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# Herbicide Drift from Genetically Engineered Herbicide-Tolerant Crops

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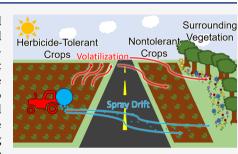


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ABSTRACT: In recent years, off-target herbicide drift has been increasingly reported to lead to damage to nontarget vegetation in the U.S. These reports have coincided with the widespread adoption of genetically modified crops with new herbicide-tolerance traits. Planting crops with these traits may indirectly lead to increased drift both by increasing the use of the corresponding herbicides and by facilitating their use as postemergence herbicides later in the season. While extensive efforts have aimed to reduce herbicide drift, critical uncertainties remain regarding the physiochemical phenomena that drive the entry of herbicides into the atmosphere as well as the atmospheric processes that may influence short- and long-range transport. Resolving these uncertainties will support the development of effective approaches to reduce herbicide drift.



KEYWORDS: herbicide-tolerant crops, herbicide drift, Dicamba, 2,4-D, herbicide volatilization

### USE OF HERBICIDES ON GENETICALLY MODIFIED CROPS

Since the commercialization of genetically modified (GM) crops in the early 1990s,¹ the ability for plants to tolerate herbicides has been among the most commonly incorporated traits in agriculture. In 2020, ~90% of all corn, cotton, and soybeans planted in the U.S. were GM variants tolerant to one or more herbicides.² Until recently, the primary herbicide used on herbicide-tolerant crops was glyphosate, which was able to control most weeds independently of other methods.³ After the release of glyphosate-tolerant crops in the 1990s,³ use of glyphosate in the U.S. increased 10-fold between 1996 and 2012, resulting in glyphosate becoming the most used herbicide in the U.S.⁴

However, increased glyphosate use coincided with widespread emergence of glyphosate-resistant weeds. These glyphosate-resistant weeds prompted the development and commercialization of GM crops that tolerate additional herbicides, including the auxin herbicides dicamba 1,4-dichlorophenoxyacetic acid (2,4-D). Importantly, these new GM crops allowed for applications of dicamba and 2,4-D after GM broadleaf plants like cotton and soybean sprouted from the soil (postemergent applications). The ability to use these herbicides postemergently on the GM tolerant crops has been embraced in the U.S.: in 2017–2018, 34% of cotton was treated with dicamba postemergently, while only 17% was treated pre-emergently.

Like glyphosate, dicamba and 2,4-D have been used more frequently after the introduction of their respective herbicidetolerant crops. In particular, the use of dicamba increased by a factor of 2.3 from 2016 to 2017 after dicamba-tolerant crops were introduced in 2015 (Figure 1).<sup>4</sup> Subsequently, both adoption of dicamba-tolerance traits and dicamba use have continued to increase. Over the 2017–2018 period, 33% of soybean and 56% of cotton planted in the U.S. expressed tolerance to dicamba, while planting of soybean and cotton that exclusively tolerated glyphosate dropped by approximately 50% and 75%, respectively. <sup>14,15</sup> Dicamba use on soybeans in the U.S. increased from 190,000 kg applied on 1.9 million acres (2% of all soybeans) in 2014–2015 to 4,780,000 kg applied on 23.8 million acres (21% of all soybeans) in 2017–2018. <sup>15</sup>

While reducing the singular reliance on glyphosate, the application of herbicides on these herbicide-tolerant crops has raised new challenges that must be addressed for their safe and sustainable use. In particular, the use of dicamba and 2,4-D on herbicide-tolerant crops has been associated with numerous incidents of damage to nontolerant vegetation, <sup>16–21</sup> which has been largely attributed to the movement of both herbicides from tolerant to nontolerant vegetation via atmospheric transport—i.e., "herbicide drift". While many herbicides undergo drift over a range of scales, short-range drift of dicamba and 2,4-D from tolerant crops is particularly associated with off-target damage because both dicamba and

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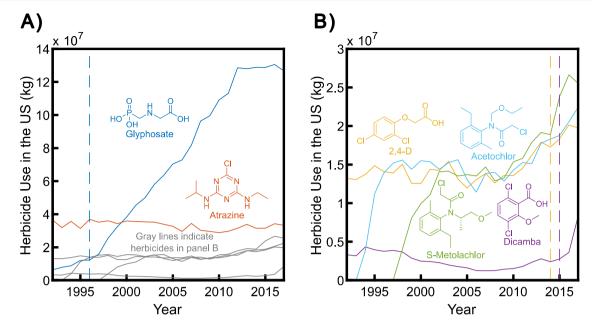


