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Mechanized and Natural Soil-to-Air Transfer of Trifluralin and Prometryn from a Cotton Field in Las Cruces, New Mexico

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Supporting Information

ABSTRACT: Two pre-emergence herbicides (trifluralin and prometryn) were applied on a cotton field in Las Cruces, New Mexico, and their atmospheric particle and gas-phase concentrations were measured during mechanized soil preparation and natural wind erosion sampling events before and after herbicide application. Air sampling was conducted using samplers mounted at various heights from the ground and at various locations on the field. During mechanized soil management with a disk harrow, sampling occurred at two distances from the tractor ("near-source", 4 m downwind and "far-source", 20−100 m from the disking tractor). Natural background (no disking) sampling events occurred during daytime and at night. Both herbicides were quantifiable for all postapplication sampling events, including background sampling that occurred 8, 38, and 40 days after herbicide application. Average concentrations in both the gas and particle phases ranged from about 10 to 350 ng/m^3. Averaging by event type, mean total prometryn concentrations were 2 (night background) to 8 (near-source) times higher than the corresponding trifluralin concentrations. Prometryn/trifluralin ratios were higher in airborne samples than in soil, indicative of trifluralin losses during daytime sampling, possibly via atmospheric reactions. Prometryn particle phase mass fractions were generally higher than those for trifluralin for all sampling events, consistent with $K_{air/soil\text{-}oc}$ partition coefficients, and particle-phase mass fractions were higher for near-source disking and daytime background sampling compared to far-source and nighttime. Daytime natural background prometryn concentrations could be as high as those measured during disking, and background samples showed significant relationships to meteorological parameters (air temperature, relative humidity, and dewpoint). Mechanical disturbance by tilling operations reduced the ability to predict airborne herbicide concentrations on the basis of meteorological conditions. Prometryn concentrations were higher for larger particle sizes (D_p > 1.8 μm), while no clear patterns with particle size were observed for trifluralin. Trifluralin concentrations in the smallest size bin ($PM_{0.18}$) were 2−50 times higher than prometryn for the three disking events where an impactor was used, indicating the importance of measuring size-resolved herbicide distributions in future studies.

KEYWORDS: *herbicide, disk harrow, prometryn, trifluralin, gas/particle partitioning, agricultural emissions, air−soil distribution, soil preparation*

INTRODUCTION

Trifluralin and prometryn are widely used pre-emergence herbicides, applied to agricultural fields prior to field planting and cultivation. The transport of these herbicides to the atmosphere via gas-phase volatilization and resuspension of particles by wind erosion ("natural" or background events), or by mechanized operations such as disking, tillage, and other agricultural operations, is of concern for downwind effects on environmental and human health. Prometryn is moderately toxic[1] and the United States Environmental Protection Agency has classified trifluralin as a Group C possible human carcinogen.[2] When in the atmosphere, herbicides distribute between the gas and particle phases depending on their concentrations, their physical and chemical properties, and atmospheric conditions such as temperature and relative humidity.[3] Knowledge of the gas/particle partitioning of herbicides is important because this process affects long-range transport of herbicides from their application sites, the potential removal of herbicides by wet and dry deposition, and the rate of atmospheric reactions such as oxidation and photodegradation.[4] Consideration of these herbicide transport processes is often overlooked due to the lack of field measurements on atmospheric gas and particle herbicide concentrations, especially during soil management practices.

Partitioning of semivolatile organic compounds (SVOCs) to aerosol particles and removal of aerosol particles through dry deposition or rainfall have been identified as key factors determining long-range transport potential and overall SVOC persistence.[5] Herbicides and pesticides present in the particle phase typically have higher atmospheric lifetimes because gas-phase compounds are more susceptible to oxidation by

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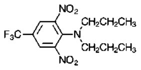
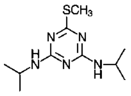
Table 1. Physical−Chemical Properties of Trifluralin and Prometryn (ref 9)

Herbicide	Chemical Structure	Molecular Weight (g/mol)	Vapor Pressure (Pa), 25° C	H (Pa.m^3/mol) 25° C	Log K_{oc}	Melting Point (° C)	Half-life in soil (day)	Half-life in air (min)	$K^{[b]}_{air/soil}$
Trifluralin $C_{13}H_{16}F_3N_3O_4$		335	1.47×10^{-2}	16.61	4.14	49	~93	25-193	4.87×10^{-7}
Prometryn $C_{10}H_{19}N_5S$		241	1.33×10^{-4}	1.39×10^{-3}	2.91	119	~60	~600[a]	6.90×10^{-10}

[a]http://www.nlm.nih.gov/pubs/factsheets/toxnetfs.html

[b] computed from H and K_{oc}

[a]http://www.nlm.nih.gov/pubs/factsheets/toxnetfs.html. [b]Computed from H and K_{oc}.

