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Evaluating methods and factors that affect dicamba volatility

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Abstract: Background: Dicamba is a herbicide with a moderate volatility profile and low dose effects on broadleaf weeds. Dicamba volatility can be strongly reduced with formulation technology and volatilization reducers.

Objective: This literature review on the dicamba herbicide aims to present new perspectives for its use, characteristics, volatilization risks, technologies to mitigate these risks and the main methods used to assess volatility in Brazil and worldwide.

Conclusions: Dicamba volatility can be mitigated with appropriate formulations and/or the use of adjuvants to reduce volatility. There has been an evolution in adapting new salts and technologies to reduce dicamba volatility. There are different methods of evaluating herbicide volatility, in particular, for the quantification of volatilized dicamba either in laboratory or field studies. Available methods can be fast and consistent and can assess volatilization from different surfaces, weather conditions and technologies to reduce volatilization. Under some conditions it is desirable to combine this method with bioassays.

Keywords: auxinic herbicide; dicamba formulation; environmental risk; volatilization

1. Introduction

Dicamba (3,6-dichloro-2-methoxybenzoic acid or 2-methoxy-3,6-dichlorobenzoic acid) is a systemic herbicide in the group of synthetic auxins, classified in group 4 according Weed Science Society of America (WSSA) used to control annual and perennial broadleaf weeds postemergence. It can be used when preplanting soybean and cotton crops not tolerant to dicamba, given that the dose and safety interval recommendations defined in the package insert are followed. More recently, through biotechnology, it has been possible to selectively apply dicamba to soybean crops without injuring them but allowing the management of broadleaf weeds that greatly damage the crops in different regions of Brazil. Dicamba contributes to a broader spectrum of broadleaf weed management, with emphasis on the control of *Conyza* spp., *Amaranthus* spp. and morning *Ipomoea* spp. in Brazil and with possible uses in the management of the various soybean cultivation stages (Cahoon et al., 2015; Montgomery et al., 2017; Osipe et al., 2017).

Dicamba is an acidic herbicide of the benzoic acid chemical group that was first registered for use in 1967, and it can form salts in aqueous solution (US Environmental Protection Agency, 2006). Dicamba is a plant auxin-mimicking herbicide that stimulates cell elongation and differentiation, causing plant disordered growth (Bunch et al., 2012; Mithila et al., 2011). This irregular plant growth cause disruption cell transport systems and can induce to plant death (US Environmental Protection Agency, 2006). Nontarget plants that are susceptible and exposed to even a small amount of dicamba may experience injury effects with deformities (cupping effect) (Figure 1) and a hyponastic response (Egan, Mortensen, 2012; Strachan et al., 2010).

In recent years, with the launch of technologies that allow the safe application of dicamba in postemergence soybean and cotton crops (Werle et al., 2018), there has been an intensification of the use of this herbicide. The Brazilian National Biosafety Technical Commission (CTNBio) has deregulated in recent years the use of dicamba tolerant soybean and cotton (Comissão Técnica Nacional de Biossegurança, 2017; 2018). The launch of this biotechnology will serve as one more important tool for the sustainable management of weeds, especially herbicide resistant weeds, and to protect the technologies and herbicides currently used in the Brazilian agriculture; however, some care should be taken to avoid problems with this herbicide due its effect at low doses on some highly sensitive species, such as soybean that does not possess the tolerance gene to this herbicide. The volatility of dicamba is a point of concern. The objective of this literature review about the dicamba herbicide is to present new use perspectives, characteristics, volatilization risks, technologies to

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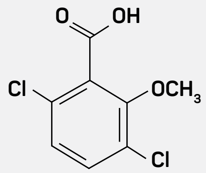
Figure 1 - Characteristic symptoms of small amounts of dicamba in nontolerant soybean

Table 1 - Characteristics of dicamba (not including its salts)

