Methods To Measure Herbicide Volatility

Thomas C. Mueller*

Herbicides are powerful chemical agents that exert strong biological activity on plants. The release of new formulations of dicamba and 2,4-D and their use in transgenic agronomic crops will probably result in many more applications during the time of year when sensitive nontarget vegetation will be present. The use of herbicides is regulated by the U.S. Environmental Protection Agency, and there are usually no negative effects on nontarget species. One negative aspect of herbicide use occurs when the application moves away from the target area and causes unwanted plant injury on susceptible species. Interest in herbicide drift is increasing, as evidenced by the number of refereed articles that investigate the mitigation or potential for herbicide drift (Figure 1). Although the topic of herbicide drift is broad, in this manuscript I will focus on an overview of off-site movement from a historical perspective and then discuss specific research protocols to examine vapor drift.

Herbicide can drift off target in basically three ways. The first is when the herbicide droplets never hit the target because the wind blows them off the target area, and this is called particle drift or physical drift. It is possible that some droplets discharged from the nozzle may evaporate before hitting the target, and these would move primarily with the fine spray particles. The second mechanism for herbicide drift occurs when the herbicide lands on the target area and then later changes back into a gaseous form and moves off-site, and this is called vapor drift. The third loss mechanism is movement with wind-blown soil, but these are normally isolated incidences under extreme climatic conditions.

The capstone research project on particle spray drift is the work of the Spray Drift Task Force, which is available online (Anonymous 2013). This report provides a wealth of information on all the factors that affect particle spray drift: boom height, wind speed, nozzle selection and the resulting droplet spectrum sizes, and so forth. Field scale particle drift studies are especially difficult to conduct accurately given the transient nature of wind under most field conditions, and those research protocols are beyond the scope of this manuscript.

The Spray Drift Task Force defines drift as the particle movement immediately after pesticide application (Anonymous 2013). One interesting note from the Spray Drift Task Force report was the following definition: ''pesticide drift does not include the movement of pesticide caused by other types of migration such as windblown soil particles or volatilization from the application site after application'' (Anonymous 2013, p 4). This direct quotation epitomizes the challenges of nomenclature in such complex scenarios as herbicide drift, where some people will include vapor drift or movement with windblown soil particles as sources of ''pesticide drift'' that contributes to off-site movement. As previously mentioned, at times, various groups are sometimes hesitant to use the words ''vapor'' or ''volatilization,'' preferring to use terms such as ''secondary loss,'' ''post application movement,'' or other terminology. For the sake of this report, the term ''vapor drift'' will denote the movement of herbicide after application after it has reached the target, the target being plant foliage or soil.

There is a wealth of historical knowledge on 2,4-D volatility, with the featured researcher being G. Staten of New Mexico State University, who showed differential volatility of 2,4-D ester, sodium salt, ammonium, and acid formulations (Staten 1946). Several others also published reports showing differential volatility, including Brown et al. (1948), Day et al. (1959), Grover et al. (1972), and Que Hee et al. (1975). Staten was a pioneering researcher who understood the importance of determining how the herbicide moved off target and what the biological consequences were. He conducted a wide variety of studies, including water carriage, spray drift, and volatility studies using a variety of innovative methods. His take-home message was that nonvolatile acid or salt formulations could be used near cotton (*Gossypium hirsutum* L.) when care was taken to avoid particle spray drift, and he concluded that highly volatile formulations could not be used in New Mexico in summer near cotton crops.

