Spark and Swift, 2002), cation exchange capacity (Wauchope and Meyers, 1985), clay mineral content (Baskaran et al., 1996), and temperature (Caro, 1976). In general, soil properties influence pesticide runoff by affecting adsorption and desorption processes. High soil organic matter contents (>5%) will typically be the most important factor influencing pesticide absorption (Caro, 1976; Spark and Swift, 2002). In soils with a low soil organic matter content (<2%) clay mineral content may be the dominant factor because of the larger surface area of clay particles (Laird et al., 1992; Jenks et al., 1998). Soil pH has been shown to influence pesticide adsorption by altering the chemical composition of a pesticide, resulting in a net positive charge (Jenks et al., 1998). For example, some pesticides (e.g., atrazine) are more adsorptive in acidic soils because they react with H^+, making the pesticide cationic and chemically attracted to cation exchange sites (Bailey and White, 1964; Weber et al., 1972; Jenks et al., 1998). Although pesticides favoring adsorption are less susceptible to runoff from a minor runoff event, they are increasingly susceptible to critical or catastrophic runoff events where sediment erosion can be significant.

Soil moisture influences adsorption and desorption of pesticides because of water competition for adsorption sites on soil particles (Hamaker and Thompson, 1972; Cole et al., 1997). As soil moisture increases (through a rain or irrigation event), water is adsorbed to the soil matrix and pesticides desorb. Subsequently, the desorbed pesticide diffuses into the water phase, where it can be more readily transported off-site. Studies examining the application of pesticides to wet versus dry soils showed that runoff losses were significantly greater for wet soils because of the lower adsorption potential (Barnett et al., 1967; Baldwin et al., 1975; Asmussen et al., 1977).

Management Strategies to Reduce Pesticide Runoff

Pesticide runoff losses are primarily a function of the type of runoff event, with the bulk of the pesticide loss occurring early in the event and decreasing exponentially with time (Buttle, 1990; Reddy et al., 1994). Seasonal runoff losses are predominantly an accumulation of single-event losses, with minor loses in-between major storm or irrigation events (Haith and Rossi, 2003). As a result, best management practices for reducing pesticide runoff losses must consider reducing pesticide concentrations in both the water phase and the sediment. Erosion control practices such as minimum tillage and grass buffers may be effective in reducing erosion and runoff water, which greatly reduce pesticide loss via sediment erosion, but are ineffective in controlling losses in the water phase (Cole et al., 1997; Shipitalo

et al., 2000). Practices for reducing pesticide losses in runoff include: (i) avoiding pesticide application during adverse weather conditions, such as when rain or high winds are anticipated within 48 h of application; (ii) determining the most appropriate pesticide type, rate, and persistence for weather and soil conditions; (iii) incorporating the pesticide if possible; (iv) using erosion control practices such as conservation tillage, contouring, and grass buffers around waterways to reduce runoff (Wauchope, 1978; Baker and Johnson, 1979; Fawcett et al., 1994; Cole et al., 1997; Shipitalo et al., 2000); and (v) avoiding pesticide wettable powder formulations where possible.

Groundwater Leaching

During the past four decades considerable effort has been made toward understanding the factors governing water and chemical transport through soil (Biggar and Nielsen, 1976; Addiscott and Wagenet, 1985; Jury and Flühler, 1992; Gish et al., 1998b; Kung et al., 2005). However, field-scale pesticide mass flux measurements of groundwater are rare. Typically, pesticide leaching studies focus on monitoring pesticide concentration profiles in soil as a function of time after application or effluent discharge from tile drains (Jury et al., 1984; Helling and Gish, 1986; Isensee et al., 1990; Kladivko et al., 1991; Harris and Catt, 1999; Novak et al., 2001). Unfortunately, uncertainty in soil water dynamics is extremely large, with soil hydraulic conductivity and soil water diffusivity parameters demonstrating coefficients of variation exceeding 200% (Libardi et al., 1980; Nielsen et al., 1973). The large uncertainty in soil water dynamics is most likely due to soil heterogeneities and preferential flow.

Preferential flow is likely the dominant flow mechanism governing pesticide movement to groundwater (Kladivko et al., 1991; Harris and Catt, 1999; Novak et al., 2001; Koplin et al., 1998; Jarvis, 2002). Preferential flow assumes that a small fraction of the total soil pore space is responsible for rapidly conducting solutes to groundwater (Germann and Beven, 1981). Preferential flow typically occurs through structureless soils by means of flow instabilities (Glass et al., 1988; Ghodrati and Jury 1992); flow through spatial voids resulting from decayed roots, shrinking clay minerals, sink holes, or created by soil fauna (Gish and Jury, 1983; Libra et al., 1984; Shipitalo et al., 1990; Ritsema and Dekker, 1995; Gish et al., 1998a; Williams et al., 2000); and/or flow along subsurface restricting layers (Kung, 1990). Unfortunately, quantifying preferential flow at the field scale is extremely difficult since there is uncertainty in identifying the location of subsurface flow pathways and when water is actually flowing in these pathways. As a result, pesticide mass fluxes are typically calculated, not monitored. Without mass flux procedures, it is impossible to quantify a total flux or the relevance of preferential flow at the field scale for various management, soil, and climatic scenarios.

Monitoring pesticide transport has been done for several decades, but with limited success. Early monitoring attempts focused on removal of soil cores and analyzing for pesticides as a function of time after application and profile depth. Unfortunately, soil field core data were found to be of limited usefulness. For example, Wyman et al. (1985, 1986) evaluated aldicarb transport through soil by collecting 48 soil cores (3.6 m long) four times during a growing season. Each soil core was segmented into 30-cm increments, homogenized, and subsampled. Because no aldicarb residues were detected below 2.4 m throughout a three-year period, it was concluded that aldicarb was completely degraded and did not pose a threat to groundwater quality. In contrast, Brasino (1986) conducted a coincident experiment which found that peak aldicarb concentrations in three groundwater monitoring wells (6-m depth) ranged from 27 to 76 ppb even though the same chemical application rate, irrigation scheme, and soil were used. As a result, early pesticide transport studies that focused on soil core data to evaluate pesticide leaching may be of limited value.

Recently, an innovative total flux monitoring procedure was evaluated in which tracers were surface applied in a narrow band (typically 3 by 25 m) parallel to a tile drain but offset by 0.3 m from the buried tile drain system (Kung et al., 2000a). Using this approach, a total mass flux for mobile tracers was monitored and the relevance of preferential and matrix flow processes were determined (Kung. et al., 2000a; Gish et al., 2004). Everts et al. (1989) and Kung et al.