Table 2. Meteorological Parameters during Sampling Events[a]

event #	event type	days after applied	mean temp (°C)	mean WS (m/s)	mean WD (deg)	mean RH (%)	stability parameter	mean T_{dew} (°C)	mean soil moisture (%)
1	preherbicide background	−4	NA	NA	NA	NA	NA	NA	NA
2	**preherbicide near-source disking**	**−1**	**19**	**3.71**	**134.1**	**NA**	**0.1**	**NA**	**1.45**
3	**near-source disking**	**0**	**23.7**	**9.6**	**264.3**	**8.4**	**1.8**	**−11.91**	**1.35**
4	**near-source disking**	**1**	**24.2**	**18.8**	**258**	**10.4**	**0.3**	**−8.85**	**2.47**
5	**far-source disking**	**5**	**13.2**	**12.4**	**258**	**13**	**-0.2**	**−14.62**	**1.76**
6	**far-source disking**	**7**	**18.3**	**2.6**	**93.3**	**9.1**	**0.7 to −0.4**	**−14.99**	**3.06**
7	nighttime background	8	8.9	4.2	125.8	18.9	NA	−13.53	2.29
8	daytime background	38	20.6	3.5	139.7	5.6	NA	−19.05	NA
9	nighttime background	40	13.7	6.5	258.4	11.9	NA	−15.29	NA

[a]WS = wind speed, WD = wind direction, RH = relative humidity, NA = not available. Stability from Kasumba et al. (2011) based on sonic anemometers used during “active” events; soil moisture measured by TDR probe and moisture cans.

hydroxyl radicals.[6] Understanding the gas/particle partitioning behavior of herbicides can thus help us understand or predict the long-range transport of herbicides to nontarget sites. Recent studies have quantified the ambient gas/particle partitioning of herbicides and pesticides,[4a,6c,7] but few studies have measured the herbicide content of airborne particulate matter (PM) from agricultural fields during mechanized agricultural operation events such as disking and tillage.[8] In addition, very few studies have measured the vertical profiles of herbicides on agricultural fields, while no studies have reported the distribution of herbicides in different airborne particle size fractions. In our previous study, pendimethalin and metolachlor concentrations were measured during disking events in California; pendimethalin but not metolachlor was found in airborne PM released during disking, and there was a measurable increase in pendimethalin's particle/gas partition coefficient with distance from the tractor.[8b]

The objectives of this study were to (1) quantify the total airborne herbicide load and gas/particle distribution of two herbicides under field conditions; (2) determine the distribution of the particle-phase herbicides as a function of airborne particle size; and (3) compare the herbicide concentrations with respect to event type (disking vs background) in order to determine the relative importance of human-induced versus natural-process herbicide emissions from agricultural fields. Airborne gaseous and particulate herbicide (trifluralin and prometryn) concentrations were measured during nine sampling events (one preherbicide daytime background, one preherbicide disking, four postherbicide disking, one postherbicide daytime background, and two postherbicide nighttime background) on a cotton field in Las Cruces, New Mexico, in March and April 2008.

EXPERIMENTAL METHODS

Herbicide Application and Sampling Events. Two pre-emergence herbicides, prometryn and trifluralin (Table 1), were applied to bare soil in a cotton field in Las Cruces, NM, in March 2008 as the trade herbicides Caparol (Syngenta, Greensboro, NC) and Trust (Dow AgroSciences, Indianapolis, IN), respectively. The active ingredient for Caparol is prometryn (2,4-bis(isopropylamino)-6-(methylthio)-1,3,5-triazine [44.4%]), while that for Trust is trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine [46%]). The applied formulation contained 0.05% Placement (AgriSolutions) a drift control and deposition agent. Prometryn and trifluralin target application rates were 0.850 lb/acre (0.095 g/m^2) and 0.518 lb/acre (0.058 g/m^2), respectively, based on the formulation mixture. The structures and physical−chemical properties of both herbicides are shown in Table 1.[9] The theoretical air−soil partition coefficients ($K_{air/soil}$) for both herbicides were calculated using Table 1 values and eq 1:

$$K_{air/soil} = \frac{K_H}{K_{oc}} \tag{1}$$

where K_H is the dimensionless 25 °C Henry's law constant, and K_{OC} is the organic carbon sorption partition coefficient. Equation 1 assumes the majority of soil sorption is due to organic matter and ignores mineral sorption that has been shown to be important for dry field conditions.[10] The air/soil partition coefficient ($K_{air/soil}$) for trifluralin is 3 orders of magnitude greater than the value for prometryn due to its much higher vapor pressure. Trifluralin's reported short half-life in air

Table 3. Average Herbicide Concentrations in Soil Samples (ng/g of soil)[a]

herbicide	Event 4 sample 1 *n* = 2	Event 4 sample 2 *n* = 2	Event 6 sample *n* = 2	Event 9 sample *n* = 2	mean conc in soil ng/g
days since application	1	1	7	40	
trifluralin (ng/g soil)	661 (754)	468 (116)	141 (154)	528 (385)	449
prometryn (ng/g soil)	127(137)	71.5 (8.4)	13.7 (16.7)	89.5 (85.4)	75.5
prometryn/trifluralin concentration ratio	0.21 (0.04)	0.16 (0.02)	0.08 (0.03)	0.15 (0.05)	0.15

[a] *n* represents number of 1 g subsamples extracted. Values in parentheses represent one standard deviation.

