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Simulating and Characterizing Agricultural Ground Applications for Soil VOC Deposition Studies

ABSTRACT: Reactive volatile organic compounds (VOCs) play a major role in the formation of photochemical oxidants in the atmosphere by reacting with oxides of nitrogen and solar ultraviolet energy producing ozone, which is a criteria pollutant regulated under the National Ambient Air Quality Standards. The United States is one of the most agriculturally productive countries in the world due in part to the use of chemical pesticides that consist of active ingredients that are typically non-volatile or semi-VOCs and inert ingredients such as solvents, emulsifiers, and diluents that may also be volatile. Presently, the VOC determination of emission factors from agricultural pesticide applications assumes that all of the inert VOC ingredients volatilize. This research focuses on the development of a laboratory methodology for applying agricultural spray formulations in accurate and measurable levels to support VOC deposition onto and loss from soil surfaces. Adapting a laboratory spray table system with a modified spray and deposition sampling scheme resulted in repeatable spray applications, with the deposition pattern being mapped across the treatment area. These mapped deposition values allow for measurements from soil samples to be correlated with actual spray deposition. This methodology provides for a rapid and repeatable means for surveying VOC deposition and losses from a variety of spray formulations under varying spray rates and spray droplet sizes.

KEYWORDS: volatile organic compounds (VOCs), spray table, spray simulation, spray deposition

Introduction

Reactive volatile organic compounds (RVOCs) play a major role in the formation of photochemical oxidants in the atmosphere. The reaction of RVOC with oxides of nitrogen (NO_x) in the presence of solar ultraviolet energy can produce ozone (O_3), a criteria pollutant regulated under the National Ambient Air Quality Standards (NAAQS) [1]. Tropospheric ozone contributes to the greenhouse gas effect, and its high levels can impair public health and welfare. In 2008, the U.S. Environmental Protection Agency (USEPA) reduced the primary and secondary 8-h NAAQSs for ozone from 80 parts per billion (ppb) to 75 ppb. It is estimated that 345 counties, many near areas of substantial agricultural production, may exceed the new standard, compared to 85 counties that exceeded the previous standard [2]. Some VOCs are non-reactive hydrocarbons, which may not contribute significantly to ozone formation. Measured VOCs are often expressed as the sum of non-methane hydrocarbons. These measurements do not give information on the photochemical reactivity of the hydrocarbon mixtures [3]. These compounds have varying maximum incremental reactivities (MIRs).

The use of chemical pesticides has helped make the United States one of the most agriculturally productive countries in the world. In 2006, the National Agricultural Statistics Service reported that each farmer in the United States provided food and fiber for 144 people compared to just 46 in 1940. This increase also corresponds to an increase in chemical use during this time period from 400 million lb in the mid-1960s to 771 million lb in 1995. Peak use of agricultural chemicals occurred in 1980 with consumption of 850 million lb [4]. Most chemicals used in agriculture can commonly be referred to as pesticides. A pesticide is defined as any agent used to kill or control undesired insects, weeds, rodents, fungi, bacteria, or other organisms. The term pesticide includes the following: Insecticides, herbicides, rodenticides, fun-

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gicides, nematicides, acaracides, disinfectants, fumigants, wood preservatives, and plant growth regulators. Most liquid pesticides consist of active ingredients, which are typically non-volatile or semi-VOCs (SVOCs) and inert ingredients such as solvents, emulsifiers, and diluents. Many of the inert ingredients in liquid pesticides are VOCs.

The AP-42 emission factors for VOCs from pesticide application are determined using an algorithm that incorporates the vapor pressure of the active ingredient and assumes that all of the VOC inert ingredients volatilize within 30 days of application [5]. However, there is very little data to back this assumption. Furthermore, not all pesticide solvents have the same potential to form ozone. According to the California Department of Pesticide Regulation, the most prevalent solvents in use in 2000 were aromatic 200 solvent, xylene range solvent, kerosene, methyl isobutyl ketone, propylene glycol, and aliphatic solvent. Kerosene, which is a mixture of alkanes, has a MIR of around 1.5 (i.e., 1 g of kerosene has the potential to form 1.5 g of ozone under the right conditions), whereas alkenes, such as xylene range solvent and propylene glycol, have MIRs of around 6.0. Therefore, the use of some pesticide solvents may lead to a greater risk of ozone formation than others.

When applying pesticides, droplet size is an important consideration and is one of the most important factors affecting spray drift. Larger droplets have less potential for drift, but smaller droplets may be needed for some chemicals to maximize chemical efficacy. While droplet size has long been recognized to affect spray drift, its effect on volatilization of active and/or inert ingredients has not been demonstrated in available literature. Pesticide tank-mix dilution levels may also affect VOC volatilization. Pesticides are applied within a specified range of application rates, but the chemical is diluted to allow for uniform application with commercially available application equipment. Most application equipment is designed to apply at application rates between 19 and 280 L/ha (2–30 gal/ac) at normal operating ground speeds, fluid flowrates, and spray pressures. Changes in the tank-mix dilution may affect the absorption of pesticides by plant tissue or adsorption of pesticides onto the soil matrix. Organic molecules, including VOCs and SVOCs, may adsorb to soil particles through van der Waals–London interactions, hydrophobic bonding, hydrogen bonding, charge transfer, ligand exchange, ion exchange, direct and induced ion-dipole and dipole-dipole interactions, magnetic interactions, or chemisorption [6]. The moisture content of the surface-air interface will be affected by the tank-mix dilution rate and may therefore affect adsorption through several of these adsorptive forces.