(2000b) also used adsorbed tracers to simulate pesticide leaching behavior. Everts et al. (1989) observed that both the nonadsorbing tracer (bromide) and adsorbed tracer (rhodamine WT) simultaneously appeared in a tile drain shortly after the initiation of irrigation, while Kung et al. (2000b) observed that the nonadsorbed (bromide) and adsorbed (rhodamine WT) tracers arrived at the tile drains at the same time and that their breakthrough curves peaked at the same time. Thus, the soil water dynamics of preferential flow can dominate transport regardless of the chemical adsorption affinity for the soil. Unfortunately, these flux procedures have not yet been used to quantify the impact of tillage, formulation, or management practice on pesticide leaching.

Since pesticide flux monitoring through the soil profile is in its infancy, field observations discussed here will focus on field observations of pesticide concentrations. However, without flux measurements there is a greater likelihood that field experiments may generate contradictory results.

Field Observations of Pesticide Leaching

As is the case for surface runoff, the timing of a rainfall event relative to application influences pesticide leaching to groundwater. Pesticide transport is especially vulnerable to preferential transport shortly after application. For example, in a sandy soil in Beltsville, MD, surface-applied atrazine and metolachlor were rarely detected in a 3-m well for months before application (Fig. 12|2). Then pesticide concentrations peaked shortly after application when a 60-mm rain event had occurred and afterward declined exponentially with time. On the

other hand, once in the subsoil pesticides may be transported predominantly by the smaller pores of the soil matrix, which would increase the time it takes for a given pesticide to reach groundwater (Kung et al., 2000b; Delphin and Chapot, 2006). Thus, it appears that the first rainfall event after application has the highest risk of pesticide leaching to groundwater, but that modeling approaches will have to include interaction between matrix and preferential flow processes.

Controlled release formulations may reduce preferential transport of pesticides. In the laboratory and in field plots atrazine leachate concentrations were reduced by as much as 80% with starch encapsulation (Gish et al., 1991b; Schreiber et al., 1993). However, Brown et al. (1995) reported unexpectedly high leaching loses with encapsulation. Later, field evaluations
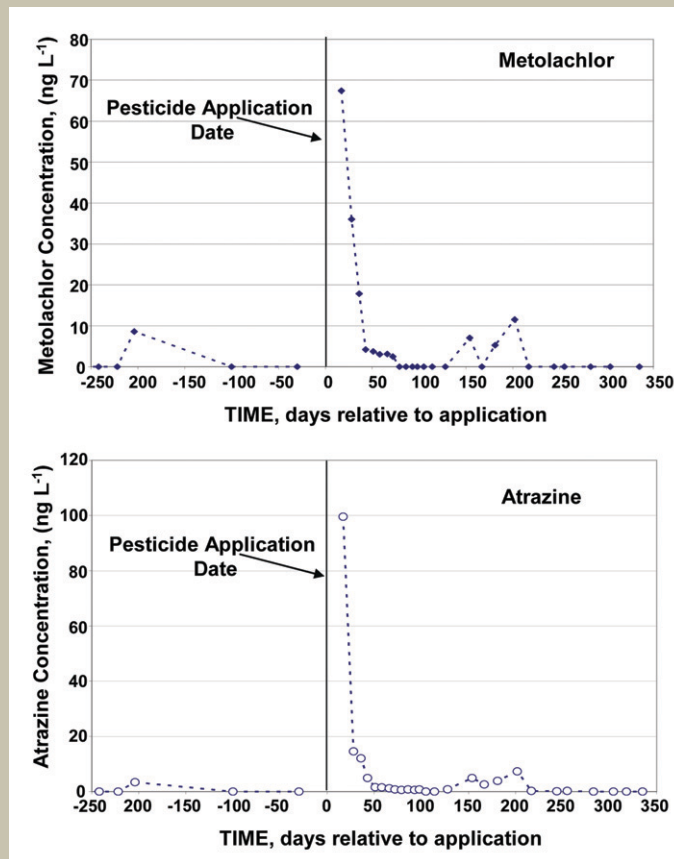

Fig. 12|2. Pesticide concentrations in a shallow 3-m groundwater well as a function of time. On the *x* axis, "0" represents the day of metolachlor application.

showed the starch encapsulated herbicides were more persistent in soil, which was attributed to being less available for leaching during rain events (Gish et al., 1994). However, pesticide chemistry must be considered when optimizing an encapsulation matrix to be effective in controlling the targeted pest and reducing environmental risks (Wienhold and Gish, 1994b).

There is some ambiguity regarding the benefit of incorporation of a pesticide relative to its leaching potential. Gish et al. (1991a) reported that soil incorporated carbofuran leached less than surface broadcast-applied atrazine, despite the much larger inherent mobility of carbofuran. However, Jones et al. (1995) suggested that soil incorporation of a pesticide after application had no impact on subsequent transport to tile drains. Obviously, more work needs to be done in this area so that the interactions among pesticide chemistry, pesticide formulation, soil type, rainfall intensity and duration, and pesticide leaching can be determined.

Preferential flow has been observed on all soils regardless of texture. However, the impact of preferential flow as a function of pesticide chemistry and soil texture has not yet been fully quantified. Initially, preferential leaching of pesticides was thought to occur on heavy or clayey textured soils via macropores or other spatial voids (Harris and Catt, 1999; Johnson et al., 1996). However, significant pesticide leaching has also been detected through loamy and silty textured soils (Kladivko et al., 1991; Brown et al., 1995; Zehe and Fluhler, 2001), as well as sandy soils (Ghodrati and Jury, 1992). On the other hand, there is some evidence that *total pesticide mass* losses in a clayey structured soil may be greater than from a sandy soil (Traub-Eberhard et al., 1995).

Management Strategies to Reduce Pesticide Leaching

Pesticide transport through soil is primarily a function of preferential flow, so for pesticides with a low solubility encapsulation will reduce leaching by increasing pesticide diffusion into the smaller pores of the soil matrix. However, reducing pesticide leaching through encapsulation may be countered by an enhanced runoff potential since encapsulation also increases soil persistence (Gish et al., 1994). Soil incorporation may also reduce leachability for pesticides that are insoluble and have low soil persistence. In addition, conservation tillage practices may temporarily enhance preferential pesticide transport through void root channels and bio-pores. In time, root channels and bio-pores will have clay and/or organic coatings where pesticide can be readily adsorbed and subsequently broken down by microbial degradation. After only a few years Gish et al. (1998b) observed higher pesticide metabolites under no-till relative to conventional tillage. This suggests that if the pesticide metabolites are less harmful than the parent compound, conservation tillage may be beneficial to groundwater quality. Farm managers should also avoid using pesticides with a long half-life or soil persistence as this will increases susceptibility to groundwater leaching.