(25−193 min) as compared to prometryn (~10 h) is likely due to a higher photodegradation or oxidation rate.[4b]

The field site, sampling events, and samplers were described previously.[11] Table 2 briefly summarizes the nine sampling events with more detailed description in the Supporting Information. Light-weight filter-polyurethane foam (filter-PUF) samplers comprised of an Apex personal air sampling pump (Casella, Amherst, NH) that had both a Teflon filter (47 mm, Pall Gelman) and a PUF cartridge at its inlet sampled particle-phase and gas-phase herbicides, respectively, at a flow rate of 4 L/min. During all the sampling events, three filter-PUF samplers were mounted at different heights on a portable platform vertical array located either in the middle, corner, or edge of the field to capture herbicide vertical profiles, while two other filter-PUF samplers were always placed at the downwind and upwind corners of the field at ~1 m height. A micro-orifice uniform deposition impactor (MOUDI, model 110-R, MSP Corp.) operating at 30 L/min was located on the platform to measure herbicide distributions in 10 particle size fractions (<0.18 to 18 μm diameter) using aluminum foil substrates. During the disking events, the disking tractor was always moving, while the samplers were stationary only for the far-source disking events. During near-source disking, the sampler platform was moved after each tractor pass to maintain a 4-m downwind distance from the disking tractor. No disking took place during "natural" background events, and the samplers were stationary. Two sonic anemometers (CSAT3, Campbell Scientific) located at the southern edge of the field at 1.34 and 8 m from the ground measured air temperature, wind speed, and wind direction at 20 Hz resolution. Because the meteorological data for Events 7, 8, and 9 were incomplete, the nearby Las Cruces International Airport meteorological data[12] summarize conditions for all nine sampling events (Table 2). Surface soil samples collected from random locations on the field during Events 4, 6, and 9 were used to determine the herbicide concentrations at various times (1, 7, and 40 days, respectively) after herbicide application (duplicate 1 g subsamples were extracted and analyzed). Samples collected by the MOUDI stages, filters, and PUFs, together with soil samples, were all stored in a −80 °C freezer after shipment to the University of Vermont until they were extracted and analyzed.

Laboratory Analysis of the Real-World Samples for the Field-Applied Herbicides. The filter-PUF, soil, and MOUDI field samples were extracted by supercritical fluid extraction (SFE) and analyzed by gas chromatography−mass spectrometry (GC/MS) for the two field-applied herbicides, prometryn and trifluralin. During extraction, the MOUDI aluminum foils were combined into four composite size fractions to obtain sufficient herbicide mass for GC/MS analysis; particles with aerodynamic diameter between 10 and 18 μm (PM_{10-18}) were extracted together, as were particles between 1.8 and 10 μm ($PM_{1.8-10}$), 0.18 and 1.8 μm ($PM_{0.18-1.8}$), and less than or equal to 0.18 μm ($PM_{0.18}$).

Using a Spe-ed 2 supercritical fluid extractor (Applied Separations, Allentown, PA), supercritical fluid carbon dioxide was used as the herbicide extraction solvent with a 10% v/v acetone modifier at 200 bar, 86 °C (MOUDI foil, 75 min, 100 mL vessel; Teflon filters, 45 min, 25 mL vessel) or 98 °C (PUFs, 120 min, 1L vessel), and a flow rate of 2 mL/min. Reproducibility of the extraction methods was ensured by extracting replicate samples of laboratory herbicide standards for each method and surrogate (terbutryn) addition prior to extraction of all samples. Herbicide standard percent recoveries ranged from 77 to 106% with relative standard deviations from 4 to 12%.

All sample extracts were analyzed by GC/MS (Agilent 6890GC/5973MSD) using methane positive chemical ionization (PCI) as the ionization mode. Exactly 2.25 μg of each of two herbicide internal standards (benfluralin, 98.7% and propazine, 99.5% (ChemService Inc., West Chester, PA) were added to each sample just before GC/MS analysis for quantification. The GC conditions were Restek (Rxi-XLB) capillary GC column (30 m, 0.25 mm i.d., and 0.25 μm film thickness), 99.999% helium carrier gas at 1 mL/min, 290 °C injector operated in splitless mode, and 290 °C detector. Particle-phase concentrations for the filters were expressed in terms of herbicide mass collected per volume of air sampled, rather than herbicide mass sampled per gravimetric mass of PM collected because some filters had preweights greater than their respective postweights, thus leading to negative PM concentrations for samples with little particle mass collected. Detailed SFE extraction procedures and GC/MS analysis conditions, including laboratory quality control and detection limits, can be found in the Supporting Information.

Measured concentrations of trifluralin and prometryn in blanks for the different sampling media were used to define minimum mass detection limits for the field samples (see Supporting Information). For each sampling medium, the herbicide concentration was considered to be *"certain"* if the sample herbicide mass was greater than the average blank mass (M_b) plus one standard deviation of the field blank mass (s_b) for the same sampling medium; *"uncertain"* if the measured herbicide mass was less than (M_b + $1s_b$), but greater than M_b; and *"below blank detection (BBD)"* if the measured herbicide mass was less than M_b. The number of samples that had detectable concentrations for prometryn (30 PUF and 33 Filter) was greater than the number of samples that had detectable trifluralin concentrations (14 PUF and 34 Filter), likely due to the higher prometryn application rate, but these data may also reflect sampling or analytical losses of trifluralin from the PUF samples. One Event 5 sample that had extremely low total volume sampled but detectable herbicide mass was omitted from statistical analysis.