One of the difficulties exploring these relationships is accurate, repeatable, and measurable methods for applying varying rates of spray product with varying droplet sizes in a laboratory manner that mimics spray and deposition patterns seen under real world applications. Laboratory methods allow for rapid application across a wide variety of formulations and application methods. There have been a number of methods developed for laboratory simulated spray applications [7–11], but most only allow for small areas to be treated. Fritz et al. [12,13] detailed a laboratory spray system that allows for larger sample areas to be treated at repeatable, quantifiable rates. Using this system, the objective of this work was to develop a repeatable methodology for applying spray deposition levels at rates and with droplet sizes that simulated typical ground application scenarios and to apply the method in a VOC soil deposition study.

Methods

Prior to the VOC soil deposition study using spray table applications, several calibration assessments of the spray table were required. These calibrations studies along with the procedures and experimental setups and data collection methods are discussed in the following sections.

Selection of Application Parameters

For this work, two spray application treatments were selected: T1, a high volume (188 L/ha (20 gal/ac)), larger droplet spray representative of residual soil applications, and T2, a lower volume (94 L/ha (10 gal/ac)), smaller droplet spray representative of foliar and insecticidal treatment applications. To this end, two nozzles were selected: The 11004 flat fan (Spraying Systems, Wheaton, IL) for T1 and the 11002 flat fan (Spraying Systems, Wheaton, IL) for T2.

A Sympatec Helos laser diffraction droplet sizing system (Sympatec, Inc., Clausthal, Germany) was used to measure droplet size. The Helos system uses a 623 nm He–Ne laser and was fitted with an R5 lens, which resulted in a dynamic size range of 0.5–875 μm in 32 sizing bins. Tests were performed within the

FIG. 1—*Spray table system.*

guidelines provided by ASTM E1260, Standard Test Method for Determining Liquid Drop Size Characteristics in a Spray Using Optical Non-Imaging Light-Scattering Instruments [14]. Measured droplet sizing data included volume median diameter (VMD) and the 10 % and 90 % diameters (DV0.1 and DV0.9) as defined in ASTM E1620 [14].

Spray Table

The spray table was $4.7 \times 2.3 \times 1.2$ m^3 with an opening for sample accessibility that was 3.0×1.4 m^2 (Fig. 1). This opening is covered with a set of glass doors (not closed in Fig. 1) on roller tracks, allowing easy access as well as a spray tight seal. The adjustable table can be positioned between 0.3 and 1.5 m below the nozzle opening and was set at 1.4 m for this work. The nozzle traverse system allows for the nozzle assembly to traverse the entire length (4.7 m) of the spray chamber.

The nozzle traverse speed is controlled by a system consisting of a photoelectric sensor, a computer, and a three-way solenoid valve. The photoelectric sensor provides a signal to monitor the position of the nozzle as it traverses the chamber, while a computer uses this signal to calculate the speed of the nozzle. The three-way solenoid valve controls the nozzle's direction of travel. The photoelectric sensor consists of a reflective photomicrosensor (EE-SB5Z-E, Omron Electronic Components, Scheumburg, IL) that rides in a steel channel as the nozzle traverses the cylinder. The channel has holes spaced every 5.1 cm (2 in.). A reflective surface was placed on the channel opposite of the sensor. As the sensor crosses a hole, the reflector causes light from the emitter portion of the sensor to be reflected back to the detector portion. This results in an electronic pulse that is counted and timed to provide the position and speed of the nozzle.

Soil Containment Boxes

Six soil containment boxes were constructed from 4.8 mm (3/16 in.) aluminum sheet metal, three for each spray rate tested. Each box was $0.61 \times 0.91 \times 0.15$ m^3 ($L \times W \times H$) ($24 \times 36 \times 6$ in.^{3}) as shown in Fig. 2. Several holes were drilled in the bottom of each box to allow for drainage. At the outset of the study, it was decided that a fine, sandy-loam soil from the Central Valley of California (near Fresno, CA) would be the test soil. However, a limited volume of this soil was available for these tests; therefore, each box could not be entirely filled with the test soil. A rigid 0.43×0.43 m^2 (17×17 in.^{2}) square aluminum form was fabricated such that the study soil could be surrounded by a "blank" soil of similar make-up (Fig. 2). Once the boxes were filled with the soils, the forms were removed. This allowed the study soil to be surrounded by a barrier of the blank soil so that temperature and moisture effects in the test soil were not overly influenced by the aluminum sides of the containment boxes. The blank soil barrier also allowed for an area at the same elevation as the study soil onto which sampling media could be placed for deposition assessment during the spray application phase of the study. The filled boxes were placed in a greenhouse in