Pesticide Volatilization

Pesticide volatilization can exceed 90% of that applied, but typical losses for many pesticides used in crop production range from 5 to 25% of that applied (Taylor and Spencer, 1990, Prueger et al., 1999; Glotfelty et al., 1989; Prueger et al., 2005). Once in the atmosphere, pesticides can be degraded or deposited in nontargeted areas via wet or dry deposition (Bidleman and Christensen, 1979; Bidleman, 1988; Burrows et al., 2002). Frequently, a portion of the applied pesticides volatilized into the atmosphere are transported and subsequently deposited in streams, rivers, and lakes (McConnell et al., 1998; Alegria and Shaw, 1999; Thurman and Cromwell, 2000; Kuang et al., 2003).

Pesticide volatilization occurs in two steps, evaporation of the pesticide from soil and plant residues followed by dispersion into the atmosphere by diffusion and turbulent mixing (Fig. 12|3) (Taylor, 1995; Prueger et al., 2005). From a thermodynamic perspective, the evaporative flux represents a phase change from liquid and/or solid phases to the vapor phase and can be described well as a diffusive process (Glotfelty and Schomburg, 1989). As a result, several methods have been developed to obtain estimates of pesticide volatilization at the field-scale. Parmele et al. (1972) developed an aerodynamic method based on gradients of wind speed, temperature, and pesticide concentrations

collected over a uniform area. Denmead et al. (1977) developed an integrated horizontal flux approach that uses pesticide concentration and horizontal wind speeds profiles. For certain conditions a theoretical profile shape method may be useful (Wilson et al., 1982) which measures wind speed and pesticide concentration at a single height above the soil. Recently, wind, temperature, water, and pesticide profile data have been used to measure pesticide volatilization where turbulent flow conditions may exist (Prueger et al., 2005; Gish et al., 2009).

Pesticide Vapor Pressure

Perhaps the most crucial pesticide property influencing volatilization is the vapor pressure of the pesticide. As the vapor pressure increases, the pesticide increasingly favors the vapor phase and is more readily volatilized. Since fumigants have larger vapor pressures they are generally more volatile than herbicides (Yagi et al.,
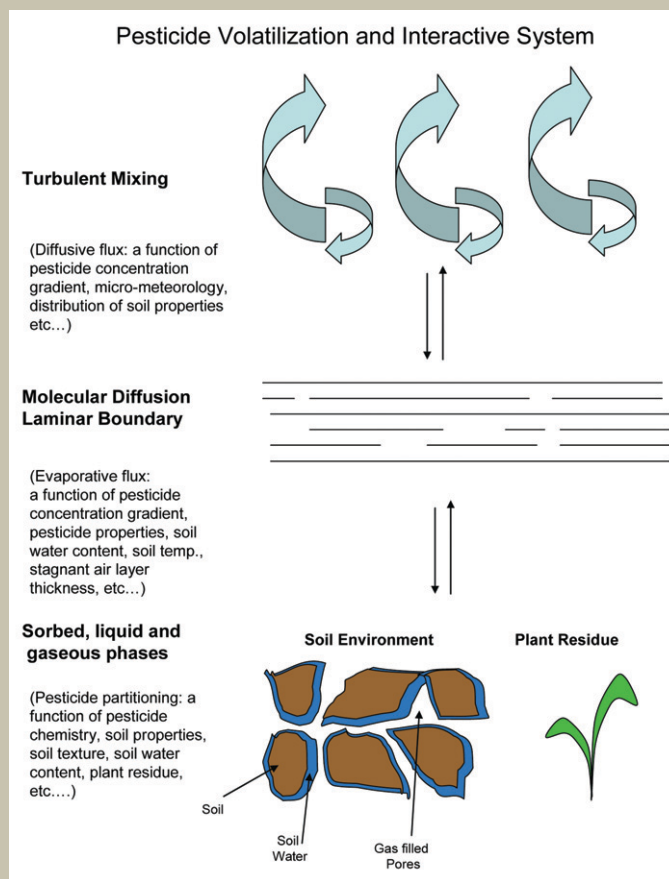

Fig. 12|3. Schematic of pesticide volatilization process. This process involves diffusive exchange of pesticide mass between the soil environment (adsorbed, gaseous pore space, liquid phase) and the atmosphere.

1995; Yates et al., 1996). In addition, in the field an "effective" pesticide vapor pressure is likely to be lower than the vapor pressure of the "pure" chemical due to interactions with the soil surface. For example, early studies detected a significant positive correlation between pesticide vapor pressure and pesticide volatilization (Farmer et al., 1972; Glotfelty et al., 1984). Later it was observed that dry soil conditions favored soil adsorption, which reduced the vapor pressure of the pesticide and lowered pesticide volatilization (Spencer and Cliath, 1974; Taylor and Spencer, 1990). In contrast, plant surfaces have a lower affinity for pesticides and as such exhibit pesticide vapor pressures that are closer to that of the "pure"

pesticide (Taylor and Spencer, 1990). For most pesticides, soil adsorption is primarily governed by the soil organic fraction (Rao and Davidson, 1980; Karickhoff, 1981). Thus, soil properties like organic matter, and to a lesser extent, texture (clay content), and soil pH, affect pesticide volatilization by increasing adsorption, thus reducing the liquid phase concentration and vapor pressure in the soil.

At the field scale, soil water content is perhaps the most critical soil property influencing herbicide volatilization. As the pesticide will be distributed among adsorbed, liquid, and vapor phases the amount of air space within a soil volume and the thickness of the water molecule

layer adsorbed onto the soil particles will influence herbicide volatilization. Spencer and Cliath (1974) measured the pesticide vapor pressures in soil at various soil water contents and demonstrated greater volatilization losses from wet than dry soils. Glotfelty et al. (1984) demonstrated that pesticide vapor losses increased more with soil water content than organic matter content or soil temperature. Furthermore, in a 5-yr field investigation, Prueger et al. (2005) demonstrated that at high soil water contents, as much as 25% of surface-applied metolachlor could be lost through volatilization, compared to as little as 5% when soils were dry. Figure 12|4 shows the impact of soil moisture on field-scale herbicide volatilization (metolachlor) where soil type, climatic inputs, formulation, and management practices were identical. In 2004 and 2005 the wet location had soil water contents and metolachlor volatilization losses that were almost twice that of the dry location. Then during 2006, using the same locations, there was no difference in surface soil water contents due to drought conditions and so the previous "wet" and "dry" locations had approximately the same soil water content. In addition, several studies have shown peaks in early morning volatilization losses that were attributed to dew formation on the soil surface (Glotfelty et al., 1989; Taylor, 1995; Prueger et al., 2005). Increases in pesticide volatilization following a rain event are also common. These spikes can be relatively large if the soil had been dry before the rainfall event (Prueger et al., 2005). Although pesticide volatilization is influenced by soil bulk density, pH, and soil texture mineralogy, the dominant soil property appears to be soil moisture.

