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## Herbicide Off-Site Transport

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### 1. Introduction

Herbicides are an important part of modern agriculture as they control weeds that would otherwise reduce yields by competing for water and nutrients. The U.S. Environmental Protection Agency estimated that 226,000 metric tons of herbicides were used in the U.S. alone during 2007, which accounts for 25% of the globally usage in 2007 (USEPA, 2011). Additionally, during 2007, 89% of the herbicide usage in the U.S. was for agriculture (USEPA, 2011). Since it has been proposed that increasing agricultural food and fiber production will be necessary to maintain political and social stability in developing countries (Tilman et al., 2002), herbicide use will become increasingly important to meet these global needs, especially as marginal lands are converted to agriculture (Helling, 1993). Although critical to production, herbicides can be toxic to humans and other organisms, even at low concentrations (Jin-Clark et al., 2002; USEPA, 2008). To maintain productive and sustainable agricultural systems there is an immediate need to understand field-scale processes governing herbicide use and off-site transport.

During the past three decades several national surveys in the U.S. have shed light on the prevalence of herbicides in the environment. One of the first national surveys was conducted by the U.S. Environmental Protection Agency (USEPA, 1990) which determined that about 10% of community water system wells contained detectable amounts of at least one herbicide. From 1993 to 1995, the National Water-Quality Assessment program monitored 20 major basins in the U.S. and found herbicides in over 50% of the sites sampled (Koplin et al., 1998). Furthermore, the U.S. Geological Survey observed that 97 percent of all streams sampled from agricultural and urban areas contain detectable concentrations of at least one herbicide, while 65 percent of the streams in undeveloped areas contained observable levels of herbicide (Gillion et al., 2006). Clearly, herbicide occurrence in streams, groundwater aquifers, and community wells are well documented, but determining the relative importance of major off-site transports processes at the field and watershed scales is still in its infancy.

As summarized in Figure 1, herbicide off-site transport occurs primarily through surface runoff (Wauchope, 1978; Shipitalo and Owens, 2006), groundwater leaching (Isensee et al., 1990; Gaynor et al., 2001; Hansen et al., 2001), and/or volatilization (Taylor and Spencer, 1990; Gish et al., 2011). Precipitation events are especially crucial for determining which loss pathways are most critical in governing herbicide off-site transport. For example, if a

precipitation event does not occur within a few weeks of application runoff and groundwater leaching losses will be negligible – however, herbicide volatilization can still be substantial (Prueger et al., 2005; Gish et al., 2011). To a large extent, how a given herbicide is partitioned between runoff, leaching and volatilization is a function of how the herbicide is distributed between three phases: 1) herbicide adsorbed to soil particles; 2) herbicide in the soil solution (liquid phase); and 3) the mass of the herbicide in the vapor phase (in soil pores and above the soil surface). Herbicides can also move from one phase to another, depending on a number of chemical and environmental factors. For example, although a particular herbicide may have a high affinity for the soil matrix, increases in soil water content move more herbicide from the adsorbed and liquid phases into the vapor phase (Prueger et al., 2005; Gish et al., 2009). Additionally, in a 2-year study (Weber et al., 2006) observed as much as 21 % of the applied metolachlor leached from field lysimeters when 316 mm of precipitation occurred during the first month after application, relative to only 2.8 % of the applied metolachlor when only 106 mm of precipitation occurred during the first month after application. Relative to a dry field conditions, a rainfall event shortly after application can enhance herbicide surface runoff (Pantone et al., 1992; Zhang et al., 1997), leaching (Gaynor et al., 2002; Weber et al., 2006), and volatilization (Prueger et al., 2005; Gish et al., 2011). As a result, if future off-site transport of herbicides is to be accurately quantified, field investigations where metrological conditions are also monitored will be essential.

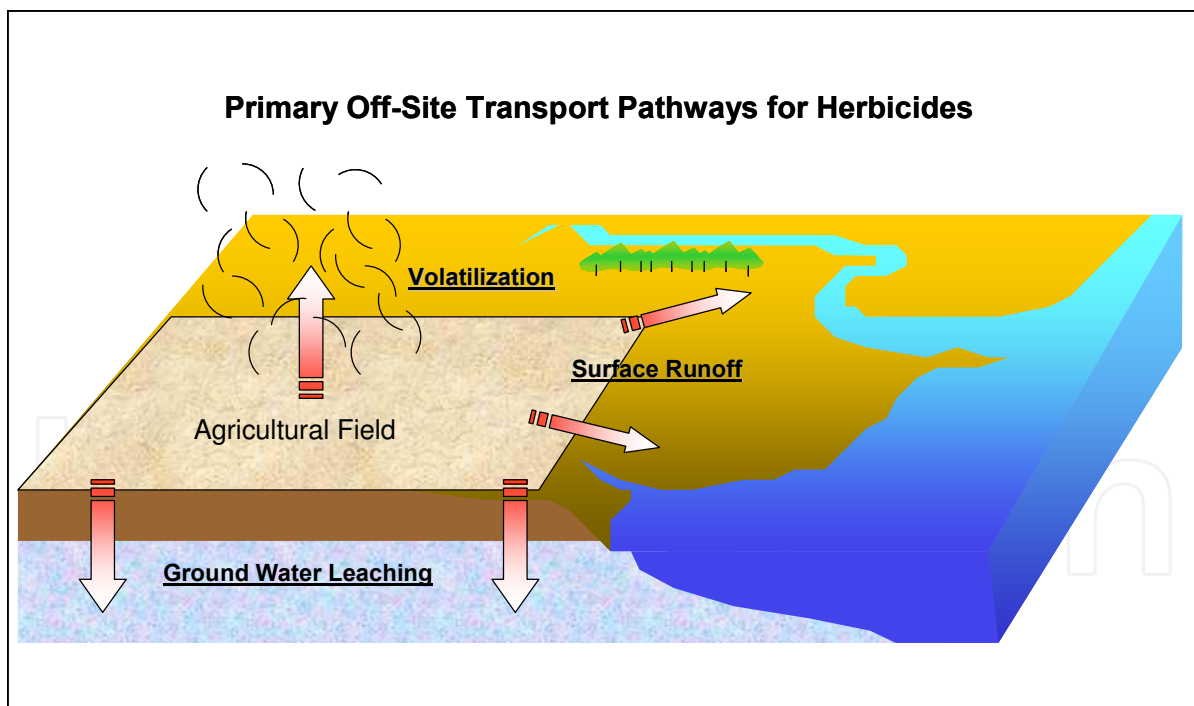


Fig. 1. Schematic of loss pathways critical to off-site transport of herbicides

As summarized in Figure 2, methods for evaluating off-site herbicide transport are expensive and difficult to interpret due to process interactions that vary both spatially and temporally and are a function of scale. The rate at which herbicides are lost from the three major loss pathways is influenced by a number of small scale factors which include soil water content, organic matter content, soil hydraulic properties, as well as larger scale

