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1995

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Timothy Gish
USDA-ARS

Ali Sadeghi
USDA-ARS

Brian J. Wienhold
University of Nebraska-Lincoln, Brian.Wienhold@ars.usda.gov

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Volatilization of Alachlor and Atrazine as Influenced by Surface Litter

Timothy J. Gish*, Ali Sadeghi**, and Brian J. Wienhold***

- * Soil Physicist, Hydrology Laboratory, Natural Resources Institute, U. S. Department of Agriculture, Agricultural Research Service, Beltsville, Maryland 20705, USA.
- ** Soil Scientist, Environmental Chemistry Laboratory, Natural Resources Institute, U. S. Department of Agriculture, Agricultural Research Service, Beltsville, Maryland 20705, USA.
- *** Soil Scientist, Northern Great Plains Research Laboratory, U. S. Department of Agriculture, Agricultural Research Service, Mandan, North Dakota 58554, USA

(Received in Germany 4 April 1995; accepted 1 June 1995)

ABSTRACT

A basic knowledge of how herbicide volatilization is influenced by agronomic practices is necessary if long-term detrimental impacts from herbicides are to be minimized. We measured cumulative herbicide volatilization losses in glass agroecosystem chambers to assess how surface residue conditions, simulated rainfall, temperature, and herbicide formulation affect volatilization of atrazine and alachlor. Research results demonstrated that herbicide volatilization before water application was greater under mulched conditions, but decreased dramatically after the first irrigation. As a result, after 35 d cumulative volatilization of atrazine from a mulched soil surface was less than half that from bare soil for both formulations. Plant litter on the soil surface and encapsulated herbicides may be viable alternatives for reducing volatilization of some herbicides in humid regions.

INTRODUCTION

Once volatilized, herbicide deposition may occur through rainfall events, fallout of particular matter to which the herbicide has become adsorbed, or by direct exchange between the atmosphere and the soil surface. To conserve natural resources, herbicide volatilization as affected by agricultural practices needs to be evaluated so as to prevent the development of management strategies which simply shift the herbicide from one part of the hydrologic cycle to another. Although no-tillage practices typically conserve water and soil, higher inputs of pesticides are frequently necessary to maintain yields (Christensen and Norris, 1983). Additionally, tillage practices affect pesticide behavior by altering soil temperature, soil water content, biological activity, and evaporation (Belvins *et al.*, 1983; Tyler *et al.*, 1983; Thomas and Frye, 1984; and Stearman *et al.*, 1989).

Conservation tillage practices typically favor the build up of an organic mulch on the soil surface. Consequently, a large portion of the surface-applied pesticide may be intercepted by plant residues (Ghadiri *et al.*, 1984). The organic mulch could have a larger surface area and greater surface roughness perhaps resulting in higher volatilization losses (Glotfelty and Schomburg, 1989). On the other hand, Wienhold and Gish (1994a) observed a 50% reduction in cumulative volatilization losses of alachlor and atrazine under no-tillage relative to tilled fields. A possible explanation for the reduction in herbicide volatility under no-tillage may be due to herbicide washoff from rainfall events that took place 3 d after application. In support of this hypothesis, Martin *et al.*, (1978) observed that the first 0.5 cm of water was effective in washing atrazine from plant litter.

Formulation can also alter herbicide volatilization behavior. Microencapsulation of chloroproham [isopropyl m-chlorocarbanilate] in nylon capsules reduced volatilization losses five fold when compared to chloroproham applied as an emulsifiable concentrate (Turner *et al.*, 1978). However, synthetic polymers may not be economical or biologically degradable, and thus not applicable to annual field use. Schreiber *et al.*, (1987) suggested that herbicide encapsulation in a starch matrix would reduce volatilization and eliminate the long-term buildup of synthetic polymers in the field. Wienhold and Gish (1994a) found a reduction in herbicide volatilization with starch-encapsulation, but the large granules used in their experiment gave questionable weed control in some areas of the mid-west U.S.. Recently, a smaller starch encapsulated granule was developed which gave favorable weed control (Schreiber *et al.*, 1994). Herbicide rates of release, for a given herbicide, increase with decreasing granule size (Wienhold and Gish, 1994b). More rapid release reduces the time over which environmental fate may be modified.

The purpose of this study was to measure the volatilization of atrazine and alachlor applied as either a commercial formulation or as the smaller starch encapsulated granules when influenced by temperature, plant residue and precipitation.