Although increased soil water contents enhance herbicide volatilization, this is not the case with fumigants. Because fumigants have a high vapor pressure, tarps are applied over the field and/or the fumigant is injected into the soil (Yagi et al., 1995; Yates et al., 1996). Higher soil water contents may reduce fumigant volatilization losses since the higher soil water contents will reduce the gas phase porosity. Recently, Yates et al. (2008) observed that the volatilization of 1,3 dichloropropene was significantly reduced when surface water was applied after fumigant injection.

Meteorological parameters are generally thought to be important only as they influence soil properties, such as surface soil water content. For example, relative humidity affects surface soil water content and can lead to enhanced pesticide volatilization if the fields are dry (Glotfelty et al., 1984; Taylor, 1995; Prueger et al., 2005). Additionally, increased solar radiation can increase air and soil temperatures, but their impact on pesticide volatility will likely depend on the surface soil water content. Rainfall can increase soil water contents, which, in turn, may increase pesticide volatilization in the short term, but depending on rainfall intensity and duration may actually move the pesticide deeper into the soil profile, where it is less likely to volatilize. Increasing wind velocity could increase pesticide volatilization if soils are wet,
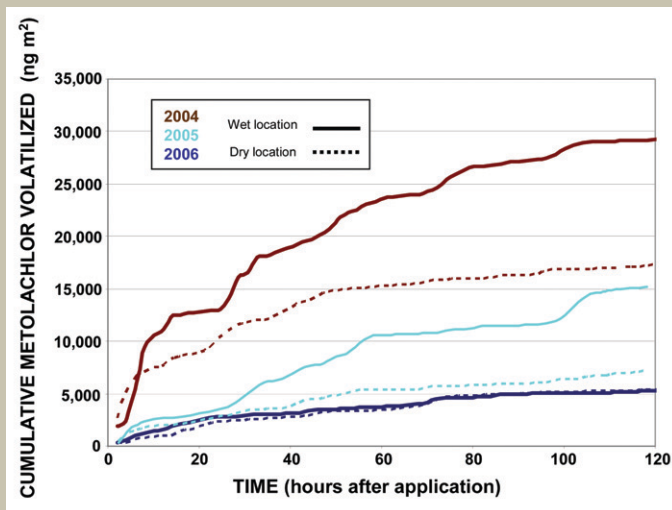

Fig. 12|4. Impact of surface oil moisture on field metolachlor volatilization. Soil water contents at the wet location were almost twice that of those around the dry location for 2004 and 2005. However, in 2006 soil water contents were not significantly different between the two locations.

but if the wind dries out the soil surface, pesticide volatilization could decrease.

Initially, soil temperature was thought to increase pesticide volatilization by increasing pesticide diffusion rates and the vapor pressure (Spencer et al., 1969). However, increased soil temperatures can also lead to a drying of the soil surface, leading to increased adsorption and a decrease in pesticide volatilization. The interaction between soil temperature and soil moisture on pesticide volatilization with identical solar radiation inputs is shown in Fig. 12|5. When the soil is "wet", increased temperatures result in a corresponding increase in pesticide volatilization (Fig. 12|5A). If, however, the soil is dry, no correlation between temperature and pesticide volatilization is observed (Fig. 12|5B). This interaction between soil temperature, soil water content, and pesticide volatilization supports the need for multi-year, field-scale investigations where soil surface and local meteorological interactions can be accurately monitored, modeled, and eventually predicted.

Fig. 12|5. Interaction of soil temperature and soil water content on metolachlor vitalization flux rates. Metolachlor fluxes were monitored simultaneously in A (wet location) and B (dry location) during 2005.

Agricultural Management

Agricultural management influences pesticide volatilization on several levels. First, soil incorporation of the pesticide decreases pesticide volatilization. Prueger et al. (1999) demonstrated that incorporating metolachlor in a band relative to a surface broadcast spray reduced pesticide volatilization losses from 22 to 6% of that applied. Although gas-phase diffusion is much greater than liquid-phase diffusion, only a small fraction of air voids is present in soil (Spencer and Cliath, 1970). Thus, by incorporating the pesticide the gas phase diffusion process is limited, and hence volatility is reduced. Second, increasing amounts of plant residue on the surface can increase pesticide volatilization since plants generally have a much lower affinity for pesticides than soil (Taylor and Spencer, 1990). Third, pesticide formulations such as control release or micro-encapsulated formulations can reduce pesticide volatility (Jackson and Lewis, 1978; Wienhold and Gish, 1994a; Gish et al., 1995). However, the effectiveness of the formulations is strongly dependent on pesticide chemistry. As pesticide solubility increases, the impact of formulation on reducing pesticide volatilization decreases (Wienhold and Gish, 1994b).
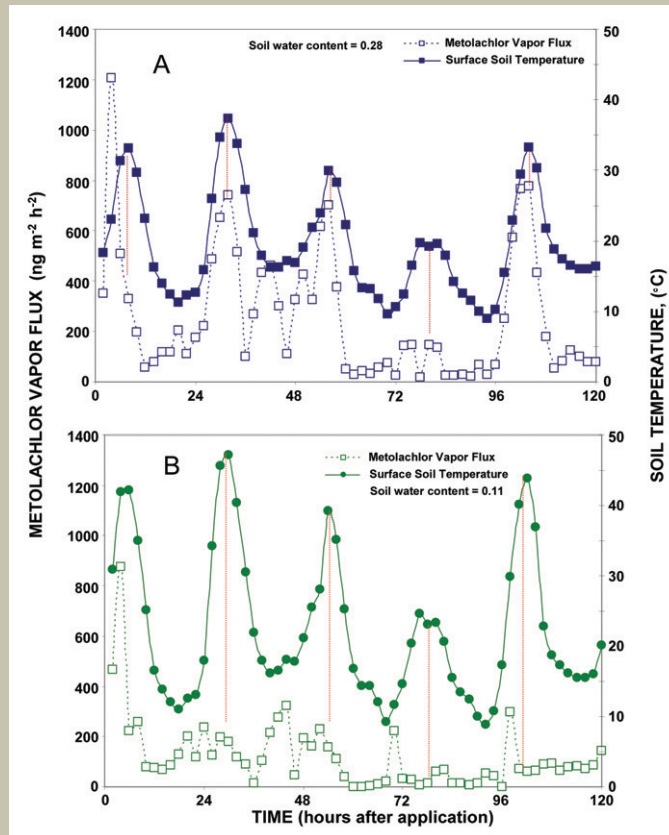
Reducing Pesticide Volatilization

Pesticide volatilization is governed by how the pesticide vapor pressure is influenced by interactions with soil properties, agricultural management practices, and local meteorology. In general, pesticides with a high vapor pressure should be avoided as they are more susceptible to volatilization. Since soil water content influences adsorption, field studies have shown that applying herbicides to a wet soil, or applying the pesticide when precipitation is anticipated (e.g., shortly after application) may be detrimental to the environment. On the other hand, rainfall or irrigation after fumigants have been injected will decrease fumigant volatilization. Best management practices for reducing pesticide volatilization also include the use of encapsulated formulations, and where possible, soil incorporation.