influences such as wind speed profiles, agricultural management practices, timing of rainfall events relative to application, and field slope (Wauchope, 1978; Mojašević et al., 1996; Gaynor et al., 2001; Shipitalo and Owens, 2006). Thus, although the impact of various soil and environmental factors on herbicide behavior have been quantified in controlled laboratory and greenhouse environments, monitoring and interpreting field-scale herbicide behavior is more ambiguous (Helling and Gish, 1986). Furthermore, in addition to the three major loss pathways, herbicide emissions can occur as spray drift in concentrated droplets or as herbicide attached to dust particles (Symons, 1977; Majewski and Capel, 1995) or from herbicides deposited directly into streams via tree wash-off (personal communication, Dr. Clifford Rice, USDA-ARS Beltsville, MD). To reduce risks associated with herbicide use, the three major loss pathways (runoff, leaching and volatilization) must be simultaneously evaluated to avoid developing herbicide formulations or practices that simply shift herbicides loss from one off-site transport pathway to another.

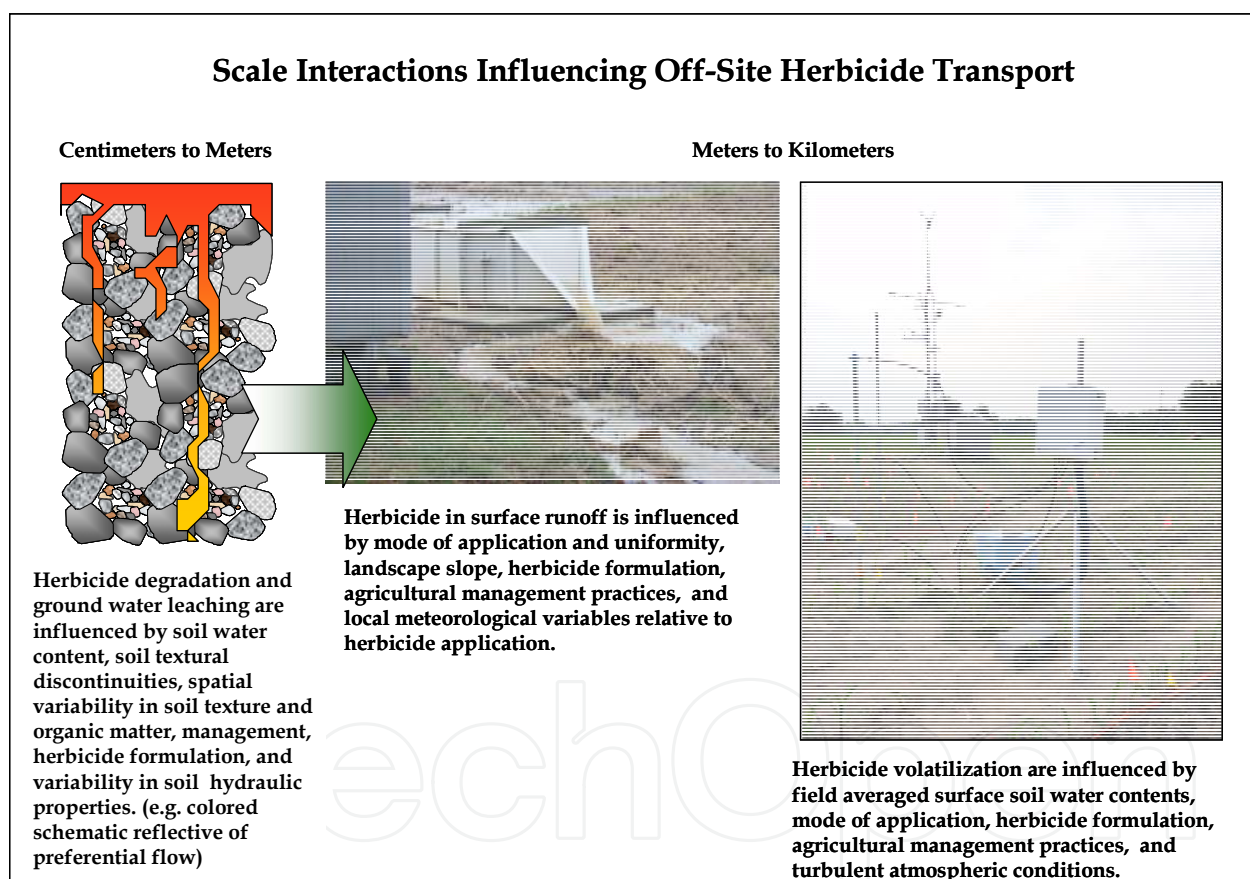


Fig. 2. Scale of properties and processes that interact to influence herbicide off-site transport

This chapter will discuss the relative importance of herbicide loss through surface runoff, groundwater leaching, and volatilization including the impact of soil properties, agricultural management, and meteorological conditions. Since local climatic and surface soil conditions influence herbicide behavior, emphasis will be given to field-scale, long-term investigations. Additionally, methods for reducing herbicide off-site transport will be briefly discussed for each loss pathway.

## 2. Surface runoff

The highest concentrations of herbicides in surface streams are typically associated with this first significant runoff event after application to agricultural fields (Thurman et al., 1991; Battaglin and Goolsby, 1999; Gentry et al., 2000; Scribner et al., 2000). As a result, herbicide surface runoff is a concern in many watersheds where intensive agriculture may be adjacent to sensitive ecosystems (Capel et al., 2008). Herbicide in surface runoff occurs through two mechanisms: 1) erosion of herbicide adsorbed to soil sediment; and 2) dissolution of the herbicide into the surface runoff water. Although herbicide concentrations in runoff sediment can be several times higher than those observed in the water phase, most of the herbicide lost in runoff is from the water phase since runoff water volumes are typically much greater than sediment losses (Wauchope, 1978). Within a single runoff event the bulk of the herbicide loss occurs early in the event and decreases exponentially with time (Buttle, 1990; Reddy et al., 1994; Shipital and Owens, 2006). Seasonal runoff losses are predominately an accumulation of single-event losses with minor losses in-between major storm or irrigation events (Haith and Ross, 2003). Although rainfall timing, intensity, and duration are the most critical factors governing herbicide runoff, the rate of application, formulation, management practice, and landscape features are also important (Caro, 1976; Baker and Johnson, 1979; Wauchope, 1978; Hall et al., 1983; Felsot, 1990; Domagalski et al., 2008). Typically, annual losses from a single rainfall event are small, < 1 % of that applied (Shipitalo and Owens, 2006; Gish et al., 2011). However, in situations, such as when a major rainfall event follows herbicide applications, herbicide losses can exceed 2 % of that applied (Baker, 1980; Haith and Rossi, 2003, Shipital and Owens, 2006). Regardless of the herbicide 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 (Baker, 1980; Capel et al., 2008; Domagalski et al., 2008).