* Professor, Department of Plant Sciences, University of Tennessee, Knoxville, TN 37996. Corresponding author's E-mail: tmueller@utk.edu
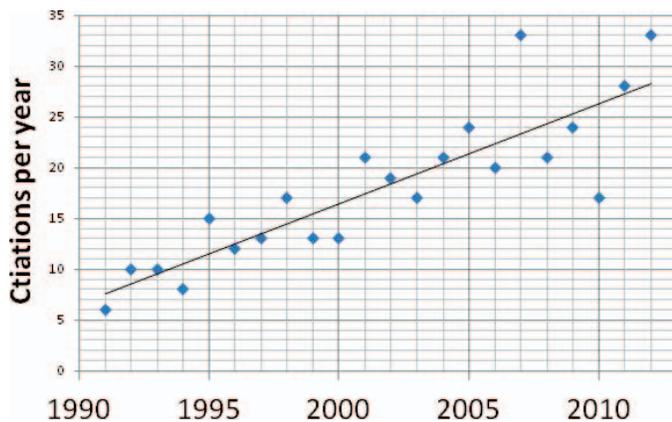
Figure 1. Number of refereed journal articles found in Web of Science using the search terms "Herbicide" and "Drift" from years 1991–2012.

One aspect of particle drift that is becoming more prominent is the idea of a very stable inversion layer in the atmosphere that allows fine spray particles (< 200 μm) to remain suspended and to move laterally for great distances (Webster 2013). This observation is an apparent contradiction to the idea that to reduce particle drift, herbicides should be sprayed when the wind is at lower velocities. There is no doubt that atmospheric conditions play a substantial role in both particle and vapor drift.

The remainder of this report deals with various attempts to quantify vapor drift of herbicides. The author fully recognizes that one of the central challenges of field research is how to separate particle spray drift from vapor spray drift, and, while some important considerations are brought forward, this discernment remains a challenge for field researchers.

Protocols and Methods

Herbicide vapor research has three basic levels of experimentation: lab, greenhouse, and field. Preliminary research is usually conducted under controlled laboratory conditions, because these studies are usually more rapid and cost less to perform. On the basis of initial laboratory and later greenhouse studies, a natural progression moves to the more difficult and costly field research methods. The ability to control the environment decreases; thus, the precision of measurements decreases and subsequent error possibilities increase as the research spectrum progresses from lab to field, which is one reason why certain observations under controlled lab conditions are not always consistent with results generated under field conditions. This does not mean that lab or greenhouse studies are not

valuable, but they do not adequately represent the real-world scenario of what happens in farmers' fields. An informative video on the subject is available from BASF (Anonymous 2012).

Lab Studies. The first general type of laboratory studies should determine the inherent propensity of a given formulation to change from the solid/liquid state to gaseous form. This can be done basically by adding a known mass of the spray solution to a very carefully weighed container, exposing the system to a various temperature/relative humidity environment, and then again weighing the container after some amount of the product has evaporated (Anonymous 2012). These studies may use radiolabeled material to track more easily how much of and where the product has moved (Strachan et al. 2013).

The specifics of how to conduct research examining the volatility of a particular compound will depend on the chemical characteristics of that molecule. In the preliminary stages of formulation screening for differences in volatility, the concentration of herbicide in the spray formulation mixture may not be a major factor, since in theory the water evaporates fairly quickly. Commonly, the herbicide dose introduced to the test chamber (glass slide, petri dish, etc.) will be at a concentration that may approximate field conditions. The conditions of the early-stage lab tests should be appropriate to discern differences between the experimental formulations under different environmental conditions, such as slightly elevated temperature, potentially altered humidity levels, or differences in air movement. If volatility of a specific herbicide is a concern, then that molecule probably has some propensity for vapor movement. A normal duration for a laboratory volatility study is 24 to 48 h. Usually the experimental formulations are compared with a standard, already registered herbicide formulation with known volatility characteristics (Anonymous 2012; Strachan et al. 2010).

Greenhouse Studies. A typical next step is to use some sort of a bioassay plant growth system that allows the researcher to place a petri dish or other vessel containing the spray solution in the immediate vicinity of a closed environment in which untreated yet sensitive bioindicator plants have been placed. These studies are often conducted inside a greenhouse. These usually have a clear plastic cover to allow light to enter and enable the plants to grow, while maintaining the vapors inside the system

(Anonymous 2012; Strachan et al. 2010). One common name for this setup is a humidome plant growth system. Although not representative of field conditions, this system provides a visual representation of actual plant responses to various formulations of different chemicals. With the appropriate untreated controls, these can provide valuable information on the relative volatility of different herbicide formulations. A major advantage of these bioassay-based systems is that no complicated, expensive analytical equipment is required. With the proper choice of sensitive bioassay plant species, this research can have sufficient sensitivity to determine volatility. However, the quantitative difference among different formulations might not be as clearly delineated as in the laboratory studies because of the variability of the bioassay species being greater than the variability of a physical loss measurement.