References

Addiscott, T.M., and R.J. Wagenet. 1985. Concepts of solute leaching in soils: A review of modeling approaches. J. Soil Sci. 36:411–424.

Alegria, H.A., and T.J. Shaw. 1999. Rain deposition of atrazine and trifluralin in coastal waters of the South Atlantic Bight. Environ. Sci. Technol. 33:850–856.

Asmussen, L.E., A.W. White, E.W. Hauser, and J.A. Sheridan. 1977. Movement of 2,4-D in a vegetated waterway. J. Environ. Qual. 6:159–162.

Aspelin, A.L. 1994. Pesticides industry and sales: 1992 and 1993 market estimates. 733-K-92-001. USEPA, Washington, DC.

Bailey, G.W., and J.L. White. 1964. Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. J. Agric. Food Chem. 12:324–332.

Baldwin, F.L., P.W. Santelmann, and J.M. Davidson. 1975. Movement of fluometuron across and trough the soil. J. Environ. Qual. 4:191–194.

Baker, J.L. 1980. Agricultural areas as nonpoint sources of pollution. p. 275–310. In M.R. Overcash and J.M. Davidson (ed.) Environmental impact of nonpoint source pollution. Ann Arbor Sci. Publ., Ann Arbor, MI.

Baker, J.L., and H.P. Johnson. 1979. The effect of tillage systems on pesticides in runoff from small watersheds. Trans. ASAE 22:554–559.

Baker, J.L., and J.M. Laflen. 1979. Runoff losses of surface applied herbicides as affected by wheel tracks and incorporation. J. Environ. Qual. 8:602–607.

Barnett, A.P., E.W. Hauser, A.W. White, and J.H. Holladay. 1967. Loss of 2,4-D in washoff of cultivated fallow lands. Weeds 15(2):133–137.

Baskaran, S., N.S. Bolan, A. Rahman, and R.W. Tillman. 1996. Pesticide sorption by allophonic and non-allophanic soils in New Zealand. N.Z. J. Agric. Res. 39:297–310.

Bidleman, T.F. 1988. Atmospheric process: Wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning. Environ. Sci. Technol. 22:361–367.

Bidleman, T.F., and E.J. Christensen. 1979. Atmospheric removal processes for high molecular weight organochlorines. J. Geophys. Res. 84:7857–7862.

Biggar, J.W., and D.R. Nielsen. 1976. Spatial variability of the leaching characteristics of a field soil. Water Resour. Res. 12:78–84.

Brasino, J.S. 1986. A simple stochastic model predicting conservative mass transport through the unsaturated zone into groundwater. Ph.D. diss. Univ. of Wisconsin, Madison, WI.

Brown, C.D., R.A. Hodgkinson, D.A. Rose, J.K. Syers, and S.J. Wilcockson. 1995. Movement of pesticides to surface waters from a heavy clay soil. Pestic. Sci. 43:131–140.

Burrows, H.D., M. Canle, J.A. Santaballa, and S. Steenken. 2002. Reaction pathways and mechanisms of photodegradation of pesticides. J. Photochem. Photobiol. B 67:71–108.

Buttle, J.M. 1990. Metolachlor in surface runoff. J. Environ. Qual. 19:531–538.

Capel, P.D., K.A. McCarthy, and J.E. Barbash. 2008. National, holistic, watershed-scale approach to understand the sources, transport, and fate of agricultural chemicals. J. Environ. Qual. 37:983–993.

Caro, J. 1976. Pesticides in agricultural runoff. p. 91–119. In B.A. Stewart (ed.) Control of water pollution from cropland. Vol. II. USEPA 600275026b.

Caro, J.H., W.M. Edwards, B.L. Glass, and M.H. Frere. 1972. Dieldrin in runoff from treated watersheds. p. 141–160. In Proc. 1970 Symp. on Interdiscipl. Aspects of watershed management, Bozeman, MT. Am. Soc. Civil Eng., New York.

Caro, J.H., H.P. Freeman, and B.C. Turner. 1974. Persistence in soil losses in runoff of soil-incorporated carbaryl in a small watershed. J. Agric. Food Chem. 22:860–863.

Cole, J.T., J.H. Baird, N.T. Basta, R.L. Huhnke, D.E. Storm, G.V. Johnson, M.E. Payton, M.D. Smolen, D.L. Martin, and J.C. Cole. 1997. Influence of buffers on pesticides and nutrient runoff from bermudagrass turf. J. Environ. Qual. 26:1589–1598.

Cousins, I.T., A.J. Beck, and K.C. Jones. 1999. A review of the processes involved in the exchange of semi-volatile organic compounds (SVOC) across the air–sol interface. Sci. Total Environ. 228:5–24.

Delphin, J.E., and J.Y. Chapot. 2006. Leaching of atrazine, metolachlor and diuron in the field in relation to their injection depth into a silt loam soil. Chemosphere 64:1862–1869.

Denmead, O.T., J.R. Simpson, and J.R. Freney. 1977. A direct field measurement of ammonia emission after injection of anhydrous ammonia. Soil Sci. Soc. Am. J. 41:1001–1004.

Domagalski, J.L., S. Ator, R. Coupe, K. McCarthy, D. Lampe, M. Sandstrom, and N. Baker. 2008. Comparative study of transport processes of nitrogen, phosphorus, and herbicides to streams in five agricultural basins, USA. J. Environ. Qual. 37:1158–1169.

Doull, J. 1989. Pesticide carcinogenicity. p. 1–5. In N. Ragsdale and R.E. Menzer (ed.) Carcinogenicity and pesticides: Principles, issues and relationships. ACS, Washington, DC.

Everts, C.J., R.S. Kanwar, E.C. Alexander, Jr., and S.C. Alexander. 1989. Comparison of tracer mobilities under laboratory and field conditions. J. Environ. Qual. 18:491–498.

Farmer, W.J., J.P. Martin, W.F. Spencer, and K. Igue. 1972. Volatility of organochlorine insecticides from soil: I. Effect of concentration, temperature, air flow rate, and vapor pressure. Soil Sci. Soc. Am. Proc. 36:443–447.