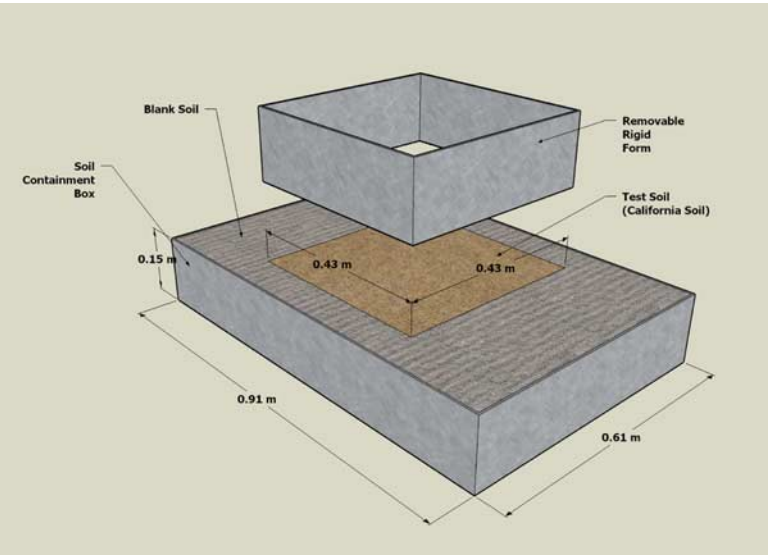

FIG. 2—*Soil containment box.*

which temperature was maintained between 15 and 27 °C. The boxes were watered over a 3 week period to "repack" the soil after being shipped so that it was close to conditions found in actual production fields.

Spray Table Setting for Desired Deposition Rates

To obtain the desired deposition rates in the spray table, an initial assessment was conducted to determine the required nozzle traverse speeds. For each treatment, the spray table was positioned such that the nozzle was 30 cm (12 in.) above the soil surface in the soil containment box. For this assessment, an additional containment box was filled completely with a blank soil to provide a sampling platform that would mimic the actual spray applications made later. The removable rigid form was used to mark a border in the blank soil surface to represent the edges of the test soil in the VOC soil deposition study boxes. Five plastic Petri dishes (8.9 cm i.d.; area of 62 cm^2) were positioned on either end of the test soil border and perpendicular to the spray nozzle traverse direction (Fig. 3).

A spray pass was made over the table with spray solution consisting of the same components at the same mix rates that were used in the actual soil application trials. The spray solutions, mixed in 4 L batches, consisted of

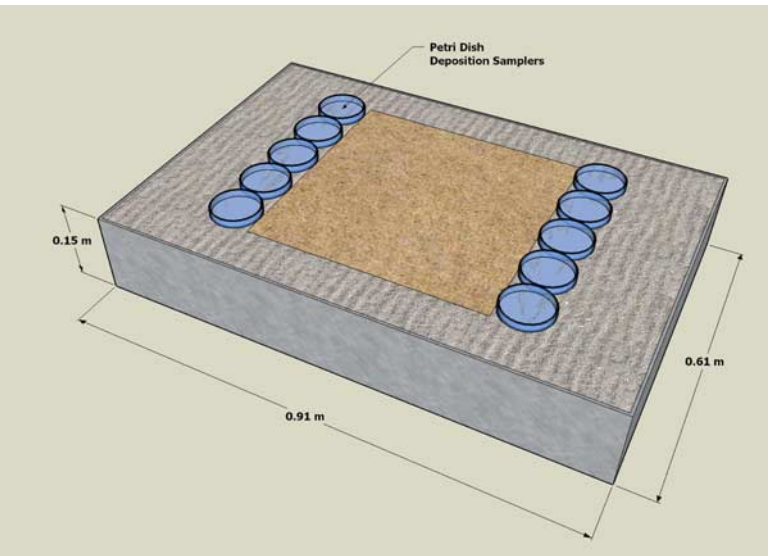

FIG. 3—*Petri dish deposition sampler setup.*

- T1 (188 L/ha rate)
  - 3890 mL water
  - 100 mL (2.5 % v/v) Aromatic 200 (Exxon Mobil Corporation, Irving, TX)
  - 3.8 mL (0.095 % v/v) Toximul 3473 (Stepan Co., Northfield, IL)
  - 5 mL (0.124 % v/v) Toximul 3474 (Stepan Co., Northfield, IL)
  - 1.08 g HCB
  - 0.5 g of Caracid Brilliant Flavine FFN, a fluorometric tracer dye
- T2: 94 L/ha rate
  - 3782 mL water
  - 200 mL (5 % v/v) Aromatic 200 (Exxon Mobil Corporation, Irving, TX)
  - 7.6 mL (0.19 % v/v) Toximul 3473 (Stepan Co., Northfield, IL)
  - 10 mL (0.25 % v/v) Toximul 3474 (Stepan Co., Northfield, IL)
  - 2.16 g HCB
  - 1 g of Caracid Brilliant Flavine FFN, a fluorometric tracer dye

Spray passes were replicated three times for spray nozzle traverse speeds of 0.5, 2.2, 4.5, and 6.7 m/s (1, 5, 10, and 15 mph). The sprayed Petri dishes were collected after each replication and placed into individually labeled plastic bags. The bags were brought back to the laboratory for processing.

Processing started by pipetting 50 mL of ethanol into each bag. The bags were then agitated by hand, and 6 mL of the effluent was poured into a cuvette. The cuvettes were then placed into a spectrofluorophotometer (Shimadzu, Model RF5000U, Kyoto, Japan) with an excitation wavelength of 423 nm and an emission wavelength at 489 nm. The fluorometric readings were converted to $\mu L/cm^2$ of spray solution using a projected area of the sampler and by comparisons to standards generated using samples of spray solution. The minimum detection level for the dye and sampling technique was 0.07 ng/cm^2.