Field Studies. Field studies are far more challenging than lab or greenhouse systems, but they can provide a direct assessment under real-world conditions. The specific weed or crop species, soil conditions, availability of application equipment, cross-contamination of different treatments with each other, and especially climatic conditions are all important parameters. Field studies are usually conducted in large areas of cropland (> 10 ha) using designated plots within that larger field. The first consideration is treated plot size, such that whatever the volatile ''signal'' you are trying to measure is adequate to provide meaningful treatment differences. Another important consideration is the buffer distance between the various plots. For instance, some research utilized 15-m by 15-m plot dimensions and a buffer distance of 120 m between plots (Mueller et al. 2013). It is also important to select an area where chemicals will not drift in from other applications.

At this point in field studies two different paths can be chosen: some type of air sampling followed by chemical analysis, or the insertion of bioassay indicator plants at a certain time interval after application. Both systems have advantages. Air sampling followed by chemical analysis provides more quantitative measurements, and the results are not dependent on the growth of the bioassay plants. The advantage of the bioassay system lies in the greater simplicity of equipment needed and the direct measurement of a plant response from the secondary movement of the chemical. Neither method can discern whether the herbicide arrives by volatility or by particle deposition.

Bioassay-Based Research. As this designation implies, indicator or bioassay plants are used to quantify herbicide effects. With respect to dicamba, Behrens and Lueschen (1979) published a comprehensive report. Many of their research techniques are still valid today, and with the introduction of new formulations of herbicides that may volatilize and move off target, these research methods are being reconsidered. In general terms, a target area is sprayed with the herbicide without the bioassay plants present. Following a predetermined interval to allow for all the spray particles to settle (thus theoretically eliminating particle drift), the bioassay plants are introduced to the target area at strategic sampling locations to ''capture'' volatile herbicide movement. The bioassay plant may be left there permanently to grow until measured, or new replacement bioassay plants may be placed at that location to examine potential vapor drift over a temporal scale. In Behrens and Lueschen's (1979) research, the field studies utilized corn plants sprayed with several different formulations of dicamba, and then soybean [*Glycine max* (L.) Merr.] plants were placed on pedestals at various locations upwind and downwind from the corn plot. The plants were then relocated to a greenhouse, allowed to grow, and then were subjected to various measurements to characterize plant growth. This system, with modifications, is still being used to examine the vapor movement of newer chemistries, including aminocyclopyrachlor and aminopyralid (Strachan et al. 2013) or older chemistries such as 2,4-D and triclopyr (Sciumbato et al. 2004b) compared with dicamba.

One aspect of the use of bioassay-based research systems is the variability of the measurement. The herbicide concentration absorbed at a specific location will cause a given effect on a bioassay species, but this given effect is dependent on how that bioassay plant grows after it is been exposed. Another factor is the difficulty, at times, in accurately quantifying the plant response from a herbicide. Strachan et al. (2013) reported bioassay plant responses as percent injury, apparent leaf surface area, and severity of leaf cupping as somewhat confounded variables (thus the term apparent leaf surface area). To quantify injury to cotton and soybean plants from exposure to auxin-like herbicides, Sciumbato et al. (2004a) published detailed descriptions of symptomology from 2,4-D, triclopyr, and dicamba. At lower herbicide concentrations the descriptions tended to be fairly precise, but at higher herbicide concentrations, as the plants

approached death and necrosis, the descriptions were more general.