Fawcett, R.S., D.P. Tierney, and B.R. Christensen. 1994. The impact of soil conservation on pesticide runoff into surface water: A review and analysis. J. Soil Water Conserv. 49:126–135.

Felsot, A.S., J.K. Mitchell, and A.L. Kenimer. 1990. Assessment of management practices for reducing pesticide runoff from sloping cropland in Illinois. J. Environ. Qual. 19:539–545.

Gan, J., S.J. Lee, W.P. Liu, D.L. Haver, and J.N. Kabashima. 2005. Distribution and persistence of pyrethroids in runoff sediments. J. Environ. Qual. 34:836–841.

Gevao, B., K.T. Semple, and K.C. Jones. 2000. Bound pesticide residue in soils: A review. Environ. Pollut. 108:3–14.

Germann, P.F., and K. Beven. 1981. Water flow in soil macropores: I. An experimental approach. J. Soil Sci. 18:363–368.

Ghodrati, M., and W.A. Jury. 1992. A field study of the effects of soil structure and irrigation method on preferential flow of pesticides in unsaturated soil. J. Contam. Hydrol. 11:101–125.

Gillion, R.J., J.E. Barbash, C.G. Crawford, P.A. Hamilton, J.D. Martin, N. Nakagaki, L.H. Nowell, J.C. Scott, P.E. Stackelberg, G.P. Thelin, and D.M. Wolock. 2006. Pesticides in the nation's streams and groundwater, 1992–2001. USGS Circular 1291. USGS, Reston, VA.

Gish, T.J., D. Gimenez, and W.J. Rawls. 1998a. Impact of roots on ground water quality. Plant Soil 200:47–54.

Gish, T.J., A.R. Isensee, R.G. Nash, and C.S. Helling. 1991a. Impact of pesticides on shallow groundwater quality. Trans. ASAE 34:1745–1753.

Gish, T. J., and W. A. Jury. 1983. Effect of plant roots and root channels on solute transport. Trans. ASAE 26:440–444, 451.

Gish, T.J., K.-J., S. Kung, D. Perry, J., Posner, G. Bubenzer, C.S. Helling, E.J., Kladivko, and T. S. Steenhuis. 2004. Impact of preferential flow at varying irrigation rates by quantifying mass fluxes. J. Environ. Qual. 33:1033–1040.

Gish, T.J., J.H. Prueger, W.P. Kustas, J.L. Hatfield, L.G. McKee, and A.L. Russ. 2009. Soil moisture and metolachlor volatilization observations over three years. J. Environ. Qual. 38:1785–1795.

Gish, T.J., A. Sadeghi, and B.J. Wienhold. 1995. Volatilization of alachlor and atrazine as influenced by surface litter. Chemosphere 31:2971–2982.

Gish, T.J., M.J. Schoppet, C.S. Helling, A. Shirmohammadi, M.M. Schreiber, and R.E. Wing. 1991b. Transport comparison of technical grade and starch-encapsulated atrazine. Trans. ASAE 34:1738–1744.

Gish, T.J., A. Shirmohammadi, C.S. Helling. K.-J.S. Kung, B.J. Wienhold, and W.J. Rawls. 1998b. Mechanisms of herbicide leaching and volatilization and innovative approaches for sampling, prediction and control. p. 107–134. In J.L. Hatfield et al. (ed.) Integrated weed and soil management. Ann Arbor Press, Chelsea, MI.

Gish, T.J., A. Shirmohammadi, and B.J. Wienhold. 1994. Field-scale mobility and persistence of commercial and starch-encapsulated atrazine and alachlor. J. Environ. Qual. 23:355–359.

Glass, R.J., T.S. Steenhuis, and J.Y. Parlange. 1988. Wetting front instability as a rapid and far reaching hydrologic process in the vadose zone. J. Contam. Hydrol. 3:207–226.

Glotfelty, D.E., M.M. Leech, J. Jersey, and A.W. Taylor. 1989. Volatilization and wind erosion of soil-surface applied atrazine, simazine, alachlor, and toxaphene. J. Agric. Food Chem. 37:546–555.

Glotfelty, D.E., A.W. Taylor, B.J. Turner, and W.H. Zoller. 1984. Volatilization of surface applied pesticides from a fallow soil. J. Agric. Food Chem. 32:638–643.

Glotfelty, D.E., and C.J. Schomburg. 1989. Volatilization of pesticides from soil. p. 181–207. In B.L. Sawhey and K. Brown (ed.) Reactions and movement of organic chemicals in soils. SSSA Spec. Publ. 22. SSSA, Madison, WI.

Hall, J.K., N.L. Hartwig, and L.D. Hoffman. 1983. Application mode and alternate cropping effects on atrazine losses from a hillside. J. Environ. Qual. 12:336–340.

Haith, D.A., and F.S. Rossi. 2003. Risk assessment of pesticides from turf. J. Environ. Qual. 32:447–455.

Hamaker, J.W., and J.M. Thompson. 1972. Adsorption. p. 49–143. In C.A. I. Goring and J.W. Hamaker (ed.) Organic chemicals in soil environment, Vol. 1. Marcel Dekker, New York.

Harris, G.L., and J.A. Catt. 1999. Overview of the studies on the cracking clay soil at Brimstone Farm, UK. Soil Use Manage. 15:233–239.

Helling, C.S. 1993. Pesticides, agriculture, and water quality. p. 235–252. In Proc. Stockholm Water Symp. Stockholm, 1992. Available at http://www.worldwaterweek.org/documents/Resources/Synthesis/1992_Proceedings.pdf (verified 11 Feb. 2011). Stockholm Vatten, Sweden.

Helling, C.S., and T.J. Gish. 1986. Soil characteristics affecting pesticide movement into groundwaters. p. 14–38. In W.Y. Garner et al. (ed.) Evaluation of pesticides in ground water. ACS, Washington, DC.

Isensee, A.R., R.G. Nash, and C.S. Helling. 1990. Effects of no-tillage vs. conventional tillage corn production on the movement of several pesticides to ground water. J. Environ. Qual. 19:434–440.

Jackson, M.D., and R.G. Lewis. 1978. Volatilization of two methyl parathion formulations from treated fields. Bull. Environ. Contam. Toxicol. 20:793–796.

Jarvis, N.J. 2002. Macropore and preferential flow. p. 1005–1013. In J. Plimmer (ed.) The encyclopedia of agrochemicals. Vol. 3. John Wiley and Sons, Chelsea, MI.

Jenks, B.M., F.W. Roeth, A.R. Martin, and D.L. McCallister. 1998. Influence of surface and subsurface soil properties on atrazine sorption and degradation. Weed Sci. 46:132–138.