The resulting data were corrected for recovery losses of the dye during processing. Clean Petri dishes were spiked with 20 μL of each spray solution (10 dishes/spray solution) and processed using the same methods. The recovery percentage for the 94 and 188 L/ha rate solutions were 93.1 % and 93.0 %, respectively. The initial deposition values were adjusted to account for these losses. The resulting deposition versus speed data were used to determine the speed required to generate the desired application rates. For both treatments, it was determined that a nozzle traverse speed of $\sim$2.7 m/s (6 mph) was needed.

Soil Sampling Layout and Spray Application and Soil Sample Collection Schedule

The three soil containment boxes available for each spray rate were divided into two groups: Volatilization samples (two boxes) and biodegradation samples (one box). For the volatilization sample boxes, the 0.43×0.43 m^2 study soil square was gridded into 20 separate sections to allow for four replicated samples over five time periods (0, 1, 4, 12, and 36 hours after treatment (HAT)) (Fig. 4). For the biodegradation sample boxes, the 0.43×0.43 m^2 study soil square was also gridded into 20 separate sections to allow for five replicated samples at 0 HAT, and three replicated samples for control samples and for 2, 4, 7, and 14 days after treatment (DAT) (Fig. 5). These sampling points were established by scientists at the ExxonMobil Biomedical Science, Inc. (EMBSI) Environmental Toxicology and Chemistry Laboratory, who processed the soil samples for VOC deposition and biodegradation. The biodegradation samples were all taken at 0 HAT and transported back to the analytical laboratory for analysis at the appropriate time intervals. The volatilization samples were taken at the appropriate time and immediately placed in a freezer to prevent biodegradation before analysis. This was also done for the 0 HAT biodegradation samples. The results from the biodegradation are not reported in this manuscript and are not essential to understanding the methods presented here.

Spray Table Applications

The volatilization and biodegradation soil containment boxes for both spray rates were treated in the spray table. Air temperature and humidity in the spray table were measured at the time of spray application using a Kestrel 4000 handheld sensor (Kielsen-Kellerman, Boothwyn, PA). Sampling protocol during these treatments followed those previously mentioned using Petri dish samplers. After application, the samples were collected, bagged, and analyzed for deposition as discussed earlier. These deposition amounts were

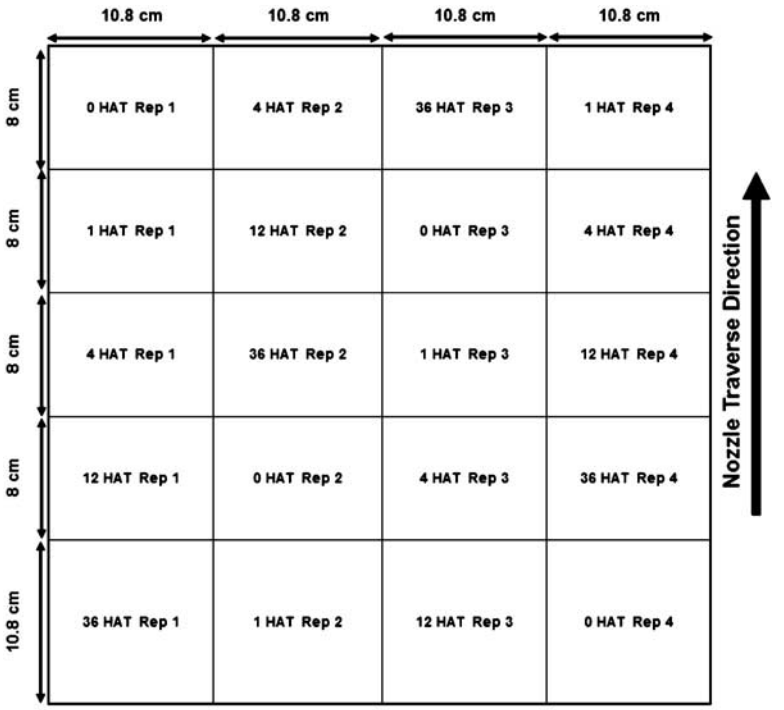

FIG. 4—*Sampling grid layout for volatilization sample boxes.*

also adjusted for sampler recovery. The deposition amounts for each soil sampling area were determined based on a linear gradient in deposition between the Petri dishes on either side of the sample soil square. Petri dish samples placed on the outside edges of the test area along the nozzle traverse during each treatment were analyzed to confirm that the deposition pattern was linear for each treatment application.

While the biodegradation samples were all collected immediately after spray application (all samples were then frozen, with the exception of the control samples, which were collected prior to spray application), the volatilization samples were collected at each of the given HAT intervals. This meant that the