### 2.1 Rainfall impact

The primary factors governing herbicide off-site transport via runoff are the intensity, duration, and timing of the rainfall events relative to application (Baker and Johnson, 1979; Baker et al., 1978). Figure 3 depicts typical herbicide surface runoff concentrations with time from a 7 ha research site in Beltsville, Maryland over 8 years (for general site description see Chinkuyu et al., 2004). The exponential decrease in runoff and lack of herbicides in runoff after 20 days may be due to the sandy textured soil which dominates this site. However, similar trends were also observed by Pantone et al, (1992) who observed higher herbicide runoff losses the first day after application than 30 days later. Additionally, Shipitalo and Owens (2006) in a 9 year study over several small watersheds demonstrated that herbicide runoff concentrations also decreased exponentially with time after application. To account for the interaction between rainfall intensity, duration, and timing, classifying three types of runoff events have been proposed: minor, critical, and catastrophic (Wauchope, 1978). Minor runoff events are a product of rain events which produce small amounts of runoff shortly after herbicide application, generally within 1-2 days. These minor events typically have high concentrations of herbicide in a relatively small amount of surface runoff and account for herbicide losses < 1 % of that applied. However, the high concentration of herbicide in these minor runoff events may affect sensitive ecosystems adjacent to agricultural land. The second type, a critical runoff event occurs within two weeks of herbicide application and has about 50 % of the rainfall exiting the field through surface



runoff. The amount of herbicide lost in a critical event is also dependent on herbicide soil persistence, adsorption affinity, and landscape features (Shipitalo et al., 2000; Ma et al., 2004). Herbicide runoff losses can be significant with a critical runoff event even if the herbicide 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 herbicide runoff loss from agricultural fields and account for 1-4 % of the applied herbicide annually (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 herbicide application (Wauchope, 1978; Schulz et al., 1998; Shipitalo and Owens, 2006). For example, catastrophic runoff events are typically caused by severe thunderstorms that produce large amounts of rainfall within three days of the herbicide application and can account for > 4% of the herbicide applied. Although a higher percentage of the applied herbicide is lost in a catastrophic runoff event, the concentration of herbicide in the water phase removed from the field is relatively low due to dilution. Occurrences of catastrophic runoff events are rare, since timing of a major storm and application of herbicide must coincide and farmers typically attempt to avoid extreme weather situations.

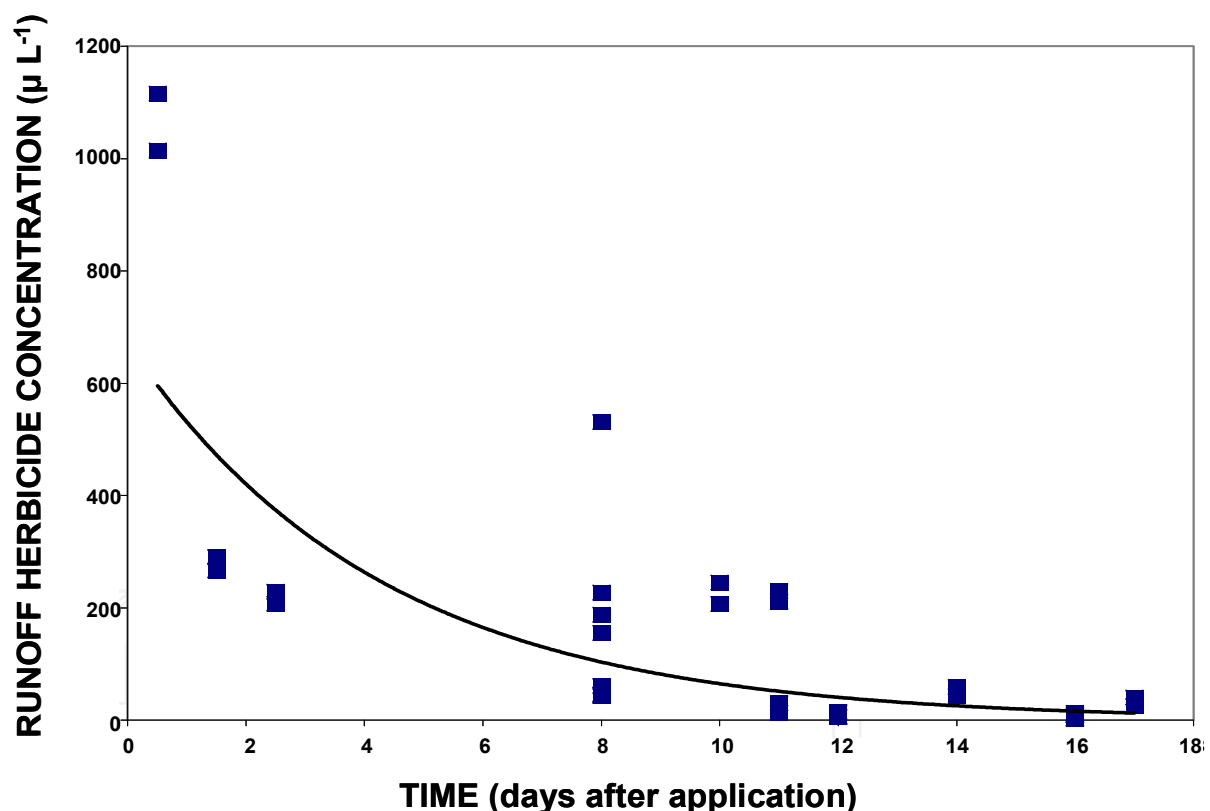


Fig. 3. Typical herbicide concentrations in surface runoff as a function of time. Data represents metolachlor and atrazine runoff over 8 years from a research site in Beltsville, Maryland (USA)

## 2.2 Management strategies

Since herbicide runoff is primarily a function of rainfall, best management practices for reducing herbicide runoff losses must consider reducing herbicide concentrations in both

the water phase and the soil 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, while less ineffective in controlling herbicide losses in the water phase (Baker et al., 1978; Baker and Johnson, 1979; Cole et al., 1997; Shipitalo et al., 2000; Caron et al., 2010). If soils are frequently wet, installing tile-drains can reduce herbicide runoff. Southwick et al. (1990) reported that installing tile drains resulted in significantly reduced herbicide runoff due to a reduction in surface runoff volumes.