MATERIALS AND METHODS

The experiment was conducted using five glass agroecosystem chambers (1.5 m long, 0.5 m wide and 1.0 m tall) as model systems (Nash *et al.*, 1977). The Monmouth sandy loam (Typic Hapludult) used in this experiment has a pH of 6.4, organic matter content of 1.1%, and a clay content of 5.6%. Soil was placed in the bottom of each chamber to a depth of 17 cm and maintained at the assigned temperature by passing water from a constant temperature bath through a jacket surrounding the soil and through copper tubes buried within the soil. Temperatures used were 25 and 35°C. The chambers were irrigated with a total of 10 cm of water, spray applied in 10, 1-cm increments during the 30 d study, in an attempt to simulate early spring rainfall common to the humid eastern U.S. The soil water potential in the top 5-cm was monitored daily in each chamber with soil tensiometers. Average surface water potentials were determined by averaging

daily tensiometer readings for the four different chambers subjected to the same environmental constraints (same temperature and plant residue condition).

Atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)-acetamide] was applied as either a commercial formulation (Bullet, Monsanto Co., St Louis, MO¹) or in a starch encapsulated formulation. Starch granules 0.425 to 0.85 mm in diameter used. Starch encapsulated atrazine contained 11.3% a.i. and alachlor 10.4% a.i. Both formulations were applied at the same rate: 1.7 kg ha⁻¹ for atrazine and 2.8 kg ha⁻¹ for alachlor. Starch encapsulated formulations were broadcast onto the soil surface while the commercial formulation was diluted in 100 mL of water and surface applied with a pump sprayer. An additional 100 mL of water, used to rinse out the sprayer, was also applied to the soil surface.

Volatilization of atrazine and alachlor for each treatment was measured in duplicate chambers. Since only five agroecosystem chambers were available, the experiment was divided into four 5 wk runs. The experimental treatments involved 2 temperatures (25 and 35°C), 2 formulations (commercial and starch encapsulated), 2 surface conditions (mulched and bare), and 2 replicates. One chamber was used as a control during each run to determine if air drawn into the chambers contained any atrazine or alachlor and to insure that the soil used did not contain any residual herbicide.

Plant litter amount for the mulched soil surface treatments was determined from field observations on an established no-tillage field being used as a herbicide control. Ten field samples, each 0.75 m², were randomly chosen and measured for plant litter. The average plant litter mass observed and subsequently used in the chambers was 521 gm. Plant residue consisted mainly of corn stubble and dried rye.

Air was continuously drawn through each chamber at a speed of 0.35 km h⁻¹ (2.9 m³ min⁻¹) using high pressure direct drive suction fan attached to a manifold at the exit of each chamber. Air entered the chamber through 12 evenly spaced holes (0.05-m diam) present in the front (0.5 by 1.0 m) wall of the chamber and exited through 12 evenly spaced holes in the back wall of the chamber. Each air entry hole was covered with glass fiber cloth to prevent the entrance of insects and dust. Each air exit hole contained a polyurethane foam plug (5-cm) that trapped any herbicide present in the vapor phase (Turner and Glotfelty, 1977).

Polyurethane plugs were replaced 2, 6 h, 1, 2, and 3 d, and 1, 2, 3, 4, and 5 wk after application. Plugs were Soxhlet extracted with 150 mL ethyl acetate for 3 h. The extract was rot-evaporated to dryness and redissolved in 10 mL of ethyl acetate containing trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl) benzenamine] as an internal standard. Atrazine and

¹Trade names or company names are included for the benefit of the reader and imply no endorsement or preferential treatment of the product listed by USDA.

alachlor concentrations were determined using a gas chromatograph equipped with a nitrogen-phosphorus detector. Operating conditions for the gas chromatograph were: 30 m x 0.32 mm id glass capillary column coated with 0.26 μm SPB-5 (Supelco Inc., Bellefonte, PA); injector temperature, 200° C; oven temperature 150° C; detector temperature, 220° C; and a He carrier gas flow rate of 2.5 mL min⁻¹.

RESULTS AND DISCUSSION

Temperature and soil water availability have a strong influence on herbicide rate of release from the starch granules. Herbicide rates of release increase with water availability and temperature (Wienhold and Gish, 1992). Average surface water potentials in the