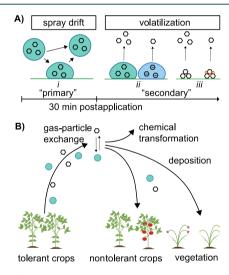
Figure 1. Use of (A) glyphosate and atrazine and (B) 2,4-D, acetochlor, S-metolachlor, and dicamba in the U.S. Data from ref 4. Low estimate data used and replotted. Dashed lines indicate the release of GM crops tolerant to the respectively colored herbicide. Gray lines in panel (A) indicate herbicide uses plotted in panel (B).

2,4-D damage susceptible plants at a fraction (~0.01% and ~0.5%, respectively) of their use rates on GM tolerant crops. <sup>22,23</sup> This effect may be exacerbated when GM tolerant crops are planted near susceptible nontolerant crops. Following the release of GM dicamba and 2,4-D tolerant crops, total herbicide drift complaints in the U.S. increased from ~1,000 complaints per year from 2013 to 2016 to over 3,000 in 2017 and 2,300 in 2018. <sup>21</sup> In response to these concerns, three low-volatility dicamba products that were previously approved for postemergence use by the U.S. Environmental Protection Agency (EPA) were restricted in June 2020. <sup>24–26</sup> Most recently, the U.S. EPA reapproved two of these products with new and modified restrictions in October 2020 for use until 2025. <sup>27,28</sup>

Herbicide drift has been and continues to be a subject of scientific, regulatory, and public discourse, requiring comprehensive understanding of the underlying physical and chemical processes that determine the entry and fate of herbicides in the atmosphere. Consequently, the ability to assess and prevent damage by drift remains limited. Herein, we define current understanding of the off-target movement of the herbicides dicamba and 2,4-D, which determines their impacts to nontarget crops and vegetation. We discuss key opportunities for environmental chemists and engineers to address critical research gaps to understand and prevent negative impacts of dicamba, 2,4-D, and other herbicides applied on herbicide-tolerant crops.

## 2. OFF-SITE HERBICIDE MOVEMENT AND U.S. REGULATION

Herbicides enter the atmosphere through multiple specific processes (Figure 2A). During initial application, sprayed droplets of herbicide solution can move off-site prior to or shortly after contacting target vegetation or soil (i.e., spray/particle drift) (Figure 2A, (i)). Spray drift is considered the major contributor to "primary drift", which has been measured within 30 min after application. <sup>21,29</sup> In contrast, damage caused



**Figure 2.** (A) Processes that initiate dicamba and 2,4-D drift including spray drift (i) and volatilization from the solution phase (ii) and solid phase (iii). Spray drift likely dominates "primary drift", which is typically considered to occur within 30 min after application, while volatilization from either phase likely dominates secondary drift, which occurs more than 30 min after application. (B) Dicamba and 2,4-D drift and subsequent atmospheric fate processes.

by "secondary drift" occurs up to days after application. <sup>21,29</sup> Both primary and secondary drift have been found to cause damage in field trials. <sup>29</sup> While physical movement of dicambaladen dust from soil or vegetation contributes to secondary drift, most secondary drift results from vapor drift upon herbicide volatilization from either the spray solution (Figure 2A, (ii)) or a solid residue formed after drying (Figure 2A, (iii)). Herbicide volatilization may be particularly exacerbated by the application of dicamba and 2,4-D as postemergent herbicides on herbicide-tolerant crops later in the growing season, during which both higher temperatures and increased deposition on vegetation instead of soil contribute to greater