Statistical Analysis. JMP software (version 9.0.0, SAS Institute Inc., 2010) was used for statistical analysis (Student's *t* tests (assuming unequal variances) and analysis of variance (ANOVA); defining "statistical significance" at the 5% level (alpha = 0.05)). To compare the herbicide concentrations based on the type of sampling event, the events were classified into four types: near-source disking (Events 3 and 4), far-source disking (Events 5 and 6), daytime background (Event 8), and nighttime background (Events 7 and 9). Herbicides were not detected in the two preapplication events (Events 1 and 2), so they are not discussed further.

RESULTS AND DISCUSSION

Soil Sample Herbicide Concentrations. Measured trifluralin concentrations in soil samples were higher than prometryn concentrations, with the ratio of prometryn to trifluralin concentrations ranging from 0.08 to 0.21 (Table 3) showing no discernible trend over time (Event 9 was 40 days after herbicide application), possibly due to sample heterogeneity across the field. The 30−40% difference in herbicide concentrations of the two different soil samples collected during Event 4 indicates the field sample heterogeneity by sampling location. The low measured prometryn/trifluralin ratios in soil samples were surprising because the ratio of prometryn to trifluralin in the applied herbicide formulation was 1.6. It is unknown to what extent the Placement deposition additive may have differentially affected the sorption and volatilization behavior of the two herbicides. This product is intended to generate positively charged micelles that encase the herbicide and reduce evaporation. It is likely that the effect of Placement would be enhanced for the lower solubility herbicide in our study, trifluralin. Trifluralin has a much higher computed $K_{air/soil\_oc}$ even given its 10 times higher organic carbon sorption coefficient compared to prometryn (see Table 1), but this computed equilibrium value assumes wet conditions, and previous studies have shown that sorption and volatilization processes depend on the soil moisture conditions.[3,10,13] The longer half-life of trifluralin in soil (93 days) compared to prometryn (60 days) is, however, consistent with the higher measured trifluralin soil concentrations. It is also important to note that there were detectable concentrations of both herbicides in the surface soil collected 40 days after herbicide application (Event 9). These data agree with previous measurements of trifluralin in soil samples over 100 days after application even in higher moisture environments.[14]

Considering the variability among samples, no decreasing trend in soil herbicide concentrations was observed, and therefore the mean soil concentrations reported in Table 3 are considered representative over all events after soil incorporation of herbicides. There was no rain during the study, so conditions were dry: soil moisture ranged from 1.3 to 3%, somewhat lower than observed in our California study[8b] (2.3–3.5%). Atmospheric conditions were also drier and colder than Clymo et al.:[8b] daytime relative humidity was 5–13%, nighttime 12–20%, and air temperature was 10–20 °C (see Table 2) vs 40–60% and 20–30 °C in our previous daytime study.

Airborne Herbicide Load. No herbicides were detected in preapplication events (Events 1 and 2), as expected. Thus, there was no carryover of herbicides from previous applications on the field, and there was no contamination from neighboring fields.

Generally, when both herbicides were detected in a given PUF or filter sample, prometryn concentrations were higher than trifluralin concentrations in both the gas and particle phases for all sampling locations and sampling events (Table S3, Supporting Information). Mean prometryn total (particle + gas phases) concentrations were statistically (alpha = 0.05) higher for near-source disking events (Events 3 and 4; mean = 351.5 ng/m^3) than far-source disking (Events 5 and 6; mean = 123.0 ng/m^3), daytime background (Event 8; mean =116.8 ng/m^3), and nighttime background events (Events 7 and 9; mean = 60.5 ng/m^3) as shown in Figure 1. For trifluralin, near-source disking total concentrations were statistically 1.5–2 times higher than the far-source and daytime background samples, but not statistically different from nighttime background (Events 7 and 9) due to higher variability in nighttime samples. For both herbicides, the event type pattern observed for total herbicide concentration was also observed for the gas-phase samples collected on PUFs, but particle-phase concentrations were not statistically different between event types for either herbicide. This latter result may be related to computing herbicide concentrations on an air-volume sampled, not PM mass, basis due to missing PM mass data for some samples.

Similar relationships were found previously for PM$_{10}$: near-source disking events had about 4–10 times higher PM$_{10}$ concentrations than far-source disking and background events.[11] Thus, soil management practices taking place on the agricultural field during sampling increase both PM$_{10}$ and herbicide airborne concentrations approximately 1–10 times above background levels, depending on the sampler distance from the tractor. No direct relationship was found as a function of tractor distance, however, suggesting airborne herbicide concentrations also depend on field meteorological conditions (temperature, wind speed, humidity) which control herbicide volatilization and soil resuspension rates.