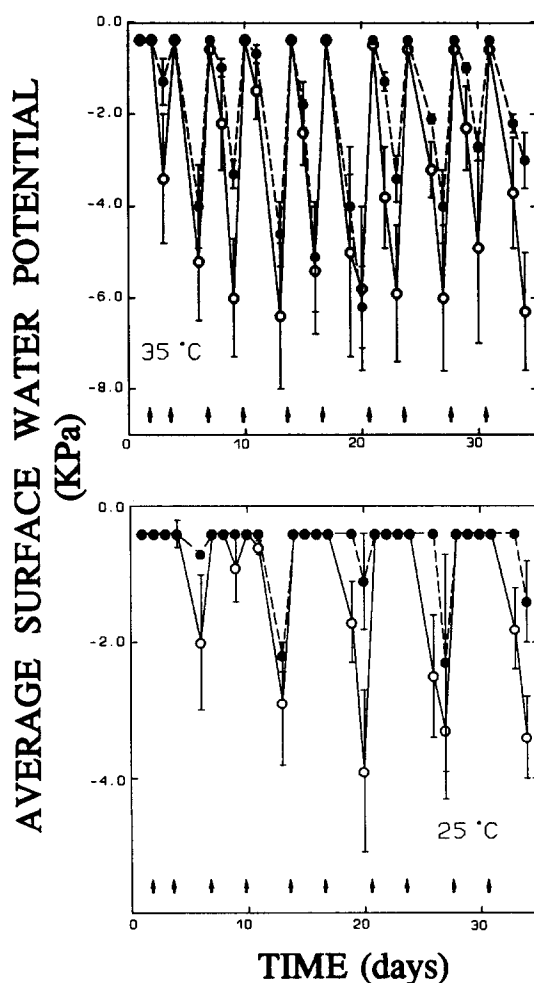


Fig. 1. Average surface soil water potential for bare (○) and mulched (●) soil surfaces as influenced by soil temperature and irrigation. Error bars indicate \pm standard error of the mean.

ecosystem chambers were less at 35 than at 25°C (Fig. 1). At 35°C, the surface soil dried out to at least -5.0 KPa twice a week, whereas at 25°C, the surface soil was moist and rarely dried out to -3.0 KPa. For both temperatures the mulched surface soil had a higher soil water potential. Additionally, standard error of the mean values for the surface water potential were less under mulched surface conditions than in bare soil.

Surface water potentials for the 25°C chambers suggest that for this water input frequency, starch granules will readily imbibe water, swell, and herbicide release will be rapid (Wienhold and Gish, 1992). At 35°C, herbicide rates of release and subsequent volatilization is more dynamic. For example, increases in temperature on a continuously moist soil lead to increased rates of

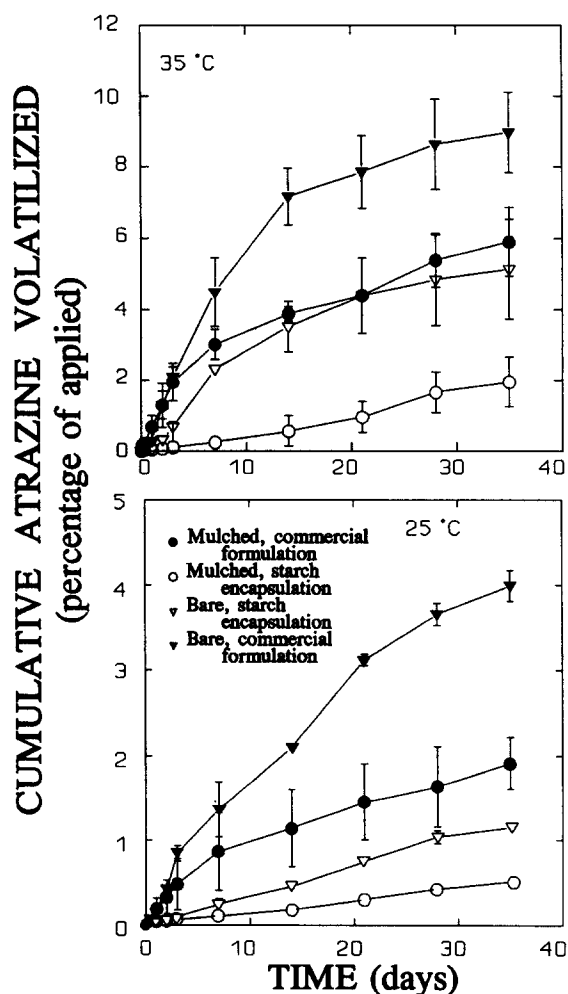


Fig. 2. Cumulative atrazine volatilization from soil as influenced by temperature, soil surface condition, and formulation. Error bars denote the range of values observed. Note differences in y-axis scale among graphs.

release and enhanced volatilization (Wienhold *et al.*, 1993). However, as the soil becomes drier, rates of release decline (Wienhold and Gish, 1992). At 35°C, evaporation rates were sufficiently high to dry the soil surface. The cyclic pattern to the surface water potential, at 35°C, indicates periods of alternating fast and slow herbicide release from the starch granules, a condition common to most field conditions.