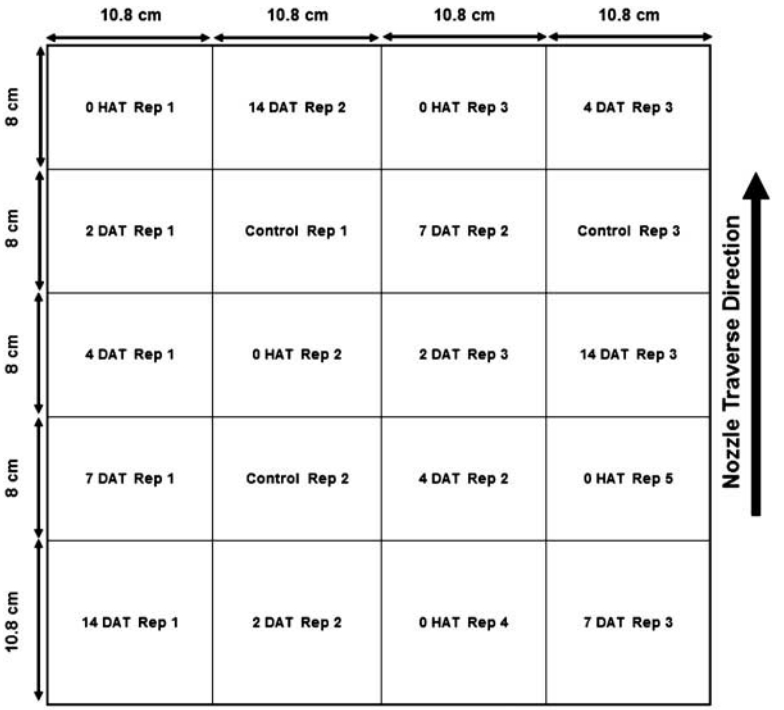

FIG. 5—*Sampling grid layout for biodegradation sample boxes.*

TABLE 1—*Study spray application and soil sampling schedule.*

Time	Spray or Soil Sample	Rate/Sample	HAT
		Day 1	
7:00 a.m.	Spray	94 L/ha volatilization box 1	0
7:30 a.m.	Spray	94 L/ha volatilization box 2	0
8:00 a.m.	Soil sample	94 L/ha volatilization box 1	1
8:30 a.m.	Soil sample	94 L/ha volatilization box 2	1
9:00 a.m.	Spray	94 L/ha Biodegradation Box 1	0
10:00 a.m.	Spray	188 L/ha Biodegradation Box 1	0
10:15 a.m.	Spray	188 L/ha volatilization box 1	0
10:40 a.m.	Spray	188 L/ha volatilization box 2	0
11:00 a.m.	Soil sample	94 L/ha volatilization box 1	4
11:15 a.m.	Soil sample	188 L/ha volatilization box 1	1
11:30 a.m.	Soil sample	94 L/ha volatilization box 2	4
11:40 a.m.	Soil sample	188 L/ha volatilization box 2	1
2:15 p.m.	Soil sample	188 L/ha volatilization box 1	4
2:40 p.m.	Soil sample	188 L/ha volatilization box 2	4
7:00 p.m.	Soil sample	94 L/ha volatilization box 1	12
7:30 p.m.	Soil sample	94 L/ha volatilization box 2	12
10:15 p.m.	Soil sample	188 L/ha volatilization box 1	12
10:40 p.m.	Soil sample	188 L/ha volatilization box 2	12
		Day 2	
7:00 p.m.	Soil sample	94 L/ha volatilization box 1	36
7:30 p.m.	Soil sample	94 L/ha volatilization box 2	36
10:15 p.m.	Soil sample	188 L/ha volatilization box 1	36
10:40 p.m.	Soil sample	188 L/ha volatilization box 2	36

spray applications for each of the sample boxes had to be scheduled such that there was no overlap in spray applications or soil sampling periods between boxes. The final spray application and soil sampling schedule is shown in Table 1.

Soil and Air Temperatures

Air temperature and humidity in the greenhouse were measured at each soil sample interval using a Kestrel 4000 handheld sensor (Kielsen-Kellerman, Boothwyn, PA). Soil temperature was measured at 2.5 and 5 cm depths (1 and 2 in.) in each soil sample location at the time the soil samples were collected using an Extech 39272 thermometer (Extech Instruments Corp., Waltham, MA). The depths are consistent with the depth of the soil collected for each volatilization and biodegradation sample. Soil moisture was measured at the same time and locations using ECH2O Check soil moisture monitor equipped with an ECH2O EC-5 moisture sensor (Decagon Devices, Pullman, WA).

Volatilization and Biodegradation Soil Sample Collection

Soil samples were collected in each location using a sharpened plug cutter (1.6 cm diameter). The plug cutter was carefully inserted through the soil surface to a depth of 2.5 cm and the sample extracted. The soil sample was then placed into a labeled glass vial with an airtight lid. Three sub-samples were collected from each sample location and placed into a single vial. The plug cutter was cleaned by rinsing in hexane after each series of sample was collected at each time point. Care was taken at each location when cutting through the soil surface as even at the high spray rate applications, spray material depositing on the surface was still in the form of individually discernable droplet impact locations. After soil samples were taken and sealed in the glass vials, the vials were placed in a freezer (with the exception of those for biodegradation at 2, 4, 7, and 14 DAT). All samples were stored in the freezer until all samples were collected. At the

conclusion of the soil sampling, vials were packed in an insulated box with dry ice and shipped (via next morning delivery) to the EMBSI Environmental Toxicology and Chemistry Laboratory.

Soil Texture Analysis

Upon completion of the study, a composite soil sample was collected from each soil containment box. The composite sample consisted of five randomly selected spots within the sample soil area from which a 100 mL sample was collected. All five samples from a single box were place in a single, labeled plastic bag. The samples were sent to the Texas A&M AgriLIFE Extension, Soil, Water and Forage Testing Laboratory, Department of Soil and Crop Services for analysis.