Characteristic	
Chemical group	Benzoic acid
Molecular weight	221.04
Name IUPAC	3,6-dichloro-o-anisic acid
CAS Name	3,6-dichloro-2-methoxybenzoic acid
Solubility in water, 20 °C (mg L^{-1})	250000
Solubility in organic solvents, 20 °C (mg L^{-1})	500000 (acetone)
	2800 (hexane)
	500000 (methanol)
	500000 (ethyl acetate)
Melting point (°C)	115
Boiling point (°C)	Decomposes before
Degradation point (°C)	230
Octanol-water partition coefficient at pH 7, 20 °C (Log P)	-1.88
Density (g ml^{-1})	1484
Dissociation constant - pKa at 25 °C	1.87 (strong acid)
Vapor pressure, 20 °C (mPa)	1.67
Henry's law constant at 25 °C (Pa m^3 mol^{-1})	1.0 X 10^{-04}
Koc* (L kg^{-1})	1.42
Chemical formula	$C_8H_6Cl_2O_3$
Chemical structure	

Source: PPDB (2022); *Comfort et al. (1992).

mitigate these risks and the main methods used to assess volatilization in Brazil.

2. Physicochemical characteristics of dicamba

Under normal conditions, dicamba usually occurs in solid form as crystals; however, it can also exist in the form of vapor or particles (Bunch et al., 2012). This herbicide has a low organic carbon partition coefficient (Koc) and, therefore, a low affinity for soil particles (Comfort et al., 1992) (Table 1). Therefore, dicamba can be available in the soil solution, absorbed by the plant root system (Silva et al., 2020) and easily leached into the soil (Oliveira Jr. et al., 2001). Furthermore, dicamba is resistant to oxidation and hydrolysis under most conditions and has a low octanol/water partition coefficient (Kow) (Krueger et al., 1991, Durkin, Bosch, 2004). Table 1 shows the physicochemical characteristics of dicamba.

Acidic dicamba is characterized as a moderately volatile compound (Bunch et al., 2012). The volatility of dicamba depends on several factors, including the amount applied, temperature, humidity, formulation and surface on which it was deposited (Nishimura et al., 2015). The herbicide is degraded in the atmosphere primarily through photolysis (Waite et al., 2005).

Because it is classified as moderately volatile, cases of dicamba injuries in susceptible plants could be reported (Bish, Bradley, 2017) if more current formulations are not used and good agricultural practices are not followed during its application. Dicamba is a strong acid, with pKa 1.87, that is formulated as a salt, and the acid form is the form susceptible to volatilization (Behrens, Lueschen, 1979; Bish et al., 2019; Macinnes, 2017); thus, the molecular state can have a important impact on volatility (Macinnes, 2017; Mueller, Steckel, 2019a).

Dicamba is used in agriculture after neutralization of this acid in a soluble salt. Among the most common salts are amine salts, dimethylamine (DMA), sodium salt, diglycolamine salt (DGA) and N,N-bis-(3-aminopropyl) methylamine (BAPMA) salt (Figure 2). Dicamba salts, produced from the DMA, DGA and BAPMA bases, result in liquid formulations with high concentrations, which cannot be obtained starting from the sodium base. Therefore, sodium base is generally used for granular formulations of herbicides.

3. Volatilization of herbicides

The movement of dicamba out of a target area can occur by physical drift (particles/droplets) at the time of application, during which part of the applied droplets is not deposited in the target area or by vapor drift with volatilization process occurring during the application and/or after deposition in the target (plants, soil, and straw). To better understand the risk or safety assessment of dicamba applications, it is necessary to differentiate drift, volatility, volatilization, transport of dicamba in the form of vapor and level of safety or risk for plants in the vicinity of the applied area.

Physical drift is the deviation of the trajectory of the particles (droplets) released by the spraying process that do not reach the target. This movement outside the target area is mitigated by the correct use of application technology, such as correct choice of spray tip, droplet size, working pressure, boom height and equipment speed, in addition to considering the ideal meteorological conditions during spraying (Bish et al., 2021).

Volatility represents the ease with which a substance moves from a liquid to a gaseous state. As will be highlighted in this document, advances in terms of formulations and adjuvants in recent years have allowed us to mitigate this characteristic, especially for ionizable substances such as dicamba.

Nevertheless, volatility is dependent on temperature, and the higher the temperature, the greater the volatility (Mueller, Steckel, 2019a; Bish et al., 2019; Mueller et al., 2013). The inverse is also true, as occurs in the production of vapor at higher temperatures and the condensation of molecules at lower temperatures.