Cumulative volatilization of atrazine increased with temperature for all surface and formulation treatments (Fig. 2). Volatilization of the commercially formulated atrazine at 35°C was twice that at 25°C for both surface conditions. For each formulation, atrazine volatilization was greatest under mulched conditions before irrigation, but dropped below the atrazine volatilization losses from a bare soil after the first irrigation (1 cm water). After 35 d, cumulative volatilization of commercially formulated atrazine under bare soil conditions ranged from about 4% of that applied at 25°C, to about 9% at 35°C. After 35 d, cumulative volatilization of commercially formulated atrazine from a mulched soil ranged from about 2% at 25°C, to about 6% at 35°C. Glotfelty *et al.*, (1989) measured atrazine volatilization losses from a fallow field and found 2.4% of the applied chemical was lost after 24 d. Wienhold and Gish (1994a) measured commercial formulated atrazine volatilization losses of 9% of that applied to a tilled soil and 4% under no-tillage. If one considers nightly cooling and drying, differences in soil properties, and precipitation these results appear reasonable for commercial formulated atrazine (Taylor and Spencer, 1990).

Atrazine is a relatively persistent herbicide (Table 1). Consequently, atrazine volatilization may also occur over long durations. Cumulative atrazine volatilization losses in this experiment do not appear to have reached asymptotic values after 35 d. Although atrazine volatilization rates are decreasing, the cumulative atrazine losses at 25 and 35°C indicate a potential source for

Table 1. Chemical properties for atrazine and alachlor at 25°C.

Chemical		
property	Atrazine	Alachlor
Solubility in		
water (mg L ⁻¹)	32	240
Henry's Law		
constant, K _H	2.5 X 10 ⁻⁷	1.3 X 10 ⁻⁶
Dissipation		
half-lives	71	42

environmental contamination. In support of these findings, Glotfelty *et al.*, (1990) observed atrazine deposition in rain near the Wye River in Maryland over a 4 to 5 month period.

Volatilization of starch encapsulated atrazine was less than the commercial formulation for both the bare and mulched soil surfaces (Figs. 2). Cumulative volatilization of starch encapsulated atrazine was nearly 3 times greater at 35°C than at 25°C for both bare and mulched soil surfaces. After 35 d, cumulative volatilization of starch encapsulated atrazine under bare soil conditions ranged from about 1% at 25°C, to about 5% at 35°C. On a mulched soil surface the 35 d, cumulative volatilization losses of atrazine was reduced to <1% of that applied at 25°C, to about 2% at 35°C. Atrazine volatilization losses from the smaller starch granules used in this study were nearly twice that reported by Wienhold and Gish (1994a). The lower volatilization losses reported earlier are the result of larger starch granules, and the subsequent slower rate of release (Wienhold and Gish, 1994b). At a water potential of 0 MPa, it takes about 30 d to achieve a 97% release of atrazine from the larger starch granules while for the smaller granules it takes only 16 d (Wienhold and Gish, 1994b). Nonetheless, volatilization of starch encapsulated atrazine was consistently lower than the commercial formulation regardless of soil moisture status and surface condition.

Cumulative volatilization losses for commercial alachlor were substantial (Fig. 3.). After 35 days, cumulative alachlor losses on a bare soil ranged from about 6% at 25°C, to about 13% at 35°C. There was no significant difference in volatilization of commercially formulated alachlor between bare and mulched soil surfaces at either 25 or 35°C. Volatilization losses of commercial alachlor were slightly less in this experiment than under the field conditions observed by Wienhold and Gish (1994a) who measured alachlor volatilization losses of about 8% under no-tillage (mulched surface) and about 13% for a tilled field. Although the same application rates of alachlor were used in both the field and this ecosystem study the water input patterns were different. In the field experiment, most of the precipitation came 6 d of application during three rain events (Wienhold and Gish, 1994a). In the greenhouse, 1-cm irrigations were spaced uniformly throughout the 5 wk period. The frequent smaller water inputs may be more effective in leaching alachlor into the soil subsurface where it would be less susceptible to volatilization (Philip, 1984).

Cumulative volatilization of starch encapsulated alachlor from the mulched soil surface was lower than all of the formulation and surface treatments. After 35 d, about 2% of the applied alachlor had volatilized at 25°C whereas about 8% had volatilized at 35°C. These alachlor losses are slightly less than those observed in the field where larger granules were used (Wienhold and Gish, 1994a). Again, it may be that the high solubility of alachlor and the frequent small irrigations favor alachlor transport into the subsoil where it is less susceptible to volatilization.