Spray versus Deposition Recovery Analysis

A series of spray trials was also conducted to quantify of the amount of spray released from the nozzle that actually deposits on the treatment surface. These trials were conducted using the same nozzles, spray solutions, nozzle traverse speeds in the spray table used for the VOC deposition study. Mylar sheet samplers (11.1×28.6 cm; 317.5 cm^2) were placed across the length of the spray table perpendicular to the nozzle traverse direction to quantify deposition across the entire width of the flat fan spray plume. This was replicated three times for both the 94 and 188 L/ha rates. Nozzle speed was determined over the width of the deposition samplers using a magnetically triggered positional timing device (constructed in-house). Nozzle flowrate was measured prior to the spray trials by spraying into a graduated cylinder for 30 s. Three replications were completed for each spray rate. The mylar sheet samples were collected and processed for deposition in the laboratory as described earlier for the Petri dishes.

Following the recovery analyses procedures mentioned earlier, the mylar sheet collectors were spiked with 40 μL of the spray solutions (10 sheets/solution) and processed for recovery analysis. The mylar sheets had a recovery of 95.3 %. This value was used to adjust the deposition values measured. To determine the measure of spray deposited versus that released, the total adjusted deposited material across all the mylar sheets across the spray fan width was compared to the amount sprayed over the width of the mylar sheet (11.1 cm), which was determined based on the traverse speed and flowrate.

Results

Nozzle Droplet Sizes and Flowrate and Spray versus Deposition

Both nozzles were operated at 21 kPa (30 psi). For the 11002 flat fan nozzle, the resulting average VMD, DV0.1, and DV0.9 values were 166.3, 84.6, and 316.0 μm, respectively. The average nozzle flowrate was 14.3 mL/s. For the 11004 flat fan nozzle, the resulting average VMD, DV0.1, and DV0.9 values were 227.5, 99.7, and 407.2, respectively. The average nozzle flowrate was 25 mL/s.

Spray versus Deposition Recovery

For the 94 L/ha spray treatment setup, 93 % of the spray applied by the nozzle over the established sampling area was recovered on the deposition samplers; likewise, 99 % was recovered for the 188 L/ha spray treatment setup.

Air Temperature and Humidity during Spray Application and Sampling Periods

Table 2 contains the air temperatures and relative humidity values measured in the spray table at the time the spray application was made for each box. Table 3 contains the air temperature and relative humidity values measured in the greenhouse during each sampling period. The zero hour volatilization and biodegradation box samples were all taken in the spray table; therefore the temperatures and relative humidity values in Table 2 correspond to those soil samples.

Soil Temperatures and Moistures

Table 4 contains the soil temperatures and moistures measured in each sampling location at the time the soil samples were collected for the volatilization boxes. Soil temperature and moisture measurements were

TABLE 2—*Air temperature and relative humidity values measured in the spray table during each spray application.*

Sample Box	Temperature (°C)	Relative Humidity (%)
94 L/ha volatilization box 1	19	44
94 L/ha volatilization box 2	18	37
94 L/ha Biodegradation	16	39
188 L/ha volatilization box 1	16	38
188 L/ha volatilization box 2	16	41
188 L/ha Biodegradation	17	39

taken at ten randomly selected locations in each of the biodegradation boxes immediately after the soil samples were collected. The soil temperature for the 94 L/ha spray rate biodegradation box was $19 \pm 0.3\,^{\circ}C$ (mean ± standard deviation), and the soil moisture at 1.5 cm was 3.5 ± 1.0 and 12.0 ± 1.3 % at 3 cm. The soil temperature for the 188 L/ha spray rate biodegradation box was $19 \pm 0.2\,^{\circ}C$ (mean ± standard deviation), and the soil moisture at 1.5 cm was 4.0 ± 0.9 and 12.9 ± 1.3 % at 3 cm. As would be expected, there was some drying out of the soil over the time of the tests with soil moisture starting out around 3 % at a depth of 1.5 cm for the beginning of the tests and dropping to around 1 % after 36 h at the same depth. The soil moisture at 3 cm depth did not noticeably change over the testing period.

Soil Texture and Physical Properties

The measured soil properties, which include *p*H, conductivity, organic matter, sand/silt/clay content, and textural class, are given Table 5.

Deposition on Soil Containment Boxes

Tables 6–11 are the adjusted (based on sampler recovery) deposition values within each sample location as defined by Figs. 4 and 5. Actual deposition on the soil surface tended to be higher than the target deposition rates of 94 and 188 L/ha in the center of the sample soil surface and lower on the outside edges. This variation in deposition across the width of the sample soil surface was a result of variation in spray pattern across the flat fan nozzles used for the applications [1]. Overall deposition mean and standard deviation for each sampling box are given in Table 12. Spray applications at the 94 L/ha rate over the three sampling boxes exceeded target application rate by 11 %, and spray application at the 188 L/ha rate over the three sampling boxes exceeded the targeted application rate by 15 %.