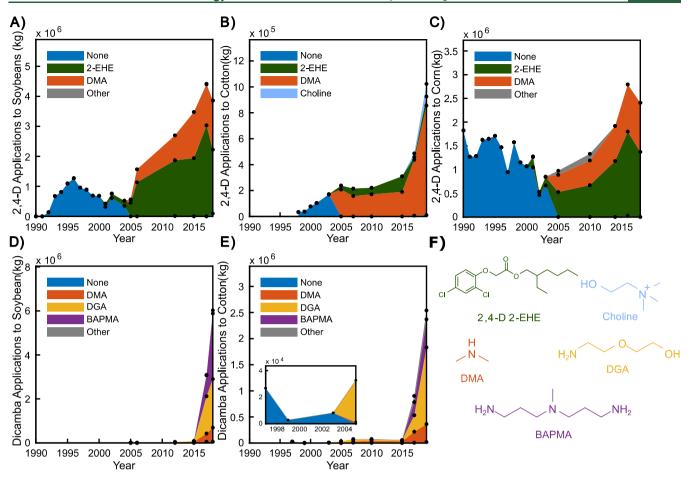


Figure 3. Use of 2,4-D on (A) soybeans, (B) cotton, and (C) corn and dicamba on (D) soybeans and (E) cotton as well as (F) the herbicide and amine structures in addition to those in Figure 1. Colors represent different formulation components. Data from USDA NASS based on survey data of region states and subject to confidentiality/privacy data gaps. "None" indicates that the product is applied as the original herbicide (free acid) without additions and was assumed to be the case when no specific formulation was listed in the data. "Other" indicates low use forms of the herbicide.

volatilization.  $^{30-32}$  The amount of herbicide that volatilizes will be influenced by processes including plant uptake,  $^{33-35}$  biodegradation,  $^{36-39}$  and photodegradation, particularly on leaf surfaces.  $^{40,41}$ 

It should be noted that off-target herbicide damage can result from other pathways beyond drift including shared equipment contamination. In triply rinsed containers, both 2,4-D and dicamba remained detectable, 42 and concentrations of dicamba remained sufficient to damage nontolerant crops. 43 In contrast, off-site transport in surface and groundwater is not widely considered for 2,4-D nor dicamba.

To prevent off-target damage from dicamba and 2,4-D drift, the U.S. EPA restricts the use of these herbicides on tolerant crops in product-specific registrations. The registrations for 2,4-D on tolerant soybeans and corn have remained largely unaltered since 2014 beyond expanding postemergent applications of 2,4-D in additional U.S. states. In contrast, comparable registrations of dicamba products for use on tolerant crops have been substantially revised from their initial time-limited registration in 2016 and subsequent reregistration in October 2018. In response to off-target damage concerns, the registrations of three postemergent dicamba products were vacated in June 2020. Two of the products were subsequently reregistered in October 2020 with new and updated requirements. A fourth dicamba product contain-

ing the herbicide S-metolachlor, originally approved in April 2019, was unaffected by the June 2020 decision and also reregistered in October 2020. 27,28

Across these registrations, common requirements intended to reduce herbicide drift include restricting nozzle types to those that generate coarse droplets that settle rapidly and prohibiting application during meteorological conditions that contribute to drift damage (i.e., high wind speeds, atmospheric inversions). <sup>32,47</sup> In addition, a required buffer area allows the herbicide to settle and dissipate before reaching surrounding vegetation. While the registration of 2,4-D products required a 30-ft (9 m) buffer area, <sup>45</sup> the 2018 registration of dicamba products required a 110-ft (34 m) zone downwind, and in cases where endangered species are present, a 57-ft (17 m) zone in the remaining directions. <sup>21</sup> In October 2020, the downwind buffer area was extended to 240-ft (73 m) generally and 310-ft (95 m) in the presence of downwind endangered species. <sup>27</sup>

The 2020 reregistrations of dicamba products also introduced additional requirements on the chemical additives included in dicamba applications. The application of all three registered products requires additional proprietary pH buffering agents (referred to as volatility reduction agents, VRAs). Two products also require a drift reduction agent (DRA) that increases droplet deposition efficiency. These

new components are required alongside product-specific formulation components (i.e., amines) that were required in prior registrations.

### 3. CHEMICAL CONTROL OF HERBICIDE DRIFT

Formulation components, both those included previously and those newly added, are integral to registrations aimed at preventing dicamba and 2,4-D drift. Herein, we describe the mechanisms by which these constituents alter drift, evidence (when available) of their impact, and remaining questions regarding their function.