Application methods such as soil incorporation can reduce herbicide runoff, leaching and volatilization losses even though persistence may increase. Soil incorporation can reduce herbicide runoff losses from 1/4 to 1/20 of the surface applied herbicide loss (Baker and Laflen, 1979; Hansen et al. 2001). Foliar applications of herbicide are to be avoided, if possible, since they tend to be easily washed off and transported off-site in runoff water before being adsorbed to the soil (Wauchope, 1978; Gevaio et al., 2000).

An important management factor which influences herbicide runoff losses is the formulation used. Some herbicides are applied as a wettable powder and have high runoff potentials, resulting in annual runoff losses generally ranging from 2 - 5% of that applied (Wauchope, 1978). Since wettable powder formulations subjected to critical and catastrophic runoff events can result in herbicide runoff losses exceeding 5% of that applied they should be avoided if at all possible. Herbicides applied as an emulsion have the next highest potential for loss in runoff, and losses are typically about 1% of that applied. Water soluble herbicides have a much greater potential of being lost in water runoff, whereas, non-water soluble herbicides often have an affinity for soil particles and will most likely be lost in the sediment portion of runoff. An example of formulation influences on pesticide runoff is observed with ester and amine salt based herbicides (Barnett et al., 1967). 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. For all other herbicide formulations (e.g., pelleted and micro-encapsulated) annual runoff losses are typically < 0.5% of that applied, except when a critical or catastrophic event occurs (Wauchope, 1978; Shipitalo and Owens, 2006).

### **2.3 Landscape and soil properties**

Landscape attributes and soil properties interact with the type of runoff event, herbicide chemistry, and formulation to influence runoff losses. All other conditions equal, herbicide runoff losses increase with increasing slope (Hall et al., 1983; Felsot et al., 1990; Celis et al., 2007). For example, herbicide runoff from a 3% slope can be as high as 2% of that applied, while slopes of 10-15% may result in herbicide runoff losses exceeding 5% of that applied (Wauchope, 1978). Soil properties which influence herbicide runoff losses include soil organic matter content (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), and clay mineral content (Baskaran et al., 1996). In general, soil properties influence herbicide runoff by affecting adsorption and desorption processes. High soil organic matter contents (> 5 %) will typically be the most important factor influencing herbicide absorption (Sparks 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 herbicide adsorption by altering the chemical composition of the herbicide resulting in a net positive charge (Jenks et al., 1998). For example, atrazine is more adsorptive in acidic soils because they react with  $H^+$ , making the herbicide cationic and chemically attracted to cation exchange sites (Bailey and White, 1964; Weber et al., 1972; Jenks et al., 1998). Although herbicides 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 herbicides due to water competition for adsorption sites on soil particles (Hamaker and Johnson, 1972; Cole et al., 1997). As soil moisture increases (through a rain or irrigation event) water is adsorbed to the soil matrix and herbicides desorb. Subsequently, the desorbed herbicide diffuses into the water phase where it can be more readily transported off-site. Studies examining the application of herbicides in wet and dry soils showed that runoff losses were significantly greater for the wet soil, because of the lower adsorption potential (Barnet et al., 1967; Baldwin et al., 1975; Asmussen et al., 1977).

Herbicides which persist in the soil for long periods of time pose an environmental threat to neighboring ecosystems simply because the window for a significant runoff event is larger. Herbicide persistence is typically quantified as a half-life ( $T_{1/2}$ ) which represents the time taken for half of the herbicide to degrade. Major factors influencing herbicide soil persistence include application method (Hall et al., 1983), herbicide chemistry and soil affinity (Jenks et al., 1998; Spark and Swift, 2002), leaching potential (Webb et al., 2008), soil water content (Mojašević et al., 1996), formulation and volatilization potential (Gish et al., 1994); and degradation processes (Gan et al., 2005). Because properties like soil moisture and organic matter content influence persistence, herbicides half-lives typically exhibit considerable variability in the field (Mojašević et al., 1996; Sparks and Swift, 2002). Where herbicide persistence is high ( $T_{1/2} > 2$  weeks) concentrations in the second and third runoff events may actually be higher than in the first runoff event (Gan et al., 2005). Furthermore, multiple applications of a particular herbicide may result in metabolic pathways being established which can increase biological degradation rates and reduce soil persistence (Kearney et al., 1969).

#### **2.4 Strategies for reducing herbicide runoff**

Practices for reducing herbicide losses in runoff include: 1) avoid pesticide application during adverse weather conditions such as when rain or high winds are anticipated within 48 hours of application; 2) use erosion control practices such as conservation tillage, contouring, and grass buffers around waterways to reduce runoff; 3) determine appropriate herbicide type, rate, and persistence for weather and soil conditions; 4) incorporate the pesticide if possible; and 5) avoid wettable powder formulations.

### **3. Groundwater leaching**

Herbicide leaching from agricultural land has long been considered a potentially serious problem. Accordingly, criteria have been introduced to regulate standards for potable water (USEPA, 2008). As with surface runoff, there is increasing evidence that the specific environmental and agricultural field conditions prevailing during herbicide application or shortly thereafter is critical in determining the extent of herbicide leaching. Additionally,



since water is the driving force for herbicide leaching, there is an inextricable link between herbicide leaching and surface and subsurface hydrology. Unfortunately, most herbicide leaching studies have focused on concentrations in soil cores or soil solution as a function of depth and time- instead of monitoring herbicide fluxes. As a result, the lack of herbicide flux data through soil has fostered debates regarding the relevance of various flow processes on herbicide transport to groundwater. Although monitoring herbicide fluxes to groundwater is still in its infancy, tile-drain studies indicate that herbicide leaching is typically less than 2 % of that applied and so are less than runoff losses (Kladivko et al., 1991, Gaynor et al., 2002).

Monitoring herbicide transport through soil to groundwater is complex and early attempts that focused on analyzing herbicides in soil cores as a function of depth had limited success. For example, Wyman et al. (1985 and 1986) evaluated aldicarb transport through soil by collecting 48 soil cores, each 3.6 m long, four times during a growing season. They observed no aldicarb below 2.4 m over a three year period and so concluded that aldicarb had 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 ppb to 76 ppb even though the same chemical application rate, irrigation scheme, and soil were used. Instead of analyzing soil cores Kladivko et al. (1991) and Gentry et al. (2002) monitored tile drains, which allowed herbicide fluxes to be calculated. Unfortunately, interpreting field-scale solute travel times from a tile drain involves considerable uncertainty since solutes applied immediately above a tile drain have a much shorter distance to travel (to exit the field) than solutes applied between the tile drains (Jury et al., 1975a, 1975b).