Conclusions

A laboratory spray table was used to mimic agricultural ground applications onto a sample soil surface to support a VOC volatilization and biodegradation study. Spray nozzles were selected to generate droplet sizes consistent with ground applications. Spray table calibration tests were conducted to determine the nozzle traverse speed that would result in spray deposition onto the soil surface at the selected levels of 94 and 188 L/ha. Soil containment boxes were constructed and the sample soil was placed into them. The boxes were then placed into a greenhouse to provide an acclimation period. During this period, watering application helped to settle the soil and to reach and maintain soil moisture levels at or near 10 %. Using

TABLE 3—*Air temperature and relative humidity values measured in the greenhouse during each soil sampling period.*

	Volatilization Boxes (Spray Rate and Replication) Temperature (°C)/Relative Humidity (%)			
HAT	94 L/ha Box 1	94 L/ha Box 2	188 L/ha Box 1	188 L/ha Box 2
1	21/39	24/33	28/31	27/25
4	29/28	28/27	29/22	24/28
12	23/28	21/30	21/30	23/26
36	23/30	21/37	23/33	23/31

TABLE 4—*Soil temperatures and moistures measured at each sampling location for each spray rate replication at each soil sampling time.*

		Volatilization Boxes (Spray Rate and Replication) Temperature (°C) Soil Moisture (%) @ 1.5/3 cm Depth			
HAT	Replication	94 L/ha Box 1	94 L/ha Box 2	188 L/ha Box 1	188 L/ha Box 2
0	1	19	19	21	20
		2.1/8.1	3.4/12.1	4.5/10.6	7.2/13.9
0	2	19	19	20	20
		1.3/7.5	2.2/7.9	3.1/9.7	5.2/10.7
0	3	19	19	20	20
		3.5/12.5	3.5/10.5	3.3/9.9	1.3/5.4
0	4	19	18	20	21
		2.5/8.7	3.5/10.9	2.8/12.3	7.1/12.7
1	1	19	20	20	21
		2.3/9.7	2.8/11.5	0.9/11.6	4.9/12.3
1	2	19	19	20	22
		2.0/10.1	2.1/7.9	1.2/8.7	10.0/13.9
1	3	19	20	21	21
		2.9/10.2	1.5/9.1	2.7/8.0	0.6/7.0
1	4	20	19	21	22
		3.5/13.0	4.6/12.5	0.3/8.7	1.5/8.4
4	1	20	22	22	24
		0.6/8.2	1.5/9.2	2.0/11.3	3.1/14.1
4	2	22	21	23	24
		3.4/11.1	3.6/11.7	3.0/10.9	2.3/6.5
4	3	20	21	22	24
		3.5/12.2	1.5/9.1	1.2/9.2	0.5/7.5
4	4	20	22	22	24
		3.3/15.5	1.8/13.0	3.7/12.3	1.5/11.3
12	1	22	23	21	23
		1.1/11.3	1.4/10.0	1.3/10.9	4.4/13.9
12	2	22	23	21	23
		1.8/12.2	2.6/11.6	0.3/7.1	2.6/8.0
12	3	22	23	20	23
		1.1/11.3	2.4/5.4	0.9/9.2	1.5/11.4
12	4	22	23	20	23
		2.5/10.9	3.1/12.2	1.7/12.5	0.6/8.7
36	1	21	22	21	23
		0.6/9.0	0.4/8.8	0.4/11.3	0.3/11.3
36	2	22	23	21	23
		0.3/7.9	1.9/10.9	1.6/7.9	1.1/8.4
36	3	22	23	21	24
		0.4/12.4	1.5/10.6	0.6/7.3	1.0/8.7
36	4	21	22	21	23
		0.8/9.1	0.7/9.4	0.5/10.1	1.8/9.2

TABLE 5—*Measured soil properties for each treatment soil container.*

Sample Box	*p*H	Conductivity (umho/cm)	Organic Matter (%)	Sand/Silt/Clay (%)	Textural Class
94 L/ha volatilization box 1	7.2	407	1.35	39/38/23	Loam
94 L/ha volatilization box 2	7.1	451	1.18	39/38/23	Loam
94 L/ha biodegradation	7.3	355	1.17	35/44/21	Loam
188 L/ha volatilization box 1	7.3	355	1.19	37/41/22	Loam
188 L/ha volatilization box 2	7.3	428	1.14	45/32/23	Loam
188 L/ha biodegradation	7.0	1060	1.14	45/32/23	Loam

TABLE 6—*Spray table deposition (L/ha) for each sampling grid location for box 1 of the 94 L/ha volatilization sample box.*

	Deposition by HAT Replication (L/ha)			
HAT	1	2	3	4
0	83.3	116.9	133.3	79.9
1	132.8	79.4	128.1	77.7
4	119.8	81.4	114.5	133.6
12	119.3	133.0	79.6	131.8
36	79.1	123.9	79.4	112.4

TABLE 7—*Spray table deposition (L/ha) for each sampling grid location for box 2 of the 94 L/ha volatilization sample box.*

	Deposition by HAT Replication (L/ha)			
HAT	1	2	3	4
0	92.3	104.2	124.3	68.3
1	120.6	67.6	131.3	103.5
4	132.4	96.2	99.1	126.0
12	109.3	122.5	68.0	130.8
36	67.3	131.8	100.1	94.6

TABLE 8—*Spray table deposition (L/ha) for each sampling grid location for the 94 L/ha biodegradation sample box.*

	Deposition by HAT Replication (L/ha)				
DAT	1	2	3	4	5
Control	114.0	118.7	108.7	⋯	⋯
0	97.2	95.9	98.9	75.4	115.9
2	124.0	74.1	100.4	⋯	⋯
4	91.5	115.0	99.6	⋯	⋯
7	113.0	113.4	75.7	⋯	⋯
14	74.9	98.1	104.3	⋯	⋯

TABLE 9—*Spray table deposition (L/ha) for each sampling grid location for box 1 of the 188 L/ha volatilization sample box.*