**Drift Reducing Adjuvants (DRAs).** DRAs (i.e., polymers, surfactants, and oil emulsions), sometimes referred to as spray/drift reducing/controlling adjuvants, are used alongside required nozzles to control droplet size.<sup>27</sup> While increasing droplet size results in higher settling velocities with reduced potential for drift, larger droplets have reduced herbicide coverage which limits weed control.<sup>51</sup> DRAs are intended to change the fluid properties (i.e., surface tension, viscosity) to achieve droplets with a specific size distribution to reduce drift and maximize herbicide coverage.<sup>51</sup>

Due to the chemical diversity of DRAs, each DRA product must be tested alongside dicamba and 2,4-D to ensure that the mixture does not increase spray drift prior to being approved. Although DRAs are required for the application of two postemergent dicamba products, evidence that DRAs prevent off-target dicamba drift remains inconclusive. Furthermore, DRAs have been observed to either increase or decrease dicamba and 2,4-D volatilization in different studies, 53,54 warranting additional evaluation of the effects of DRAs on herbicide volatilization after deposition.

Free Acid and Ester Variants. Apart from DRAs, most chemical additives are intended to prevent herbicide volatilization rather than spray drift. The tendency of the active agent to volatilize will depend on its chemical properties. In principle, herbicides can volatilize from the solution phase (i.e., the deposited droplet, Figure 2A, (ii)), relating to Henry's constant of the herbicide, or from the solid residue formed after the droplet dries (Figure 2A, (iii)), relating to their vapor pressure. Alone, the so-called "free acid" forms of dicamba and 2,4-D are both semivolatile organic compounds (SVOCs) with moderately high Henry's constants  $(1.0 \times 10^{-4} \text{ Pa m}^3 \text{ mol}^{-1})$ and  $9.9 \times 10^{-3}$  Pa m<sup>3</sup> mol<sup>-1</sup>, respectively) and vapor pressures  $(1.7 \times 10^{-3} \text{ Pa and } 1.9 \times 10^{-5} \text{ Pa, respectively}).^{55,56} 2,4-D \text{ can}$ also be applied as an ester variant (e.g., the 2-ethylhexyl ester (2-EHE)), which has a higher Henry's constant (1.8 Pa m<sup>3</sup>  $\mathrm{mol}^{-1}$ ) and vapor pressure (4.8  $\times$  10<sup>-2</sup> Pa) than 2,4-D free acid.<sup>56</sup> 2,4-D-2-EHE, which is more bioactive than the free acid,<sup>57</sup> is widely used, accounting for 64% of total 2,4-D applied to corn in 2016 and 69% of total 2,4-D applied to soybeans in 2017 (Figure 3A,C).<sup>58</sup> However, 2,4-D-2-EHE is not registered for postemergent use on 2,4-D-tolerant

Amines. Amines are included in formulations at a 1:1 molar ratio with dicamba and 2,4-D to form lower volatility salts upon drying to a residue (Figure 2A, (iii)), as well as increase aqueous solubility of 2,4-D in particular.<sup>59</sup> Each herbicideamine pair is registered independently by the U.S. EPA. Since 2005, most 2,4-D applications on cotton include dimethylamine (DMA), second only to the 2-EHE product for soybean and corn (Figure 3A,C).<sup>58</sup> In 2014, a 2,4-D choline salt, which also includes glyphosate, was approved by the U.S. EPA.<sup>44</sup> From 2017 to 2019, the 2,4-D choline almost doubled in use

on cotton in the U.S.<sup>58</sup> Experiments evaluating damage to susceptible bioassay cotton plants indicated that amounts of 2,4-D that volatilize from DMA and choline products are similar to one another and lower than the 2-EHE form.<sup>60</sup>

Like 2,4-D, dicamba products are applied as amine salts. Formulations containing diglycolamine (DGA) $^{61,62}$  and N,N-bis(3-aminopropyl)methylamine (BAPMA) $^{63}$  made up 80% of dicamba applications to cotton and soybeans in 2017 (Figure 3D,E). The remaining 20% is applied as the DMA salt (15%), while products with no reported counterion (5%) or sodium and isopropylamine salts (<1%) are minor parts of the market share. St Only DGA and BAPMA salts, which are less volatile than DMA salts,  $^{32,47,64,65}$  are currently approved for postemergent dicamba use,  $^{48-50}$  which may account for their market dominance in recent years.