Sampler-Based Research. Several challenges are inherent in the use of air sampling systems followed by chemical analysis in field research to examine herbicide volatility. How long is the interval after applying the herbicide to start sampling? How can the samplers be moved into the plot area without becoming contaminated by previously sprayed chemicals from physical contact? How many samplers should be used and at what height should they be placed (Hapeman et al. 2013)? What is the time frame to collect samples? Many times there are limitations on the availability of electricity in a field situation, so battery life may determine how long samplers run to collect any potential vapors. Another pertinent question is: Can the volatile emissions be captured on something that can be used for chemical analysis? This will depend on the chemical you are measuring. Preliminary assays need to be conducted. Once the capture of the volatile residues has been proven, it must be verified that the residues can successfully be extracted and quantified using a reproducible analytical technique, such as liquid chromatography–mass spectrometry (LC-MS). Other factors to consider include total airflow through the samplers, total duration of sampling interval, stability of analytes on the storage medium, cross-contamination of the different treatments under sometimes challenging field conditions, chemical stability under field storage conditions, and other factors.

The air samplers are normally placed inside or very near the treated area. Multiple measurements often are taken from a single treated plot if the air samplers are small and battery operated. If the air sampler is larger and collects a larger volume of air from the treated area, there may be fewer or only one sampler per plot. The sampling medium varies but can range from a cellulosic filter paper to combinations of paper filters in series with more absorptive matrices such as polyurethane foam (PUF).

Another challenge is the interpretation of the chemical concentration on whatever collection medium is used. What does this value mean? Caution should be used in making assessments of the magnitude of vapor drift based on these types of studies, since many factors will influence nontarget effects under real-world field conditions. However, these types of test systems can reliably determine the relative propensity of different formulations to volatilize and move under field conditions. To make a prediction that a certain percentage of a particular chemical would vaporize under certain parameters is speculative and not supported by this type of data. This type of experiment will elucidate the relative volatility of different treatments under a specific set of field conditions and experimental design (e.g., formulation X is Y% less volatile than formulation Z under a given set of field parameters).

A Case History for an Example. Although not the only valid test system, a recent study was designed to examine differential dicamba formulations under field conditions (Mueller et al. 2013). In subsequent research the authors optimized and refined some characteristics of their test system, so this discussion is provided as a guide.

Soybeans or the target crop is planted such that the plants will be 10–20 cm in height at the time of POST herbicide application, where possible vapor drift will be studied. Plot size was 15 m by 15 m. Applications were made using a 3.3-m-wide handheld boom, and 12-L stainless steel can was used for each respective treatment. TTI nozzles (Turbo TeeJet Induction nozzles, TeeJet www.teejet.com) sprayed a very coarse droplet spectrum (> 500 μm), which reduced the amount of fines. Mueller et al. (2013) routinely made their applications at 6 A.M., when the wind is usually calm (< 2 km hr^{-1}) in the tested geography. They proceeded to spray the respective treatments, each representing a different formulation, a different adjuvant system, or whatever the test was based upon. Normally they could spray three to five treatments in about 30 min. By this time, they made the assumption that all the very fine droplets had settled onto the target. Some scientists believe that some small droplets are still suspended in the atmosphere, introducing a possible error in this system. This may be a potential error, but it is the same error for all respective treatments, so if this error occurs it is canceled out by all treatments having the same or comparable error.

A single, high-volume air sampler (HI-Q Environmental, hi-q.net) is placed in the middle of each plot. Depending on the requirements of the test, Mueller et al. (2013) sometimes put two of the same treatments immediately adjacent to each other for ease of conducting the experiment. Air samplers were powered by electricity from propane-powered generators that can run up to 4 d on a single 45-kg tank of propane. The air samplers were equipped with a detachable solid sampling tube, which has a

Mueller: Research methods—herbicide volatility • 119

microfiber filter on the exterior inlet and a PUF plug encased in a glass housing in-line ahead of the air pump. At various time intervals, they collected each respective sample and placed it into immediate storage in a cooler and then a freezer. Typical time intervals for the research were 0 to 6, 6 to 12, 12 to 24, and 24 to 36 h after initial treatment. The samplers have digital readouts for cumulative values for time and air volume, which are reset at each sampling interval.