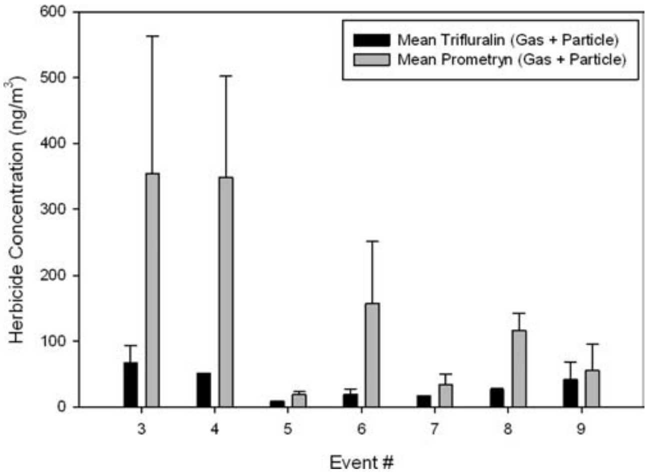


Figure 1. Mean total (gas + particle phases combined) herbicide concentrations measured in Apex filter-PUF samplers by sampling event. Error bars represent one standard deviation.

Averaging over all the filter-PUF samplers by event type, the *total* (gas + particle) prometryn concentrations were 2–8 times higher than the corresponding trifluralin total concentrations, the gas-phase prometryn concentrations were 2–4 times higher than the gas-phase trifluralin concentrations, and the particle-phase prometryn concentrations were 2–14 times higher than the particle-phase trifluralin concentrations. These differences in herbicide concentrations in airborne samples likely result from a combination of (1) different herbicide application rates; (2) the shorter half-life of trifluralin in the air, which means that more trifluralin than prometryn would decompose after entering the atmosphere; (3) differences in prometryn/trifluralin ratio by particle size (MOUDI, see below); and (4) higher loss of gas-phase trifluralin than prometryn during storage or breakthrough during sampling due to its higher vapor pressure. The higher number of PUF sample nondetects for trifluralin compared to prometryn suggests losses during air sampling for some samples, but samples with uncertain PUF concentrations did not always have low filter concentrations, and no data are available to assess PUF breakthrough during sampling. Trifluralin loss during laboratory handling is unlikely because very good recoveries were obtained for spiked PUFs and filters.

The higher prometryn/trifluralin concentration ratios measured in the gas and particle phases cannot be fully accounted for by the herbicide target application rates determined from the spray formulation. Prometryn was applied at a rate of 0.85 lb/acre, while trifluralin was applied at a rate of 0.52 lb/acre, a ratio of 1.6. Compared to the application rate, the higher ratio in air samples and lower ratio measured in surface soil samples (see Table 3) suggest processes occurred to modify the prometryn/trifluralin ratio either prior to or during air sampling, assuming laboratory losses can be ruled out. Loss of trifluralin during air sampling would explain the higher prometryn/trifluralin ratios measured in the airborne samples. We do not have field data to further quantify the possible herbicide loss mechanisms, but the herbicides' physical–chemical properties (Table 2) imply that trifluralin might degrade more quickly than prometryn when both herbicides were either resuspended (as dust-bound herbicide) or volatilized into air from the soil surface particles; thus trifluralin measured air concentrations would always be lower than those for prometryn. For example, trifluralin photolysis is known to be fast, and it also reacts with atmospheric hydroxyl radical with lifetimes of 15 min to 8.5 h, respectively.[4b,15] For the soil samples, either prometryn was preferentially lost from the soil samples prior to sample collection (Event 4) or trifluralin was more easily extracted from the soil, the latter is unlikely based on the relative properties in Table 2. More data, such as the relative rates of soil biodegradation of the two herbicides during soil sample storage, would be needed to evaluate these possible explanations of why the herbicide mass concentration ratio varied with sample type.

Given that prometryn/trifluralin ratios in filter/PUF samples were generally greater than 1, prometryn should have a longer atmospheric residence time and therefore longer transport distance probability than trifluralin after being released to the atmosphere via agricultural disking or natural daytime resuspension. The total airborne concentrations of trifluralin and prometryn were not statistically different for Events 7 and 9, the two nighttime passive sampling events ($p = 0.1487$). Nighttime concentrations were also typically lower than daytime for both herbicides. The observed similar concentrations of the two herbicides for nighttime sampling could be explained by higher in-soil prometryn degradation/loss given that these nighttime events occurred days after herbicide application (8 days for Event 7, and 40 days for Event 9). Appreciable soil degradation did not occur, however, evidenced by the high airborne prometryn concentrations measured during the daytime background event (Event 8), 38 days after herbicide application. It is more likely that time-of-day affected the resuspension, volatilization, and degradation of the two herbicides differently in the absence of soil management. Either more prometryn than trifluralin volatilized or was resuspended from the soil during daytime Event 8 than for nighttime Events 7 and 9, or photodegradation of trifluralin preferentially removed trifluralin from the atmosphere during daytime Event 8, but not at night. Meteorological parameters such as temperature, wind speed, and relative humidity could also have played a role in affecting the relative concentrations of both herbicides during day and night background sampling events. The mean temperature during Event 8 (20.6 °C) was higher than the temperatures for Events 7 (8.9 °C) and 9 (13.7 °C) (Table 2) and could have resulted in higher volatilization and dust resuspension during Event 8. Trifluralin's higher air/soil partition coefficient is consistent with greater gas-phase trifluralin loss in air relative to prometryn only during the day due to higher photodegradation and/or gas-phase oxidation *after* release from the soil. Further examination of the gas and particle phase behavior of these herbicides may shed light on these competing processes.