Volatilization is the process of converting a herbicide from the liquid to the gaseous state by transferring herbicide from the spray droplet, soil, straw or plant surface to the atmosphere (Schreiber et al., 2015; Yates, 2006). The intensity of the volatilization depends on the volatility of the compound, which is also affected by temperature and the force of attraction of the volatile compound by other nonvolatile substances present in the solution. The vapor pressure of the pesticides is the property that most influences the volatilization. An increase in the vapor pressure of a pesticide favors the vapor phase, and the pesticide is more readily volatilized. In the field, herbicide volatilization under real use conditions may be lower due to interactions with the soil surface or other environmental components (Gish et al., 2011). There is a positive and significant correlation between the vapor pressure of a pesticide and the volatilization of that pesticide (Farmer et al., 1972); however, it has been observed that dry soil conditions, for example, favor soil sorption, which reduces the vapor pressure of pesticides and decreases their volatilization (Taylor, Spencer, 1990; Schneider et al., 2013).

Volatilization can be reduced by creating barriers for the dispersion of volatilized molecules, such as mechanical incorporation into the soil, which is widely used for the herbicide trifluralin (Bedos et al., 2006). Incorporation increases the binding of the compound of interest to soil colloids, reducing volatility and hindering the escape of volatilized molecules from the soil, further reducing volatilization losses (Bedos et al., 2006; Ouyang et al., 2012).

Transported volatilized molecules in the form of vapor outside the application area can reach sensitive plants, depending on the dimensions and shape of the treated area, the temperature, the presence of winds and many other variables. It should also be noted that the risk to neighboring crops may be associated with the production of vapor and condensation of the herbicide as well as with the deposition of droplets that experienced drift at the time of application.

Thus, the volatility of a herbicide is a controllable factor and not a characteristic exclusively inherent to the active ingredient. It is possible to mitigate volatility with appropriate formulations or even with the combination of volatility-reducing products, and it is essential that each formulation or technique employed for this purpose be specifically evaluated as to its potential to produce or avoid the production of vapor.

There are several examples of mitigating volatility with advances in herbicide production and formulations. In this document, aspects that affect volatility and the technologies related to reducing dicamba volatility are discussed in greater depth. However, this scenario is not specific only to dicamba. Other herbicides with a history of problems related to volatilization, such as 2,4-D and clomazone, have experienced important advances in formulations that have drastically reduced the risk of these losses in the form of vapor.

Comparing the emulsifiable concentrate (EC) formulation and the new microencapsulated (CS) formulation technologies for clomazone, both commercially available in Brazil, Schreiber et al. (2015) observed lower volatilization losses for the CS formulation of clomazone than for the EC formulation and concluded that the SC formulation allows safer use regarding the environmental contamination of this herbicide. In this case, most of the ingredient is retained in the polymer capsule while it is not broken. Similarly, in a laboratory study with continuous air flow, Mervosh et al. (1995) observed that the volatilization of clomazone from the soil was reduced by microencapsulation with starch-based polymer and starch or clay granules. These authors also observed that the size of the particles (capsules) influenced volatilization, which demonstrates that it is possible to interfere with and minimize the volatility of clomazone with adjustments and technologies related to its formulation.

For 2,4-D, there have been substantial changes in the safety of this herbicide regarding the risk of volatilization since its commercial launch more than 70 years ago. Peterson et al. (2016) in a review for 2,4-D herbicide, described the different formulations of this herbicide. The authors describe that there are important differences in the volatility of the formulations (esters and amine and choline salts). Esterification of 2,4-D acid with an alcohol forming an alkyl chain of four carbons or less are considered highly volatile. This group includes methyl, isopropyl and butyl esters. These formulations were removed from most uses and markets in the early 1980s which significantly reduced the risk of volatilization of this herbicide. Despite the differences between the ester formulations in terms of volatility, the esters are more volatile than the salt-based formulations and are no longer used in Brazil. The amine salt formulations of 2,4-D (isopropylamine, triisopropanolamine, diethanolamine and dimethylamine) reduced the herbicide absorption efficiency but increased safety regarding the risk of volatilization. The most recent formulation introduced the 2,4-D choline salt, which also contributed to greater reductions in volatility and physical drift.