The two major processes governing herbicide transport through soil to groundwater are matrix and preferential flow. In matrix flow, the movement of the herbicide is governed by adsorption to soil particles, hydrodynamic dispersion, and convection processes (Jury et al., 1984; Helling and Gish, 1986). Hydrodynamic dispersion accounts for both molecular diffusion and a spreading out of the herbicide as the moving soil solution interacts with soil pores of various sizes. Convection is the bulk transport of the herbicide with the moving soil solution. Typically, matrix flow processes are well described by the classical convective-dispersion equation, which is the back bone of many transport models (Pachepsky et al., 2006). On the other hand, preferential flow is poorly described by the classical convective-dispersion equations, since it assumes that a small fraction of the total soil pore space is responsible for rapidly conducting solutes and herbicides to groundwater (German and Beven, 1981; Gish and Jury, 1983; Isensee et al., 1990; Jarvis, 2002; Gish et al., 2004). Preferential flow typically occurs through structureless soils by means of flow instabilities (Glass et al., 1989; Ghodrati and Jury, 1992); flow through spatial voids resulting from decayed roots, shrinking clay minerals, sink holes, or created by soil fauna (Gish et al., 1983; Libra et al., 1984; Gish et al., 1998; Shipitalo et al., 1990; Ritsema and Dekker, 1995; 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 no way of knowing where these flow pathways are or when samples should be collected, so a mass flux is typically calculated, not monitored. Without a mass flux procedure, it is nearly impossible to quantify the *relevance* of preferential flow at the field scale for various management, soil and climatic scenarios. However, due to the rapid transport of herbicides to groundwater, it appears that preferential and not matrix flow is likely the dominate flow

mechanism governing herbicides leaching (Kladivko et al., 1991; Flury, 1996; Harris and Catt, 1999; Novak et al., 2001; Koplín et al., 1998; Jarvis, 2002; Vereecken, 2005).

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

### 3.1 Rainfall impacts

Herbicide leaching is a function of local meteorology, management practice, herbicide formulation, soil type, soil hydraulic properties, and several environmental factors (Jury, 1986; Helling and Gish, 1986). Like surface runoff, the timing of a rainfall event relative to application greatly influences herbicide leaching to groundwater. Specifically, herbicide transport to groundwater is especially vulnerable to preferential transport shortly after application (Gaynor et al., 2002; Weber et al., 2006). However, variability in groundwater herbicide concentrations can be considerable as spatial variability of soil properties can influence herbicide transit times. As depicted in Figure 4a, surface applied atrazine and metolachlor were rarely detected in one observation well (3 m depth) at a sandy field site located in Beltsville, Maryland over an eight year period. However, in the same field, during the same sampling times herbicide concentrations were consistently larger in another 3 m observation well where preferential flow was more dominant (depicted in Figure 4 B). If rainfall occurs within a few days of application, herbicide well concentrations will typically display peaked concentrations shortly after application then decrease with time, until fall/winter recharge. When little or no rainfall occurred after application, herbicide groundwater concentrations were low throughout the year. Additionally, the low herbicide concentrations after a few months supports the hypothesis that once solutes or herbicides reside in the smaller pores of the soil matrix it will move predominantly by matrix rather than preferential flow (Kung et al., 2000b; Delphin and Chapot, 2006). Consequently, the first rainfall event after application has the highest risk of herbicide leaching to groundwater, but to account for low concentrations and fall/winter recharge new modeling approaches must include interaction between matrix and preferential flow processes.

### 3.2 Management impacts

With regard to agricultural management, there is some ambiguity regarding their benefits. For example, 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 herbicides after application had no impact on herbicide transport to tile-drains. In addition, conservation tillage practices may temporarily enhance preferential herbicide transport through void root channels and bio-pores. However, in time these same root channels and bio-pores will have clay and/or organic coatings where herbicides can readily adsorbed and subsequently broken down by microbial degradation. After only a few years Gish et al. (1998) observed

higher herbicide metabolites under no-till relative to conventional tillage. This suggests that if the herbicide metabolites are less harmful than the parent compound, conservation tillage may be beneficial to groundwater quality.