Jin-Clark, Y., M.J. Lydy, and K.Y. Zhu. 2002. Effects of atrazine and cyanazine on chlorpyrifos toxicity in *Chironomus tentans* (Diptera: Chironomidae). Environ. Toxicol. Chem. 21:598–603.

Johnson, A.C., A.H. Haria, C.L. Bhardwaj, R.J. Williams, and A. Walker. 1996. Preferential flow pathways and their capacity to transport isoproturon in a structured clay soil. Pestic. Sci. 48:225–237.

Jones, R.L., G.L. Harris, J.A. Catt, R.H. Bromilow, D.J. Mason, and D.J. Arnold. 1995. Management practices for reducing movement of pesticides to surface water in cracking clay soils. Weeds 2:489–498.

Jury, W.A., and H. Flühler. 1992. Transport of chemicals through soil: Movement, models, and field application. Adv. Agron. 47:141–202.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behavior assessment model for trace organics in soil: I. Model description. J. Environ. Qual. 12:558–564.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1984. Behavior assessment model for trace organics in soil: IV. Review of experimental evidence. J. Environ. Qual. 13:580–586.

Karickhoff, S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments. Chemisphere 10:833–846.

Kearney, P.C., R.G. Nash, and A.R. Isensee. 1969. Persistence of pesticide residues in soils. p. 54–67. In M.W. Miller and G.G. Berg (ed.) Chemical fallout. Current research on persistent pesticides. Charles C. Thomas Publ., Springfield, IL.

Kladivko, E.J., G.E. Van Scoyoc, E.J. Monke, K.M. Oates, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. J. Environ. Qual. 20:264–270.

Koplin, D.W., J.E. Barbash, and R.J. Gillion. 1998. Occurrence of pesticides in shallow groundwater of the United States: Initial results from the National Water-Quality Assessment Program. Environ. Sci. Technol. 32:558–566.

Kuang, Z., L.L. McConnell, A. Torrents, D. Meritt, and S. Tobash. 2003. Atmospheric deposition of pesticides to an agricultural watershed of the Chesapeake Bay. J. Environ. Qual. 32:1611–1622.

Kung, K.-J.S. 1990. Preferential flow in a sandy vadose zone: 1. Field observations. Geoderma 46:51–71.

Kung, K.-J.S., M. Hanke, C.C. Helling, E.J. Kladivko, T.J. Gish, T.S. Steenhuis, and D.B. Jaynes. 2005. Quantifying pore-size spectrum of macropore-type preferential pathways. Soil Sci. Soc. Am. J. 69:1196–1208.

Kung, K.-J.S., E.J. Kladivko, T.J. Gish, T.S. Steenhuis, G. Bubenzer, and C.S. Helling. 2000a. Quantifying preferential flow by breakthrough of sequentially applied tracers: Silt loam soil. Soil Sci. Soc. Am. J. 64:1296–1304.

Kung, K.-J.S., T.S. Steenhuis, E.J. Kladivko, T. Gish, G. Bubenzer, and C.S. Helling. 2000b. Impact of preferential flow on the transport of adsorbing and non-adsorbing tracers. Soil Sci. Soc. Am. J. 64:1290–1296.

LaFleur, K.S., W.R. McCaskil, and D.S. Adams. 1975. Movement of prometryne through Congaree soil into groundwater. J. Environ. Qual. 4:132–133.

Laird, D.A., E. Barriuso, R.H. Dowdy, and W.C. Koskinen. 1992. Adsorption of atrazine on smectites. Soil Sci. Soc. Am. J. 56:62–67.

Libra, R.D., G.R. Halberh, G.G. Resmeyer, and B.E. Hoyer. 1984. Groundwater quality and hydrogeology of Devonian-carbonate aquifers in Floyd and Mitchell Counties, Iowa. Iowa Geol. Surv. Open File Rep. 84-2. Part I. Iowa Geological Survey, Iowa City.

Libardi, P.L., K. Reichardt, D.R. Nielsen, and J.W. Biggar. 1980. Simple field methods for estimating soil hydraulic conductivity. Soil Sci. Soc. Am. J. 44:3–6.

Ma, Q.L., R.D. Wauchope, L. Ma, K.W. Rojas, R.W. Malone, and L.R. Ahuja. 2004. Test of the root zone water quality model (RZWQM) for predicting runoff of atrazine, alachor, and fenamiphos species from conventional-tillage corn mesoplots. Pest Manage. Sci. 60:267–276.

Majewski, M.S., and P.D. Capel. 1995. Pesticides in the atmosphere, distribution, trends, and governing factors. Ann Arbor Press, Inc., Chelsea, Michigan, USA.

McConnell, L.L., J.S. LeNoir, S. Datta, and J.N. Seiber. 1998. Wet deposition of current-use pesticides in the Sierra Nevada mountain range, California, USA. Environ. Toxicol. Chem. 17:1908–1916.

Muir, D.C., and B.E. Baker. 1976. Detection of triazine herbicide and their degradation products in tile-drain water from fields under intensive corn (maize) production. J. Agric. Food Chem. 24:122–125.

Ng, H.Y.F., J.D. Gaynor, C.S. Tan, and C.F. Drury. 1995. Dissipation and loss of atrazine and metolachlor in surface and subsurface drain water: A case study. Water Res. 29:2309–2317.

Nielsen, D.R., J.W. Biggar, and K.T. Erh. 1973. Spatial variability of field measured soil water properties. Hilgardia 42:215–259.

Novak, S.M., J-M. Portal, and M. Schiavon. 2001. Effects of soil type on metolachlor losses in subsurface discharge. Chemosphere 42:235–244.

Parmele, L.H., E.R. Lemon, and A.W. Taylor. 1972. Micrometeorological measurement of pesticide vapor flux from bare soil and corn under field conditions. Water Air Soil Pollut. 1:433–451.

Posner, J.L., M.D. Casler, and J.O. Baldock. 1995. The Wisconsin integrated cropping system trial: Combining agro-ecology with production agronomy. Am. J. Alt. Agric. 10:98–107.

Prueger, J.H., T.J. Gish, L.L. McConnell, L.G. McKee, J.L. Hatfield, and W.P. Kustas. 2005. Solar radiation, relative humidity, and soil water effects on Metolachlor volatilization. Environ. Sci. Technol. 39:5219–5226.

Prueger, J.H., J.L. Hatfield, and T.J. Sauer. 1999. Field-scale metolachlor volatilization flux estimates from broadcast and banded application methods in central Iowa. J. Environ. Qual. 28:75–81.

Rao, P.S.C., and J.M. Davidson. 1980. Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models. p. 23–67. In M.R. Overcash and J.M. Davidson (ed.) Environmental impact of nonpoint source pollution. Ann Arbor Sci. Publ., Ann Arbor, MI.