Although the inclusion of amines in dicamba and 2,4-D formulations is near-ubiquitous, the underlying phenomena that result in reduced herbicide volatilization remain an active area of inquiry. When the sprayed herbicide solution dries to a solid residue, intermolecular bonds between the herbicide and the amine are thought to form that span a continuum from electrostatic interactions (i.e., between charged molecules formed upon proton transfer from the herbicide carboxylic acid to the amine) to hydrogen bonds (i.e., between the neutral molecules involving the same functional groups). 66,67 As organic molecules that participate in more extensive solid-phase hydrogen bonding tend to have greater sublimation enthalpies, 68,69 formation of these intermolecular bonds in the herbicide residue may contribute to decreased herbicide volatility.

Another key question is why amines vary in their ability to suppress herbicide volatilization. For example, larger amines with multiple hydrogen bonding moieties (i.e., DGA, BAPMA, diethanolamine, tallow amine) tend to reduce dicamba volatility relative to DMA, which contains one hydrogen bonding moiety. Previously, we compared a series of amines to understand which amine properties are associated with greater suppression of herbicide volatilization. Our results suggested that the number of intermolecular bonds that an amine could form with herbicide molecules was of greater importance than other characteristics including molecular weight, amine order, or  $pK_a$ . Further characterization of the intermolecular bonds between amines and herbicide may yield greater insight into this trend.

**Volatility Reducing Adjuvants (VRAs).** Dicamba products reregistered in 2020 by the U.S. EPA are required to be sprayed with a VRA to buffer solution pH.<sup>27</sup> Buffering pH above dicamba's p $K_a$  (1.87) is expected to retain dicamba in a nonvolatile anionic form, preventing volatilization from the solution phase (Figure 2A, (ii)).<sup>71</sup> One approved postemergent dicamba-BAPMA formulation requires a VRA to be added prior to use.<sup>50</sup> Other products with dicamba-DGA contain a proprietary VRA within the formulation.<sup>48,49,62</sup>

VRAs appear to be effective at reducing dicamba volatilization in multiple trials,  $^{52}$  although uncertainties remain regarding the underlying phenomena. Whereas dicamba-DGA without a VRA was more volatile than dicamba-BAPMA,  $^{65}$  dicamba-DGA with the aforementioned VRA resulted in comparable air concentrations after application to dicamba-BAPMA alone.  $^{47}$  While VRAs are designed to buffer the pH of the spray solution above the herbicide's p $K_{\rm a}$  (Figure 2A, (ii)), their role once the sprayed droplets dry to a solid-phase residue is unclear. One study found that dicamba still

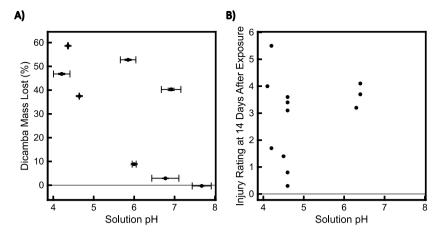


Figure 4. (A) Dicamba mass loss due to volatilization from the herbicide residue prepared with different amines at a 1:1 amine:dicamba molar ratio. Mass loss is measured as the difference between a measured initial and final value of dicamba mass after 48 h at 60 °C. Data from ref 70. (B) Damage to bioassay soybean plants at 14 days after 36 h of exposure to dicamba. Exposure was to dicamba volatilized from soil sprayed with dicamba-BAPMA formulation alone or combined with three different adjuvants and two additional herbicides. Data from ref 54.

volatilized from solid-phase residues generated from high pH solutions (Figure 4A).<sup>70</sup> Data collected by aggregating overall volatilization from both phases also indicated that solution pH was a poor predictor of damage to susceptible bioassay soybeans (Figure 4B),<sup>54</sup> indicating that pH control of the solution phase alone may insufficiently suppress volatilization. Further research into the specific roles of VRAs in the solution and solid phases may provide a greater understanding of how these components reduce herbicide volatilization.

Additional Herbicides. Beyond components added to prevent drift, some dicamba and 2,4-D formulations contain other constituents including additional herbicides that can influence herbicide drift. In particular, glyphosate has been found to increase the volatility of dicamba, 47,70,72 although one study found that the effect of glyphosate was decreased when a VRA was included.<sup>72</sup> The effect of glyphosate on 2,4-D volatility has not been directly investigated, although glyphosate was included in a study comparing the volatilization of 2,4-D products including the DMA, choline, and 2-EHE forms. 60 Because glyphosate itself is often formulated with counterions such as ammonium, potassium, and isopropylamine, its coapplication with dicamba or 2,4-D salt may generate unintended salt pairs. Beyond glyphosate, other herbicides included in certain products (e.g., S-metolachlor)<sup>49</sup> or pesticides approved for tank mixtures with 2,4-D and dicamba 45,48-50 may also impact herbicide drift but have not been investigated.