After conducting this research for several years, the greatest problem encountered was rainfall events during field air sampling. The samplers are not built to withstand rainfall, so plastic shields were constructed to protect them during heavy rain. Rainfall also will obviously alter the amount of potential herbicide vapor to move off the plant or soil since the rainwater could wash the chemical off leaves, move it into the soil, or both.

A dedicated weather station in close proximity to the field site is essential to the interpretation of results. Minimum climatic data include temperature, rainfall, wind speed, and wind direction. Other environmental parameters such as light intensity can be helpful, but these are the minimum. The weather station should be set to collect data at a 15-min time step. Shorter time intervals (e.g., 1 min) result in excessively large data sets that will be difficult to interpret, whereas longer time intervals lack refinement to help describe observations.

After samples are collected, they are extracted with organic solvents, followed by chemical analysis. Most research utilizes LC-MS, and the concentrations using the field methods of Mueller et al. (2013) have normally been substantially above analytical limits of detection. For different herbicides that might not volatilize as much or if the sampling intervals are much shorter, then sensitivity or lack of sensitivity could become a problem.

Parting Comments

Research to determine the relative secondary loss amounts of respective formulations can provide guidance for their use. Glyphosate resistance will continue to be a major factor in weed control, and the use of auxinic chemistries can result in production systems that are effective at controlling weeds and economical to the point at which farmers are profitable and environmentally sustainable such that nontarget effects are reduced.

Literature Cited

Anonymous (2012) The Making of an Advanced Dicamba Formulation. http://www.agro.basf.us/information/video-library/dicamba.html. Accessed August 25, 2013

Anonymous (2013) Spray Drift Task Force Report. www.agdrift.com. Accessed August 25, 2013

Behrens R, Lueschen WE (1979) Dicamba volatility. Weed Sci 27:486–493

Brown CA, Holdeman QL, Hagood ES (1948) Injuries to Cotton by 2,4-D. Baton Rouge, LA: Louisiana State University and Agricultural and Mechanical College, Agricultural Experiment Station Bull. 426. 19 p

Day BE, Johnson E, Dewlen JL (1959) Volatility of herbicides under field conditions. Hilgardia 28:255–267

Grover R, Maybank J, Yoshida K (1972) Droplet and vapor drift from butyl ester and dimethlyamine salt of 2,4-D. Weed Sci 20:320–324

Hapeman CJ, McConnell LL, Potter TL, Harman-Fetcho J, Schmidt WF, Rice P, Schaffer BA, Curry R (2013) Endosulfan in the atmosphere of South Florida: transport to Everglades and Biscayne National Parks. Atmos Environ 66:131–140

Mueller TC, Wright DR, Remund KN (2013) Effect of formulation and application time of day on detecting dicamba in the air under field conditions. Weed Sci 61:586–593

Que Hee SS, Sutherland RG, McKinlay KS, Saha JG (1975) Factors affecting the volatility of DDT, dieldrin, and dimethylamine salt of 2,4-D from leaf and glass surfaces. Bull Environ Contamin Toxicol 31:284–290

Sciumbato AS, Chandler JM, Senseman SA, Bovey RW, Smith KL (2004a) Determining exposure to auxin-like herbicides. I. Quantifying injury to cotton and soybean. Weed Technol 18:1125–1134

Sciumbato AS, Chandler JM, Senseman SA, Bovey RW, Smith KL (2004b) Determining exposure to auxin-like herbicides. II. Practical applications to quantify volatility. Weed Technol 18:1135–1142

Staten G (1946) Contamination of cotton fields by 2,4-D or hormone-type weed sprays. Agron J 38:536–544

Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B, Lindenmeyer RB, Shaner DL, Westra P, Brunk G (2010) Vapor movement of synthetic auxin herbicides: aminocyclopyrachlor, aminocyclopyrachlor-methyl ester, dicamba, and aminopyralid. Weed Sci 58:103–108

Strachan SD, Ferry NM, Cooper TL (2013) Vapor movement of aminocyclopyrachlor, aminopyralid, and dicamba in the field. Weed Technol 27:143–155

Webster EP (2013) Herbicide drift: past, present, future. Proc South Weed Sci Soc 66:46