Reddy, K.N., M.A. Locke, and C.T. Bryson. 1994. Foliar washoff and runoff losses of lactofen, norflurazon, and fluometuron under simulated rainfall. J. Agric. Food Chem. 42:2338–2343.

Ritsema, C.J., and L.W. Dekker. 1995. Distribution flow: A general process in the top layer of water repellent soils. Water Resour. Res. 31:1187–1200.

Schreiber, M.M., M.V. Hickman, and G.D. Vail. 1993. Starch-encapsulated atrazine—Effects and transport. J. Environ. Qual. 22:443–453.

Shipitalo, M.J., W.A. Dick, and W.M. Edwards. 2000. Conservation tillage macropore factors that affect water movement and the fate of chemicals. Soil Tillage Res. 53:167–183.

Shipitalo, M.J., W.M. Edwards, W.A. Dick, and L.B. Owens. 1990. Initial storm effects on macropore transport surface-applied chemicals in no-till soil. Soil Sci. Soc. Am. J. 54:1530–1536.

Schulz, R., M. Hauschild, M. Ebeling, J. Nankodrees, J. Wogram, and M. Liess. 1998. A qualitative field method for monitoring pesticides in the edge-of-field runoff. Chemosphere 36:3071–3082.

Spark, K.M., and R.S. Swift. 2002. Effect of soil composition and dissolved organic matter on pesticide sorption. Sci. Total Environ. 298:147–161.

Sparling, D.W., G.M. Fellers, and L.L. McConnell. 2001. Pesticides and amphibian population declines in California, USA. Environ. Toxicol. Chem. 20:1591–1595.

Spencer, W.F., and M.M. Cliath. 1970. Desorption of Lindane from soil as related to vapor density. Soil Sci. Soc. Am. Proc. 34:574–578.

Spencer, W.F., and M.M. Cliath. 1974. Factors affecting vapor loss of trifuralin from soil. J. Agric. Food Chem. 20:987–991.

Spencer, W.F., M.M. Cliath, and W.J. Farmer. 1969. Vapor density of soil-applied dieldrin as related to soil-water content, temperature, and dieldrin concentration. Soil Sci. Soc. Am. Proc. 33:509–511.

Symons, P.E.K. 1977. Dispersal and toxicology of the insecticide fenitrothion; predicting hazards of forest spraying. Residue Rev. 68:1–36.

Taylor, A.W. 1995. The volatilization of pesticide residues. p. 257–306. In T.R. Roberts and P.C. Kearney (ed.) Environmental behavior of agrochemicals. Vol. 9. John Wiley and Sons, New York.

Taylor, A.W., and W.F. Spencer. 1990. Volatilization and vapor transport processes. p. 213–269. In H.H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA Book Ser. 2. SSSA, Madison, WI.

Thurman, E.M., and A.E. Cromwell. 2000. Atmospheric transport, deposition, and fate of triazine herbicides and their metabolites in pristine areas at Isle Royale National Park. Environ. Sci. Technol. 34:3079–3085.

Tilman, D., K.G. Cassman, P.A. Matson, R. Naylor, and S. Polasky. 2002. Agricultural stability and intensive production practices. Nature 418:671–677.

Traub-Eberhard, U., K.-P. Henschel, W. Kordel, and W. Klein. 1995. Influence of different field sites on pesticide movement into subsurface drains. Pestic. Sci. 43:121–129.

USEPA. 1990. National pesticide survey: Project summary. EPA Rep. 570990NPSg.

USEPA. 2008. Drinking water contaminants. EPA 816-F-03-016. Available at http://www.epa.gov/safewater/contaminants/index.html (verified 29 Nov. 2010).

USEPA Biological and Economic Analysis Division. 2004. Pesticide industry sales and usage: 2000 and 2001 Market estimates. http://www.epa.gov/oppbead1/pestsales/.

Wauchope, R.D. 1978. The pesticide content of surface water draining from agricultural fields. A review. J. Environ. Qual. 7:459–472.

Wauchope, R.D., and R.S. Meyers. 1985. Adsorption–desorption kinetics of atrazine and linuron in

freshwater sediment aqueous slurries. J. Environ. Qual. 14:132–136.

Webb, R.M.T., M.E. Wieczorek, BT. Nolan, T.C. Hancock, M.W. Sandstrom, J.E. Barbash, E. R. Bayless, R.W. Healy, and J. Linard. 2008. Variations in pesticide leaching related to land use, pesticide properties, and unsaturated zone thickness. J. Environ. Qual. 37:1145–1157.

Weber, J.B., S.B. Weed, and T.J. Sheets. 1972. Pesticides—How they move and react in the soil. Crops Soils 25(1):14–17.

Wienhold, B.J., and T.J. Gish. 1994a. Effect of Formulation and tillage practice on volatilization of atrazine and alachlor. J. Environ. Qual. 23:292–298.

Wienhold, B.J., and T.J. Gish. 1994b. Chemical properties influencing rate of release of starch encapsulated herbicides: Implications for modifying environmental fate. Chemosphere 28:1035–1046.

Williams, A.G., D. Scholefield, J.F. Dowd, N. Holden, and L. Deeks. 2000. Investigating preferential flow in a large intact soil block under pasture. Soil Use Manage. 16:264–269.

Wilson, J.D., G.W. Thurtell, G. Kidd, and E. Beauchamp. 1982. Estimation of the rate of gaseous mass transfer from a surface source plot to the atmosphere. Atmos. Environ. 16:1861–1867.

Wyman, J.A, J.O. Jensen, D. Curwen, R.L. Jones, and T.E. Marquardt. 1985. Effects of application procedures and irrigation on degradation and movement of aldicarb residues in soil. Environ. Toxicol. Chem. 4:641–651.

Wyman, J.A., J. Medina, D. Curwen, J.L. Hansen, and R.L. Jones. 1986. Movement of aldicarb and aldoxycarb residues in soil. Environ. Toxicol. Chem. 5:545–555.

Yagi, K., J. Williams, N.Y. Wang, and R.J. Cicerone. 1995. Atmospheric methyl bromide (CH_3Br) from agricultural soil fumigations. Science 267:1979–1981.

Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and M.V. Yates. 1996. Methyl bromide emissions from a covered field. II. Volatilization. J. Environ. Qual. 25:192–202.

Yates, S.R., J. Knuteson, F.F. Ernst, W. Zheng, and Q. Wang. 2008. Effect of sequential surface irrigations on field-scale emissions of 1,3-dichloropropene. Environ. Sci. Technol. 42:8753–8758.

Zehe, E., and H. Fluhler. 2001. Slope scale variation of flow patterns in soil profiles. J. Hydrol. 247:116–132.