#### 4. ATMOSPHERIC FATE AND TRANSPORT

While the entry of herbicides to the atmosphere offers the greatest potential to prevent drift, the impact of herbicides undergoing drift will also be determined by processes including atmospheric transport, transformation, and deposition (Figure 2B).<sup>73</sup> Field-to-field herbicide movement is typically studied on a scale of <100 m,<sup>31,64</sup> limiting the impact of slower atmospheric processes such as chemical transformation. However, these processes may be relevant to the atmospheric fate of dicamba and 2,4-D on the regional scale.<sup>74</sup> Furthermore, atmospheric processes will be influenced by the distribution of herbicides between the gas and particle phases. This distribution may differ depending on whether the herbicide enters the atmosphere via either spray drift or

volatilization, as well as further altered within the atmosphere if dicamba and 2,4-D, both SVOCs, 55,56 exchange between these phases at atmospherically relevant temperatures and pressures. 75

Atmospheric Photolysis and Oxidation. In the atmosphere, chemical transformation by photolysis  $^{76,77}$  or oxidants  $^{78,79}$  in the gas and particle phases limits the persistence of agrochemicals like dicamba and 2,4-D. Daytime oxidants in the atmosphere include the hydroxyl radical (\*OH) and, in some environments, ozone (O<sub>3</sub>), while the nitrate radical (NO<sub>3</sub>) may be relevant at night.<sup>78,79</sup> Among these reactions, rate constants for gas-phase reactions of \*OH with 2,4-D analogs mecoprop-p and 2-methyl-4-chlorophenoxyacetic acid have been experimentally measured to be 1.5  $\times$  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } 2.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, in good agreement with a modeled rate constant for the gas-phase reaction of  ${}^{\bullet}OH$  with dicamba (3  $\times$  10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).<sup>80-82</sup> Given typical atmospheric OH concentrations, these chemicals have estimated half-lives of several days by this pathway,82 which is sufficiently long to allow mesoscale transport. 73 In the particle phase, dicamba and 2,4-D may also undergo heterogeneous oxidation, which should be considered when determining their persistence in the atmosphere.83,84

**Deposition.** The distribution of 2,4-D and dicamba between the gas or particle phase will also influence their deposition onto nontarget vegetation surfaces and surrounding soils. Both dry and wet deposition contribute to herbicide removal from the atmosphere; however, the contribution of wet deposition will vary by season and location. In general, dry deposition velocities of particle-associated organic compounds tend to exceed those of gas-phase organic compounds. This trend has been invoked to explain relatively large and variable dry deposition velocities of dicamba (0.53–1.50 cm/s) and 2,4-D (0.29–4.89 cm/s), which may result from the specific distribution of these herbicides between the gas and particle phases when the measurements were performed. 74,86

**Phase Partitioning.** While phase partitioning of dicamba and 2,4-D is critical to determining both its atmospheric fate and ultimate impact on nontarget vegetation, the distribution of dicamba and 2,4-D between phases is not well-characterized. Field measurements often aggregate atmospheric concentrations of herbicides in the gas and particle phases. In one study,

airborne dicamba concentrations over a field site reached 220 ng/m³-air at 6–12 h after dicamba application but decreased to 2–12 ng/m³-air at 58–72 h postapplication.³² These reported air concentrations were composites of dicamba extracted simultaneously from fiber filter papers and polyurethane foam (PUF) media placed in series, representing dicamba in the particle phase and gas phase, respectively. Damage to bioassay soybean plants, which has been used to detect atmospheric movement of dicamba, ³1,64,88 is expected to result from the total exposure to dicamba in the gas and particle phases, with unknown contributions of each.