Gas- and Particle-Phase Herbicide Concentrations by Event Type. Figure 2 shows the average particle-phase and gas-phase concentrations of both herbicides in each sampling event for the three filter-PUF samplers located on the tower/platform. Prometryn mean concentrations were typically higher than trifluralin mean concentrations for all filter and PUF samples in each event (Figure 2, note *y*-axis scales), and airborne herbicide concentrations appreciably decreased with time after herbicide application. Events 7, 8, and 9 occurred 8, 38, and 40 days after herbicide application, respectively, and the concentrations of both herbicides during Event 9 were lower than those for the earlier nighttime background event (Event 7). The 2–4 times higher prometryn particle-to-gas concentration ratio for daytime Event 8 compared to Events 7 and 9 supports the hypothesis that daytime conditions released more surface soil particles and particle-bound herbicides from the soil compared to nighttime conditions. Such natural erosion conditions are not uncommon in dry climates where solar insolation heats the ground and leads to development of vertical convection currents that incorporate fine soil particles into the atmosphere ("dust devils").

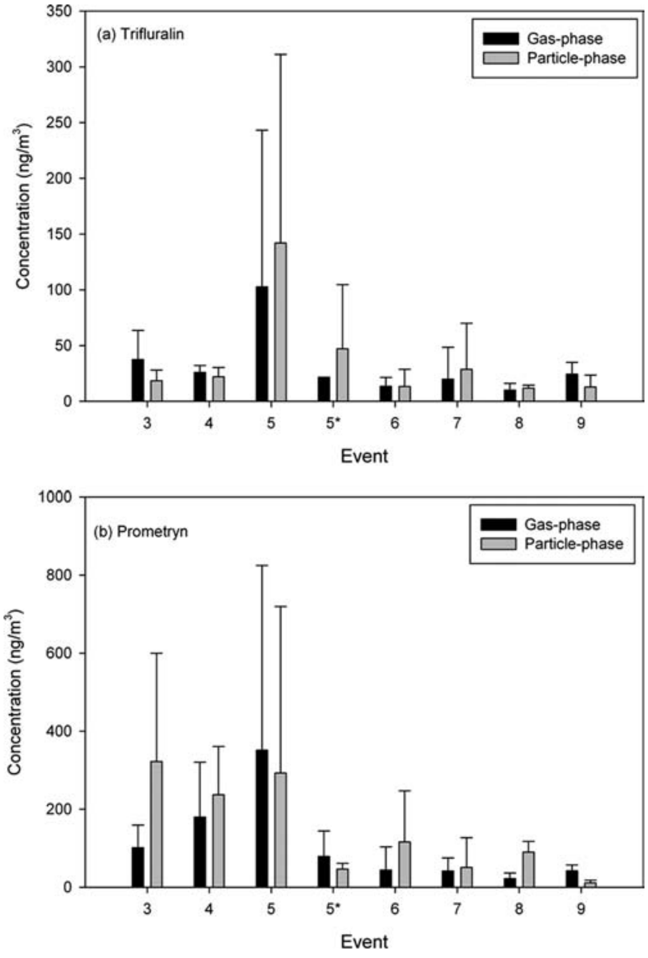


Figure 2. Average gas and particle-phase concentrations of (a) trifluralin and (b) prometryn (for the three filter-PUF samplers on the tower). The * indicates Event 5 data plotted without the outlier concentration.

During Event 5 disking, the DustTrak sampler located at 5.5 m height measured unusually high PM_{10} concentrations compared to the other DustTraks.[11] Samplers located at this spot on the platform were apparently exposed to more herbicide and particles than other samplers for an unknown reason, possibly due to a localized dust devil soil disturbance event during this relatively windy far-source disking event (see Table 2). Because the filter-PUF sampling unit located at the

5.5 m height of the platform during Event 5 clogged, these data were not included in statistical analyses.

Herbicide Concentrations and Sampler Height. On the basis of our PM_{10} study,[11] vertical profile patterns of decreasing herbicide concentrations with sampling height were expected, especially for the near-source disking events. For PM_{10}, concentrations decreased with height from the ground for near-source disking events, while there were no consistent vertical profile shapes for far-source disking events and background events.[11] The vertical profiles observed for both herbicides differed from event to event for both gas and particle-phase herbicides (Supporting Information, Figures S1 and S2). Even replicate types of sampling events (near-source disking Events 3 and 4; far-source disking Events 5 and 6), however, did not have similar vertical herbicide profiles. Thus, no distinct vertical profile patterns existed for the herbicides trifluralin and prometryn despite being found for PM_{10}.