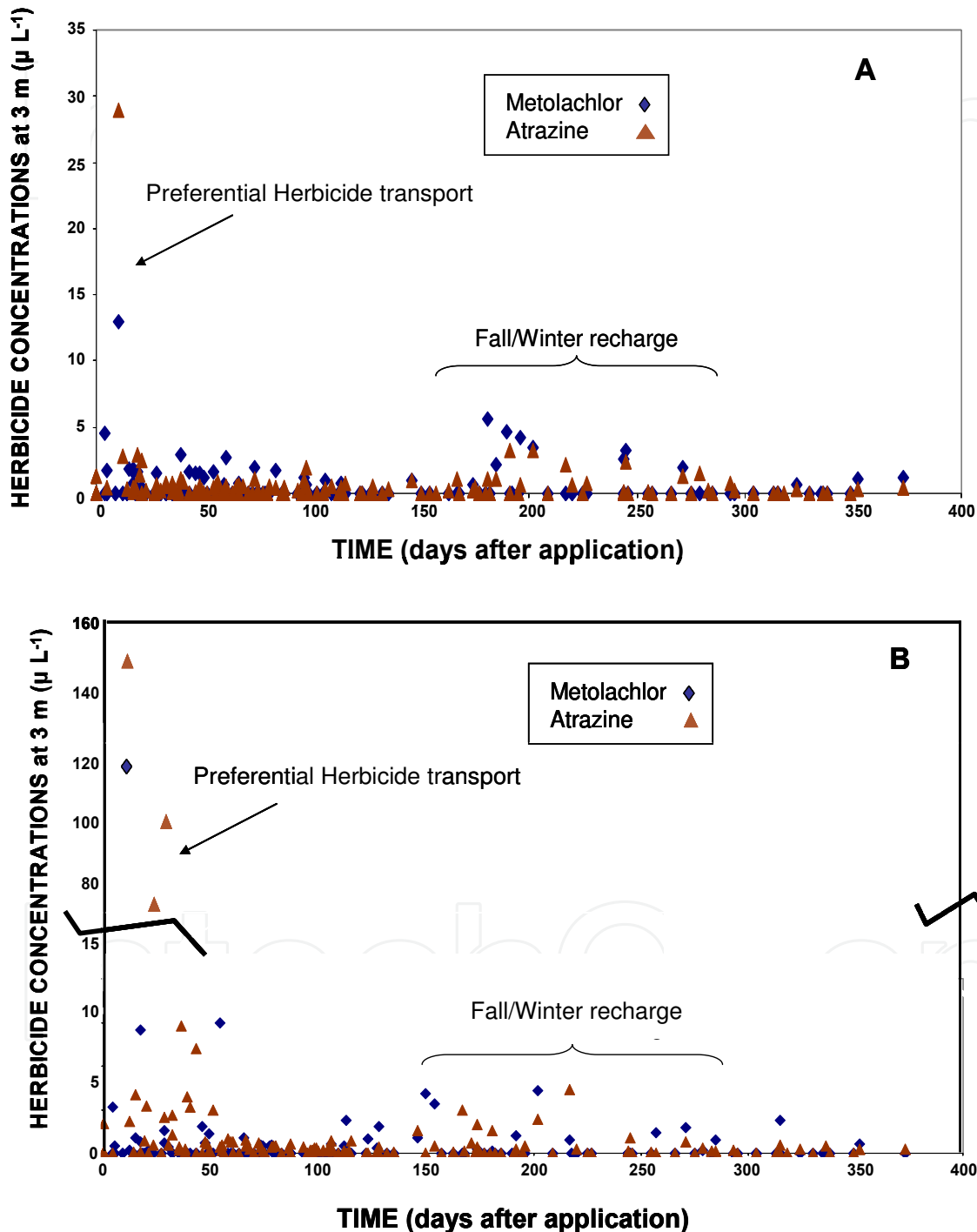


Fig. 4. Variability of atrazine and metolachlor well concentrations over eight years at a depth of 3 m. Figure 4A is representative of well locations where preferential has minimal impact, while Figure 4B denotes areas where preferential flow is more dominant. Notice scale change in Figure B

Controlled release formulations may reduce preferential transport of herbicides. 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). Surprisingly, Brown et al., (1995) reported unexpectedly high leaching losses with encapsulation. Later, field evaluations 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). Naturally, herbicide chemistry must be considered when optimizing an encapsulation matrix in order to be effective in controlling the targeted pest, as well as reducing environmental risks (Wienhold and Gish, 1994b).

### 3.3 Management strategies to reduce herbicide leaching

Herbicide transport through soil is primarily a function of preferential flow, so for herbicides with a low solubility encapsulation will reduce leaching by increasing diffusion into the smaller pores of the soil matrix. Reducing herbicide leaching through encapsulation may be countered by an enhanced runoff potential since encapsulation also increases soil persistence. Soil incorporation may also reduce leachability for some herbicides that are insoluble and have low soil persistence. Farm managers should avoid applying herbicide if rainfall is anticipated within 48 hours of application and should avoid using herbicides with a long half-life as this could increase susceptibility to groundwater leaching.

## 4. Herbicide volatilization

Volatilization is perhaps the principal loss pathway by which herbicides are transported off-site. Although herbicide volatilization can exceed 90% of that applied, typical losses for many herbicides range from 5 to 25% of that applied (Taylor and Spencer, 1990; Prueger et al., 1999; Glotfelty et al., 1989; Rice et al., 2002; Prueger, et al., 2005). The impact of herbicide volatilization generally decreases with time after application, but unlike surface runoff and groundwater leaching, volatilization occurs regardless of soil type, landscape features, or local meteorology – although these factors influence *how much* herbicide is volatilized. In an eight year field investigation in Beltsville, Maryland, volatilization losses of atrazine and metolachlor always exceeded runoff losses (details of the site set-up and for this multi-year investigation depicted in Figure 5 are given in Gish et al., 2011). Furthermore, once in the atmosphere, herbicides can be degraded or deposited in non-targeted areas via wet or dry deposition (Bidleman and Christensen, 1979; Bidleman, 1988; Burrows et al., 2002). Frequently, a portion of the applied herbicide volatilized into the atmosphere is 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).

As depicted in Figure 6, herbicide volatilization occurs in two steps, evaporation of the herbicide from soil and/or plant residues followed by dispersion into the atmosphere by diffusion and turbulent mixing (Taylor, 1995; Prueger et al., 2005). Several methods have been developed to obtain estimates of herbicide volatilization at the field-scale. Parmele et al. (1972) developed an aerodynamic method based on gradients of wind speed, temperature and herbicide concentrations collected over a uniform area. Demmead et al. (1977) developed an integrated horizontal flux approach which uses herbicide concentration and horizontal wind speeds profiles. For certain conditions a theoretical profile shape method (Wilson et al., 1982) may be useful which measures wind speed and herbicide