4. Chemical factors influencing dicamba volatilization

In the case of dicamba, simply changing the pH of the solution can modify the proportion of ionized molecules. The pKa of dicamba is 1.87 (Table 1), indicating that at this pH, the number of nonionized and ionized molecules are equivalent. The increase of pH reduces he participation of nonionized molecules that are more prone to volatilization. Therefore, the volatility of dicamba is dependent on pH. The use of nonvolatile cations with strong binding to dicamba to neutralize this acid and compose commercial formulations is a very effective practice to reduce volatility as illustrated in Figure 2. In summary, the increase in pH will increase the amount of dicamba anion, and the use of nonvolatile cations with strong binding to the dicamba anion has also been shown to be a highly effective option to reduce the volatility of this herbicide.

Volatilization is one of the main challenges encountered with the use of auxinic herbicides. One of the main ways to reduce the volatility of products is related to the type of salt and formulation used (Vidal, Merotto, 2001). For dicamba, as already reported for 2,4-D, the ester formulation is more volatile than the amine formulation.

Currently, there are some dicamba formulations, including DMA salt, DGA salt, sodium salt and BAPMA salt, that differ significantly in terms of volatility (Figure 2). While the efficacies of different salts may be equivalent, the volatilities of the different dicamba salts are different. The literature indicates that the DGA or BAPMA dicamba salts are less susceptible to volatilization than the DMA dicamba salt under controlled or field conditions (Mueller et al., 2013; Egan, Mortensen, 2012; Carbonari et al., 2020; Mueller, Steckel, 2019a). The volatilization of dicamba applied in the form of DGA salt was reduced by 94% compared to that of dicamba applied in the form of DMA salt (Mueller et al., 2013).

Additionally, Egan and Mortensen (2012) observed a positive and significant correlation between relative humidity and the distance at which plant injury was observed, as well as for the amount of dicamba deposited from the volatilized fraction. The authors concluded that the estimates of vapor losses outside the treated area were drastically reduced for the DGA formulation compared to the DMA formulation and that the distance curves achieved by volatilization indicated that the mean exposures were