Herbicide Gas/Particle Fractionation. The mass fraction of herbicide measured in the particle phase (Φ_p) was determined (eq 2) to evaluate the gas-particle behavior of the two herbicides by event type:

$$\Phi_p = \frac{M_p}{M_p + M_g} \qquad (2)$$

where M_p is the herbicide mass in the particle phase (filter sample) and M_g is the herbicide mass in the gas phase (PUF sample). The measured Φ_p for prometryn was generally higher than Φ_p for trifluralin in individual samples, in agreement with the herbicides' relative air/soil partition coefficients. Over all sampling events, Φ_p ranged from 0.08 to 0.90 (mean = 0.44 ± 0.21) for trifluralin and from 0.13 to 0.99 for prometryn (mean = 0.55 ± 0.26). For prometryn, there was a significant difference in the particle mass fraction by event type, with Φ_p greater than 0.5 for the daytime background and near-source disking events and less than 0.5 for far-source and nighttime events (Figure S3, Supporting Information). High Φ_p during disking events was expected because herbicide-bound particles were mechanically resuspended from the ground. There apparently was not sufficient time for prometryn to desorb from the dust during near-source disking, resulting in increased mass fractions in the particle phase. During background sampling, in contrast, no particles were mechanically disturbed from the ground, and thus the concentration of herbicide-bound particles in the atmosphere was determined by natural wind erosion and compound volatilization from the soil. The significantly (at 95% probability level) lower Φ_p ratios for nighttime background and far-source disking compared to near-source and daytime background sampling suggest volatilization processes were greater than wind erosion of particle-bound herbicides under nighttime background sampling. In contrast, for the single daytime background sampling (Event 8), wind erosion of herbicide-bound dust dominated over volatilization of prometryn to generate the observed high particle mass fractions.

Event 8 was the only event with a distinct pattern of increasing Φ_p with increasing sampling height (Figure S3, Supporting Information), suggesting that high near-ground gas-phase volatilization from soil at low ambient air relative humidity and high temperature (Event 8; see Table 2) combined with intermittent events of soil particle erosion under these daytime background conditions. The increase in particle mass fraction with height indicates prometryn was preferentially sorbed to particles as they were transported away from the ground-level source. The highest sampling height (9 m) had the highest Φ_p measured in the study and the lowest PUF concentrations of all passive events. Thus, prometryn was either lost from the gas-phase, relative to particle phase, as soil particles were vertically transported from the ground or gas-to-particle readsorption of (near-ground) volatilized prometryn may have occurred under conditions of daytime soil heating and dust resuspension. Natural wind erosion may resuspend different particle sizes compared to active mechanical disking and the tendency of prometryn to desorb from airborne particles may be a function of particle size and organic matter content. With increasing height, the volume fraction of smaller particles with higher f_{oc} typically increases; both these factors would explain the higher Φ_p with sampler height. As discussed below, however, prometryn concentrations were not higher in the smaller size fractions during the disking events where particle size distribution was measured. Future studies should examine the distribution of herbicides as a function of particle size and sampling height concurrently to better quantify these background herbicide transport processes.

The background events (7, 8, and 9) showed statistically significant relationships between airborne prometryn total concentrations and Φ_p with mean event meteorological parameters, but disking event relationships to meteorological conditions were not as strong. For example, total airborne prometryn increased with (i) increased ambient air temperature ($R^2 = 0.61$, $p = 0.0048$), (ii) decreased relative humidity ($R^2 = 0.51$, p = 0.0127), and (iii) decreased dewpoint ($R^2 = 0.61$, $p = 0.0048$) for *background* events, whereas mean temperature explained 50% of the variability ($R^2 = 0.50$, p = 0.0015), humidity had no significant relationship to total prometryn concentration, and dewpoint ($R^2 = 0.33$, $p = 0.0165$) explained only 33% of the variability for *disking* events. These data indicate that mechanical disturbance by tilling operations reduces the ability to predict airborne herbicide concentrations on the basis of meteorological conditions alone.

The measured gas/particle relative herbicide concentrations were consistent with the calculated air/soil partition coefficients. Prometryn particle phase mass fractions were generally higher than those for trifluralin during all events (see Figure S3, Supporting Information). More research on a wide range of herbicides is needed to achieve better quantitative understanding of the factors that influence gas/particle partitioning of herbicides under field conditions. The findings of the gas/particle partitioning of trifluralin in the present study are consistent with previous studies. For instance, in a Strasbourg, France gas/particle partitioning study of 71 pesticides, trifluralin was one of the pesticides found to mostly partition to the gas phase with an average mass fraction in the gas phase of 66.5%.[7a]

The range of herbicide particle-phase mass fractions measured in this study were similar to those measured by Clymo et al. (2005)[8b] for pendimethalin, but not metolachlor, during near-source disking in California. Relationships between herbicide properties and Φ_p were examined but not found to be significant except for a distinct increase in the range of measured Φ_p for herbicides with log K_{oc} greater than 2.5 (see Figure S4, Supporting Information). Other properties, including vapor pressure, $K_{air/soil}$, Henry's constant, Abraham's H acceptor/donor parameters showed no relationship. Compound polarizability, as quantified by ACD Laboratories iLab2 software (http:/ilab/acdlabs.com/iLab2/index.php), and which may be indicative of compound sorption to both organic matter and mineral surfaces in soil particles, showed a nonlinear relationship to Φ_p, with a distinct increase in Φ_p for polarizability less than 31×10^{-24} cm^3. Data from more herbicides are needed to better predict Φ_p as a function of chemical properties.