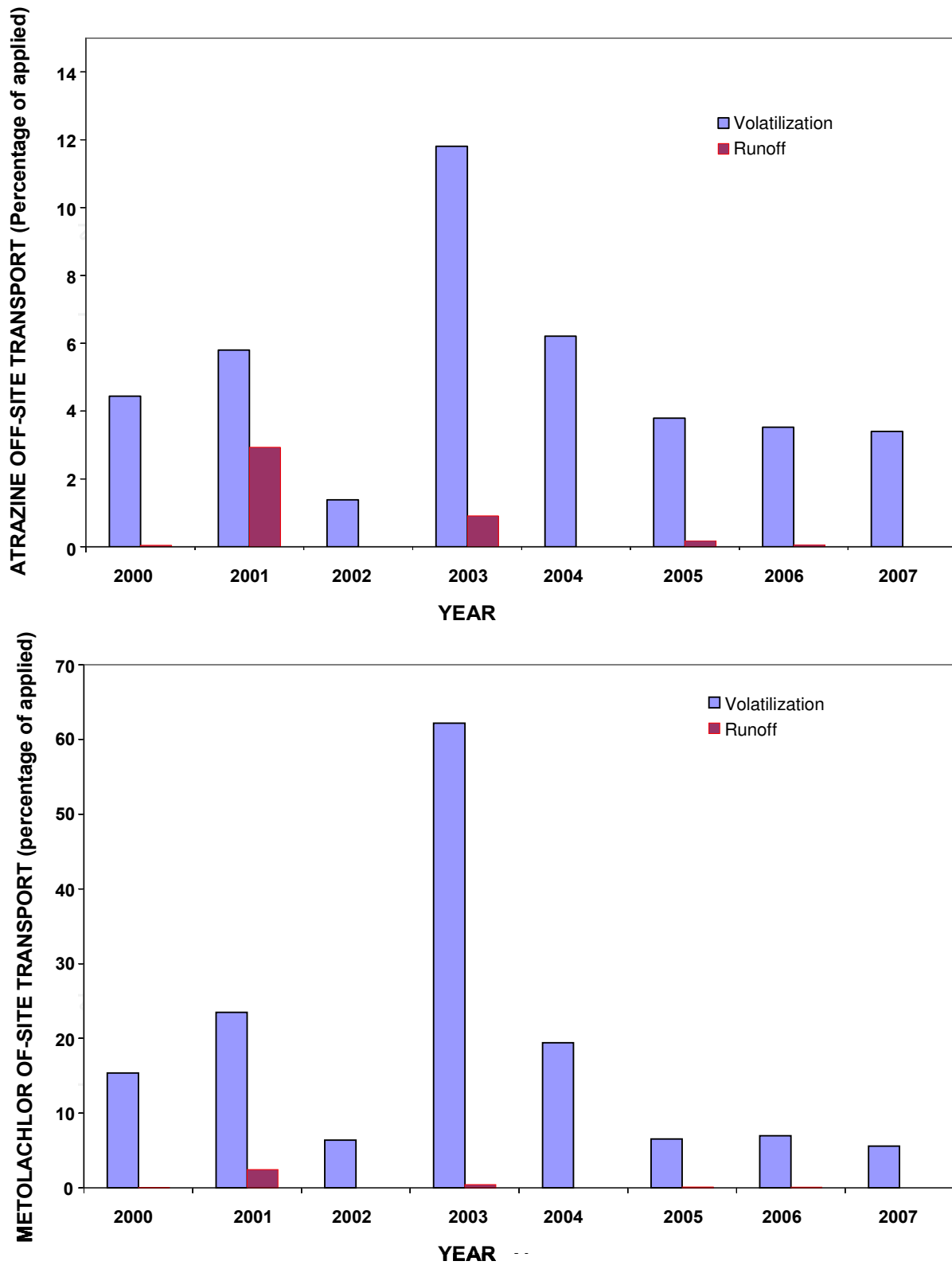


Fig. 5. Comparison of annual volatilization and runoff losses of atrazine and metolachlor on the same site over eight years. Runoff was monitored from early May (before planting) through November (well after harvest) while volatilization losses were monitored for only the first 5 days after application



concentrations at a single height above the soil to calculate herbicide vapor losses. Recently, eddy covariance measurements of wind, temperature, and water vapor have been linked to and herbicide concentration profiles above the soil surface to quantify herbicide volatilization fluxes where turbulent flow conditions in the field may exist (Prueger et al., 2005, Gish et al., 2009).

Since herbicides are generally applied around crop planting, mass applications of herbicide within a given agricultural region may contribute to a large nonpoint pulses of herbicide entering the atmosphere. A regional signaling of herbicide volatilization, along with wet and dry deposition has been observed by Kuang et al. (2003) in the Chesapeake Bay, by Goolsby et al. (1997) and Majewski et al. (1998) in the Midwestern United States, and by Nations and Halberg (1992) and Hatfield et al. (1996) in Iowa. Factors influencing herbicide volatilization include vapor pressure of the herbicide, meteorological conditions, soil properties, and agricultural management practices.

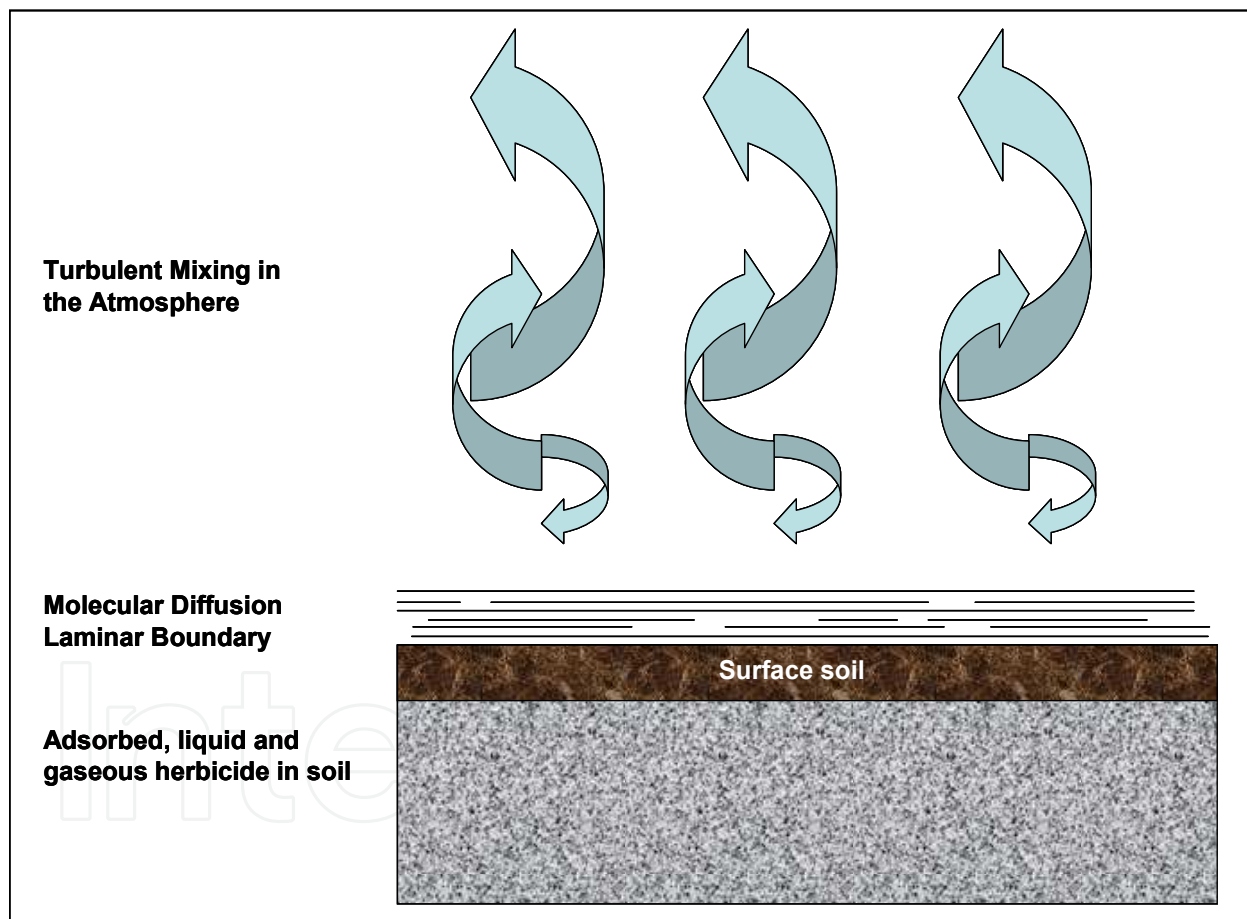


Fig. 6. Schematic of herbicide volatilization processes

#### 4.1 Vapor pressure

Perhaps the most crucial *herbicide property* influencing volatilization is its vapor pressure. As the vapor pressure increases, the herbicide increasingly favors the vapor phase and is more readily volatilized. In the field an “effective” herbicide vapor pressure is likely to be lower than the vapor pressure of the “pure” chemical due to interactions with the soil. For

example, early studies detected a significant positive correlation between the pesticide vapor pressure and insecticide 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 herbicide and lowered herbicide volatilization (Spencer and Cliath, 1974; Taylor and Spencer, 1990). By contrast, plant surfaces have a lower affinity for herbicides and as such exhibit vapor pressures that are closer to that of the “pure” herbicide (Taylor & Spencer, 1990). For most herbicides, 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 herbicide volatilization by increasing adsorption, thus reducing the liquid phase concentration and vapor pressure in the soil.