The greatest herbicide volatilization losses occurred with starch encapsulated alachlor from a bare soil surface. After 35 d, about 8% of the applied starch encapsulated alachlor had

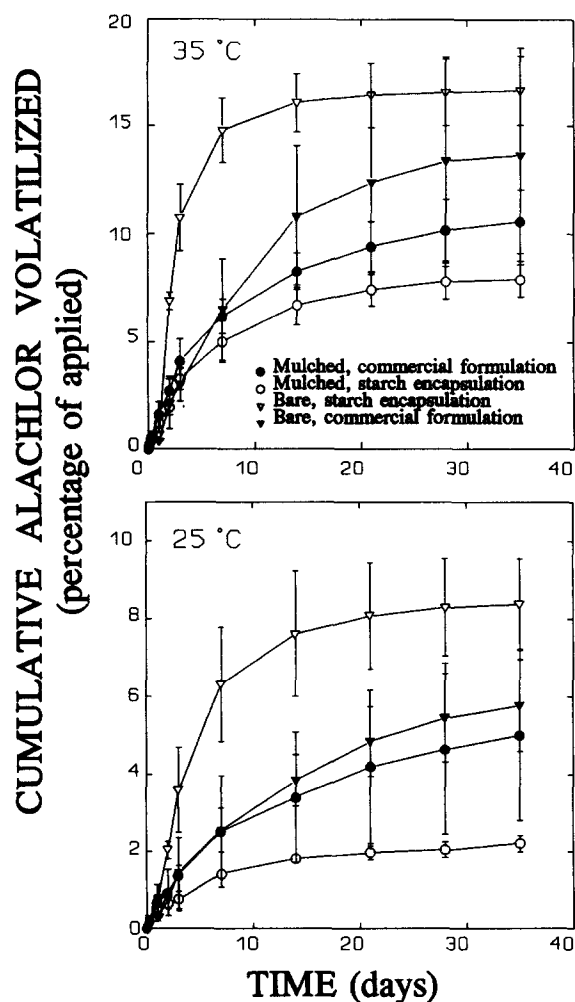


Fig. 3. Cumulative alachlor from soil as influenced by temperature, soil surface condition, and formulation. Error bars denote range in values observed. Note differences in y-axis scale among graphs.

volatilized at 25°C while about 17% had volatilized at 35°C. High volatilization losses of starch encapsulated alachlor from bare, moist soils have been observed before (Wienhold *et al.*, 1993; Wienhold and Gish, 1994a). The higher volatilization losses of alachlor relative to atrazine from bare soils have been attributed to granule effects (localized high concentrations, low affinity of the granule for alachlor) and pesticide characteristics (solubility and K_d) (Table 1).

Alachlor volatilization losses appear to reach asymptotic values by 35 d. Although alachlor is more volatile it is also less persistent (Table 1). As a result, alachlor volatilization rates will be

greater during the first two weeks after application, but will also reach asymptotic levels before atrazine. Glotfelty *et al.*, (1990) found that while atrazine in rain water lasted over many months, alachlor was present in the atmosphere for only short periods of time. Alachlor levels in rain water dropped to undetectable levels within 1 to 2 wks after application.

Volatilization of atrazine and alachlor were strongly influenced by the presence of surface litter and herbicide formulation. In this experiment, a 1-cm irrigation appears to wash herbicides off plant residue. Once below the surface litter, the herbicides had to diffuse through a stagnant air region below the surface litter. Reduced air movement at the soil-atmosphere interface reduced volatilization though soil moisture conditions favored volatilization under mulched conditions when compared to bare soil (Fig. 2 and 3). However, it also appears that the mulched surface has less of an impact on volatilization of commercially formulated alachlor than atrazine. The relatively larger K_H value for alachlor reduces the impact of the stagnant boundary layer which formed under mulched conditions. Spencer *et al.*, (1988) also found that volatilization of organics with low K_H values are controlled by the air-boundary layer above the soil surface, while those with higher K_H values are less influenced by a stagnant air layer. In addition, starch encapsulation also appears to reduce herbicide volatilization when used in combination with a mulched soil surface. The decrease in starch encapsulated alachlor volatilization with the mulched conditions may be related to the micro-environment of the pesticide after application. From field tests, >60% of the recovered spray-applied alachlor was associated with the surface plant litter, while <5% of the starch-encapsulated alachlor was associated with the surface litter.

In comparison to larger starch granules, the smaller granule size appears to increase atrazine volatilization, but had little impact on alachlor volatilization. It may be that the reduction in granule size was negligible when compared to the fast release rates associated with alachlor's solubility. To ascertain whether or not the smaller granule size is shifting the herbicide to other parts of the hydrologic cycle, both field runoff and leaching studies should be conducted.

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