Particle Size and Herbicide Concentration. The sorption capacity of particulate organic matter has been previously found to be controlled by the size of PM because of a greater number of sorptive sites associated with a greater surface-to-volume ratio with decreasing particle size.[16] Size-resolved airborne particles were collected here for disking Events 4, 5, and 6 only. For the combined MOUDI-binned particle size fractions, prometryn concentrations increased with increasing particle size fraction for most of the sampling events, while no clear pattern was observed for trifluralin (Figure 3).

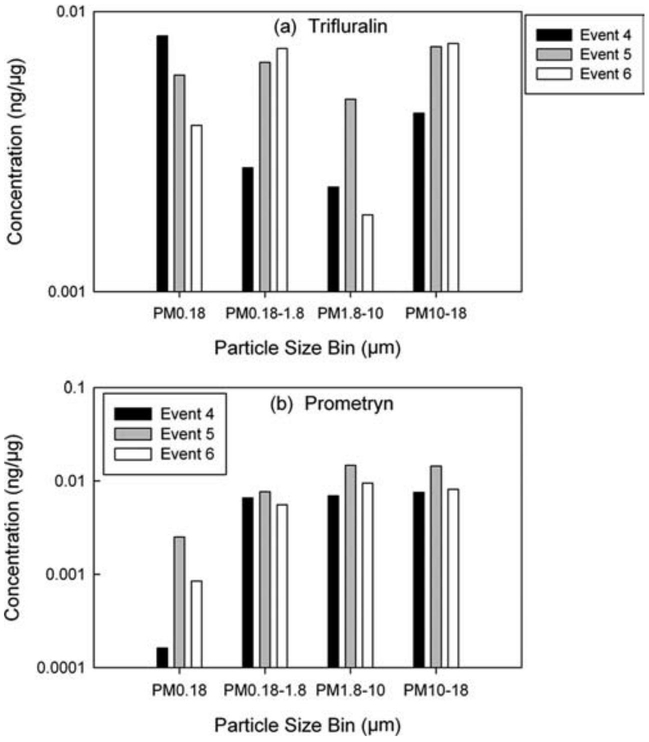


Figure 3. (a) Trifluralin and (b) prometryn concentrations measured on the particles sampled by the MOUDI (ng/μg of total MOUDI mass sampled). Note that the *y*-axis is on a log scale.

Prometryn concentrations were usually higher than trifluralin concentrations in all size fractions except in the smallest fraction, $PM_{0.18}$. Because trifluralin is more hydrophobic than prometryn, it was expected that trifluralin concentrations in the smallest size fraction, $PM_{0.18}$ (expected to have the highest organic matter content) would be higher than prometryn concentrations, and this was observed (Figure 3). The trifluralin concentration in $PM_{0.18}$ was 50 times higher than that for prometryn during Event 4, about 2 times higher during Event 5, and about 5 times higher during Event 6. Given the observed relationship for prometryn with particle size, it is unlikely that the increase in Event 8 particle mass fraction was due to size-fractionation of particles during resuspension events, unless convection due to daytime soil heating under low humidity, high temperature atmospheric conditions preferentially suspends larger diameter particles than are suspended during mechanical tilling. Data are needed to compare the particle size distributions of herbicides during *natural background erosion* events to those associated with managed soil activities (disking, cultivation, etc.).

Previous field studies have used high volume samplers in order to sample considerable mass of herbicides and pesticides during sampling. For example, flow rates ranging from 31 to 38 m^3/h sampled gaseous and particle-bound PAHs in air at a deciduous forest in Borden, Ontario;[17] 15 m^3/h sampled gaseous and particulate phase pesticides (83 pesticides) at two sites in Quebec, Canada;[7b] and 10−15 m^3/h flows were used to sample gas and particle-phase herbicides at three sites in France.[4a] Here, the 0.24 m^3/h flow rate for the lightweight filter-PUF samplers enabled sampling gas- and particle-phase herbicides at different heights from the ground (0−9 m), but also resulted in low measured mass of herbicides, especially trifluralin, during some events despite sampling very close to the source compared to other studies. It is not known to what extent the number of trifluralin PUF samples below detection were the result of the low sample flow rates employed vs atmospheric oxidation/photolysis. It should be noted that an intermittent source was sampled in this study: except during the short periods of time when the disking tractor passed immediately upwind of the tower, background ambient air was being sampled, even during the disking events (Events 3−6). This may explain why background event herbicide concentrations could be of similar magnitude to those measured during both near- and far-source mechanized events that greatly disturbed the dry soil.

This work suggests two important avenues for future real-world measurement of airborne herbicides downwind of agricultural operations: extensive background gas/particle sampling as a function of height and as a function of particle size should be conducted for a wider range of herbicide compounds. These studies should also examine the effects of herbicide formulation on volatilization and particle resuspension processes. Higher sampler flow rates and methods to quantify filter "blow-off" artifacts should be employed in future field campaigns. Collection of this data will enable calculation of pre-emergent herbicide fluxes downwind after soil application.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Field sampling details, laboratory QA/QC procedures, filter and PUF herbicide concentrations by event, and mass fractions for individual samples are documented separately. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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