#### 4.2 Soil moisture and meteorological impacts

At the field-scale, the surface soil water content is perhaps the most critical *soil property* influencing herbicide volatilization. As the herbicide will be distributed among adsorbed, liquid, and vapor phases the amount of airspace 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 herbicide 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 herbicide vapor losses increased more with soil water content than organic matter content or soil temperature. Furthermore, in a 5-year field investigation, Prueger et al. (2005) demonstrated that at high soil water contents, as much as 25% of surface applied herbicide metolachlor could be lost through volatilization, compared to as little as 5% when soils were dry. In a three year field investigation, Gish et al. (2009) compared metolachlor volatilization from two locations where soil texture, climatic inputs, formulation, and management practices were identical, but where soil moisture and surface organic matter content differed. They observed that when the “wet” location had surface soil water contents nearly twice that of the “dry” location that metolachlor volatilization losses were also doubled relative to the “dry” location. These results were surprising since the “wet” location had significantly higher organic matter content than the “dry location”. Furthermore, when there was no significant difference in surface soil water contents between the two locations, both locations generated nearly identical metolachlor volatilization losses. As a result, it appears that surface soil moisture is more important than organic matter content (Gish et al., 2009). Several additional studies have shown the importance of soil moisture as peaks in early morning herbicide volatilization losses have been attributed to dew formation on the soil surface (Glotfelty et al., 1989; Taylor, 1995; Prueger et al., 2005). Lastly, increases in herbicide volatilization following a rain event are common and these spikes can be relatively large if the soil was dry prior to the rainfall event (Prueger et al., 2005). Although herbicide volatilization is influenced by soil bulk density, pH, soil mineralogy, and soil organic matter content, the dominant soil property appears to be soil moisture.

The impacts of meteorological conditions on herbicide volatilization were initially 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 herbicide volatilization if the fields are dry (Glotfelty et al., 1984; Taylor, 1995; Prueger et al.,

2005). Soil temperature was thought to increase herbicide volatilization by increasing diffusion rates and vapor pressure. However, increased soil temperatures can lead to drying of the soil surface, resulting in increased adsorption and a decrease in herbicide volatilization. Increased solar radiation can increase air and soil temperatures which influence herbicide volatilization, but the impact is dependent on the surface soil water content. Gish et al., (2009) demonstrated that when the surface soil was moist, increases in temperature led to sharp increases in metolachlor volatilization. However, when soils were dry increases in soil temperature had no discernible impact on metolachlor volatilization. Rainfall increases soil water contents, which in turn may increase pesticide volatilization, but depending upon rainfall intensity and duration it may actually move the herbicide deeper into the soil profile where it is less likely to volatilize. Increasing wind velocity could increase herbicide volatilization if soils are wet, but if the soil dries out the soil surface volatilization could decrease.

#### 4.3 Management impacts

Agricultural management influences herbicide volatilization on several levels. First, soil incorporation of the herbicide decreases herbicide volatilization. Prueger et al. (1999) demonstrated that incorporating metolachlor in a band relative to a surface broadcast spray reduced herbicide 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, 1970). Thus, by incorporating the herbicide gas diffusion may be limited, and volatility reduced. Second, increasing amounts of plant residue on the surface can increase herbicide volatilization since plants generally have a much lower affinity for pesticides than soil (Taylor & Spencer, 1990). Third, herbicide formulations such as control release or micro-encapsulated formulations can reduce volatility (Jackson and Lewis, 1978; Wienhold and Gish, 1994a; Gish et al., 1995). The effectiveness of the formulations is strongly dependent upon herbicide chemistry and the matrix encapsulating the herbicide. As herbicide solubility increases, the impact of formulation on reducing volatilization decreases (Wienhold and Gish, 1994b).

#### 4.4 Reducing herbicide volatilization

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

### 5. Summary

Among the major loss pathways, herbicide runoff has been the most rigorously studied. In general, herbicide annual runoff losses are less than 1% of that applied, with the largest

portion of this loss occurring near the time of application; however as much as 5% annually is common for worst case runoff scenarios' (Haith and Rossi, 2003; Shipitalo and Owens, 2006). Enhanced herbicide runoff relative to leaching from tile-drained fields supports the hypothesis that herbicide runoff is more detrimental to the environment than herbicide leaching (Lafleur et al., 1975; Muir and Baker, 1976; Ng et al., 1995). Unfortunately, field-scale herbicide leaching losses in non-tile-drained fields is difficult to quantify due to soil heterogeneity. Estimates of herbicide leaching are generally <1% of that applied and in a worst case scenario herbicide leaching losses are probably << 5% of that applied. The third loss pathway, volatilization, is a major environmental concern with herbicide losses commonly exceeding 15 % of that applied (Taylor and Spencer, 1990, Prueger et al. 1999; Prueger et al., 2005; Gish et al., 2009; Gish et al., 2011). Herbicide vapor pressure, soil moisture and meteorological interactions dominate herbicide volatility. Determining the impact of field scale off-site transport where all three major loss pathways are being monitored is rare and requires additional research on this critical topic.

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## **Soil Health and Land Use Management**

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Soils play multiple roles in the quality of life throughout the world, not only as the resource for food production, but also as the support for our structures, the environment, the medium for waste disposal, water, and the storage of nutrients. A healthy soil can sustain biological productivity, maintain environmental quality, and promote plant and animal health. Understanding the impact of land management practices on soil properties and processes can provide useful indicators of economic and environmental sustainability. The sixteen chapters of this book orchestrate a multidisciplinary composition of current trends in soil health. Soil Health and Land Use Management provides a broad vision of the fundamental importance of soil health. In addition, the development of feasible management and remediation strategies to preserve and ameliorate the fitness of soils are discussed in this book. Strategies to improve land management and relevant case studies are covered, as well as the importance of characterizing soil properties to develop management and remediation strategies. Moreover, the current management of several environmental scenarios of high concern is presented, while the final chapters propose new methodologies for soil pollution assessment.

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