Generally, phase partitioning dynamics of SVOCs in the atmosphere are influenced by the molecule's vapor pressure and concentration, atmospheric relative humidity and temperature, concentration of absorbing particulate matter, and chemical composition of the particulate matter.<sup>83</sup> Based on models of neutral organic compounds partitioning in the atmosphere, 89,90 only a small fraction (<1%) of dicamba as the neutral species is predicted to be associated with the particle phase at equilibrium. However, dicamba and 2,4-D have been reported to primarily undergo regional-scale transport in the particle phase.<sup>74</sup> This observation may result from dicamba and 2,4-D's low p $K_a$  values (1.87 and 2.73, respectively)<sup>56,71</sup> that enable greater partitioning to the particle phase to charge balance alkaline components. Alkaline components of atmospheric particles include ammonium, which is often elevated in agricultural regions, 91,92 and amines, which may be elevated due to the use of amine-based formulations to control volatilization. Amines may also contribute to new atmospheric particle formation 93 or contribute to the formation and growth of secondary aerosol upon their oxidation in the atmosphere. 94-96 Consequently, the agricultural context in which dicamba and 2,4-D are applied may influence their distribution between the gas and particle phases and therefore their movement to nontolerant vegetation.

#### 5. OUTLOOK

To address the challenges posed by the drift of these herbicides applied to tolerant crops, continued progress is needed both to improve practices that prevent drift including the design of chemical formulations and to understand the impact of herbicides after their entry into the atmosphere by clarifying their fate. Additional efforts to understand phenomena including those described below may support the development and prioritization of increasingly effective solutions to prevent herbicide drift.

Defining the Phenomena That Contribute to Herbicide Drift. To prioritize strategies to prevent drift, we should build on past studies comparing drift at time intervals after herbicide application<sup>29</sup> to better define the contributions of spray drift and volatilization, particularly for recently updated herbicide registrations. Furthermore, the extent of volatilization from the solution or from a solid residue generated after evaporation should be disaggregated. Determining the dominant phase from which volatilization occurs would help to clarify the roles of formulation components such as amines, which are targeted at reducing solid-phase volatility, and newly required pH-buffering VRAs, which are primarily reducing liquid-phase volatility with unknown impacts on solid-phase volatility. 70 An advanced understanding of the phenomena controlling herbicide volatilization may also support a broader framework to consider the unintended impacts of other chemical components (e.g., herbicides like glyphosate and their

associated counterions, surfactants, adjuvants). Future efforts could extend this framework to consider constituents originating naturally on leaves or soil surfaces or formed via transformation (e.g., photodegradation<sup>40,41</sup>). We anticipate that laboratory research, which enables controlled experiments, advanced characterization of chemical phenomena, and comparison among numerous conditions, will complement field experiments capturing environmental realistic behavior.

Characterizing Atmospheric Processes That Influence the Impact of Herbicide Drift. In addition to greater understanding of the input of herbicides to the atmosphere, the fate of the herbicides in the atmosphere is also important to the short- and long-range impacts of drift. Current understanding of the atmospheric fate of 2,4-D and dicamba has largely relied on the time-integrated filter and sorption samplers that average single samples over many hours to days with offline laboratory processing and analysis. 32,47,72 In comparison, online tools that perform with high timeresolution are equipped to better relate observations of dynamic processes (e.g., phase partitioning) to changing conditions (e.g., meteorology, emissions, particle composition). These tools include the aerosol mass spectrometer (AMS), to assess speciation of major organic and inorganic particle components, 97 and the thermal desorption chemical ionization mass spectrometer (TDCIMS), to assess the composition of new particles. Gas-phase species may be investigated by various CIMS methods such as the proton transfer reaction mass spectrometer (PTRMS)<sup>101</sup> and Vocus PTR-ToF. 102 Furthermore, quantification of organic molecules in both gas and particle fractions can be performed simultaneously by the semivolatile thermal desorption aerosol gas chromatograph (SV-TAG), <sup>103,104</sup> a type of in situ GC/MS system. <sup>105–107</sup> These methods are also suited to track the multiphase oxidative evolution of both the herbicides and their formulation components, including formation of reaction products that may be toxic and/or contribute to the generation of secondary organic aerosols. 80,81

Overall, the impacts of dicamba and 2,4-D to nontarget vegetation in recent years exemplify how new challenges can emerge from changes to the application of herbicides upon the introduction of their tolerance traits, even when the herbicides have been used in another context for decades previously. Because emerging herbicide-tolerance traits dramatically alter how their corresponding herbicides are applied, the new application context must be considered to understand and mitigate environmental impact of these herbicides.

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#### Notes

The authors declare no competing financial interest.

#### **Biography**



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