	Deposition by HAT Replication (L/ha)			
HAT	1	2	3	4
0	193.8	246.0	250.4	188.0
1	260.4	199.6	273.1	167.2
4	267.6	184.6	240.1	245.9
12	251.9	255.4	193.4	275.6
36	205.7	270.3	175.4	234.9

TABLE 10—*Spray table deposition (L/ha) for each sampling grid location for box 2 of the 188 L/ha volatilization sample box.*

	Deposition by HAT Replication (L/ha)			
HAT	1	2	3	4
0	153.9	256.3	249.0	199.3
1	243.8	205.1	265.3	148.2
4	285.9	151.9	246.7	251.3
12	266.0	246.4	202.0	256.2
36	208.1	275.6	150.0	238.1

TABLE 11—*Spray table deposition (L/ha) for each sampling grid location for the 188 L/ha biodegradation sample box.*

	Deposition by HAT Replication (L/ha)				
DAT	1	2	3	4	5
Control	206.4	236.3	234.7	···	···
0	131.0	234.6	137.8	159.0	231.4
2	237.1	164.6	239.6	···	···
4	229.6	219.6	140.6	···	···
7	193.2	235.5	154.1	···	···
14	170.2	134.3	244.1	···	···

TABLE 12—*Mean and standard deviation of spray deposition over the entire sampling area for each soil containment box.*

Sample Box	Overall Deposition (L/ha), Mean ± Standard Deviation
94 L/ha volatilization box 1	107 ± 23
94 L/ha volatilization box 2	105 ± 23
94 L/ha biodegradation	100 ± 16
188 L/ha volatilization box 1	229 ± 36
188 L/ha volatilization box 2	225 ± 45
188 L/ha biodegradation	197 ± 43

the selected application parameters, a spray mixture containing an aromatic solvent and a fluorometric tracer dye was applied to the soil surface using the spray table setup. Actual spray volume deposited across the surface of the soil was measured using depositional sampling methods. Depositional amounts over the whole study were close to the targeted rates, exceeding them by approximately 15 %. Soil samples were collected from the soil boxes following established times after treatment and replication locations across the soil surface. The developed methodology proved to be one that can be adapted to desired spray rates and spray droplet sizes with good repeatability and spray uniformity across the soil surface.

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References

[1] Cooper, C. D. and Alley, F. C., *Air Pollution Control: A Design Approach*, 3rd ed., Waveland Press, Inc., Prospect Heights, IL, 2002.

[2] USEPA, Counties with Monitors Violating the 2008 8-hour Ozone Standard of 0.075 parts per million (ppm), 2008. Available at http://www.epa.gov/air/ozonepollution/pdfs/2008_03_monitors_violating_2008.pdf (Last accessed 12 Aug 2008).

[3] Munari, F., Mapelli, G. P., Kotzias, D., and Duane, M., "Performance and Characteristics of a Trace Gas Analyzer for the Determination of Volatile Organic Compounds in Air," *J. High Resolut. Chromatogr.*, Vol. 19, 1996, pp. 333–338.

[4] Aspelin, A. L., *Pesticide Industry Sales and Usage: 1994 and 1995 Market Estimates*, United States Environmental Protection Agency, Washington, D.C., 1997.

[5] U.S. Environmental Protection Agency (USEPA), 1995, *Emission Factor Documentation for AP-42 Section 9.2.2—Pesticide Application*, USEPA, Office of Air Quality Planning and Standards, Emission Factors and Inventory Group, Research Triangle Park, NC.

[6] *Organic Chemicals in the Soil Environment*, C. A. I. Goring and J. W. Hamaker, Eds., Marcel Dekker, Inc., New York, 1972, Vol. 1.

[7] Potter, C., "An Improved Laboratory Apparatus for Applying Direct Sprays and Surface Films, with Data on the Electrostatic Charge on Atomized Spray Fluids," *Ann. Appl. Biol.*, Vol. 39(1), 1952, pp.

1–28.
[8] Mason, E. B. B. and Adamson, R. M., "A Sprayer for Applying Herbicides to Pots or Flats," *Weeds.*, Vol. 10(4), 1962, pp. 330–332.
[9] Burnside, O. C., "A Laboratory Sprayer Flamer," *Weed Sci.*, Vol. 17(1), 1969, pp. 102–104.
[10] Davis, E. A., "Laboratory and Greenhouse Spray Chamber," *Weed Sci.*, Vol. 25(3), 1977, pp. 221–223.
[11] Bouse, L. F. and Bovey, R. W., "A Laboratory Sprayer for Potted Plants," *Weeds.*, Vol. 15(1), 1967, pp. 89–91.
[12] Fritz, B. K., Parker, C. T., López, J. D., Jr., Hoffmann, W. C., and Schleider, P. G., "Deposition and Droplet Sizing Characterization of a Laboratory Spray Table," *Appl. Eng. Agric.*, Vol. 25(2), 2009, pp. 175–180.
[13] Fritz, B. K., Hoffmann, W. C., and López, J., "Development and Testing of a Laboratory Spray Table Methodology to Bioassay Simulated Levels of Aerial Spray Drift," *J. ASTM Int.*, Vol. 6(6), 2009, paper ID JAI102125.
[14] ASTM E1260–03, 2009, "Standard Test Method for Determining Liquid Drop Size Characteristics in a Spray Using Optical Non-Imaging Light-Scattering Instruments," *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.