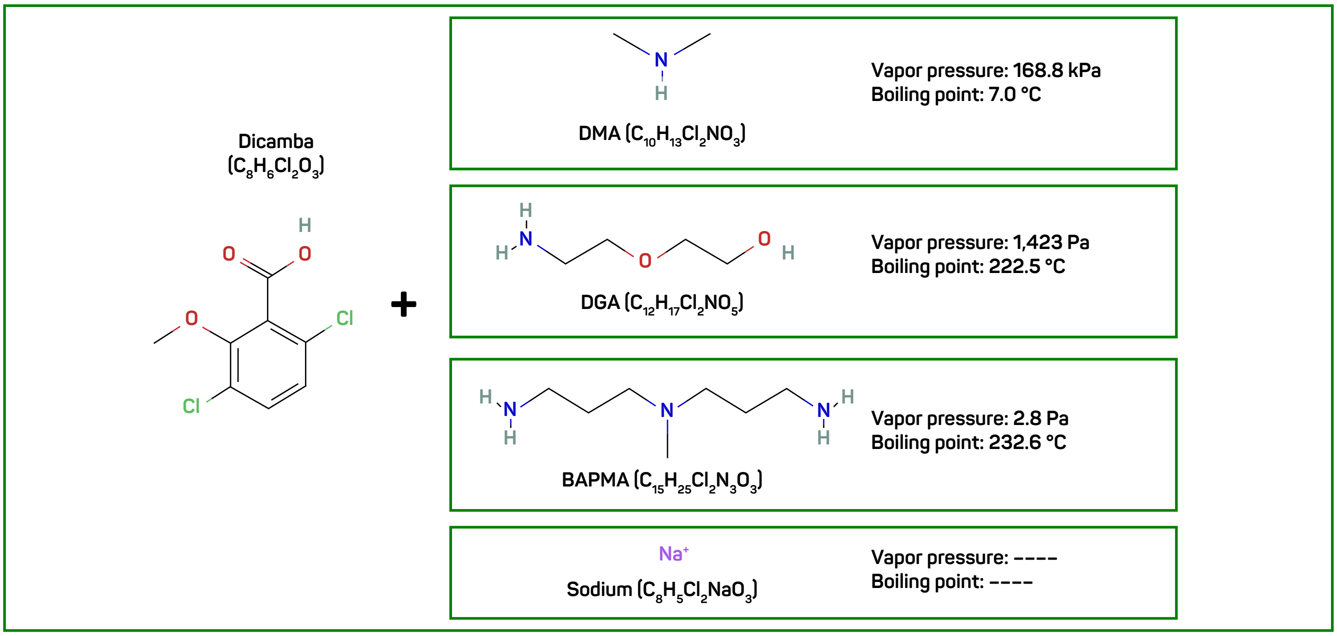


Figure 2 - Characteristics of dimethylamine salt (DMA), sodium salt, diglycolamine salt (DGA) and N,N-bis-(3-aminopropyl) methylamine salt (BAPMA) used in dicamba formulations (European Chemicals Agency, 2022a; 2022b; 2022c)

close to zero at only the short distances from the area treated with the DGA formulation.

This difference in the volatility between DMA salt compared to DGA and sodium salts results from the property of the base used in the neutralization of the acid. Dicamba salts produced with diglycolamine, BAPMA or sodium bases, which have higher boiling points and lower vapor pressures, result in salts with lower volatility (Riter et al., 2021). The molecular weight of the BAPMA salt and the force of the bond with the acidic part reduce dicamba dissociation from the salt and seek free hydrogen protons in an aqueous solution (Westberg, Adams, 2017).

The equation below represents the dissociation of the DMA dicamba salt in a aqueous solution:

$$DCH + DMA \leftrightarrow DC^{-} + DMAH^{+}$$

where DCH = dicamba neutral acid; DMA = neutral dimethylamine base; DC^{-} = dissociated dicamba acid; $DMAH^{+}$ = protonated dimethylamine base

In a neutral pH solution, the equilibrium is shifted to the right, showing dicamba anions and DMA cations. However, due to the volatility of the DMA, it leaves the solution in the form of vapor, and the equilibrium gradually shifts to the left side of the equation. The loss of DMA is irreversible, and the equilibrium of the equation is maintained on the left. This shift to the left means that dicamba begins to accumulate in its acidic form, causing a decrease in the pH of the solution. Since the dicamba in its acidic form is volatile, this displacement in the equation causes volatilization of the substance. Therefore, if the dicamba acid is neutralized with a nonvolatile base, such as sodium DGA or BAPMA, the displacement of the equation is maintained to the right, preventing the formation of dicamba in its volatile form.

5. Effects of formulations, volatility reducers and mixtures with other products on dicamba volatilization

Volatilization reducers can be used in formulations or spray solutions to mitigate risks. When a dicamba formulation is diluted in the tank, the dicamba can pass to the acidic form and cause volatilization after spraying. The currently available volatility reducer (VR) can prevent the dicamba ions from combining with hydrogen ions (H^{+}), significantly reducing the volatility potential (Abraham, 2018) and providing farmers with more options for safely using dicamba.

A VR based on acetic acid/acetate (VaporGrip® in the USA and XtendProtect®) in Brazil was developed to further decrease the volatility profile of dicamba, eliminating hydrogen ions (H^{+}) in dicamba spray solution (Hemminghaus et al., 2017).

There are many reports in the literature showing that DGA or BAPMA salts of dicamba is much less volatile than DMA salt of dicamba and that VRs further reduces the risks of volatilization. Egan and Mortensen (2012) found 94% less dicamba volatility using the dicamba DGA salt compared to dicamba DMA salt. Behrens and Lueschen (1979) evaluated the volatility of different dicamba formulations under laboratory conditions. DMA dicamba was significantly more volatile than the DGA or BAPMA dicamba formulations. Behrens and Lueschen (1979) also observed that the pH of a dicamba spray solution from different formulation affects volatilization. In experiments in a growth chamber, these authors found that the volatilization of the dicamba DMA salt was reduced from 71-54% on glass surfaces when the pH of the spray solution was increased from 4.7 to 8.8.

Typically, dicamba is applied by farmers with glyphosate in tank mixtures to broaden the spectrum of weed control. Mueller and Steckel (2019a) evaluated the application of DGA dicamba + glyphosate (potassium salt), DGA + glyphosate + VR and DGA + VR in soil at different temperatures. They showed DGA + glyphosate and DGA + glyphosate + VR volatility was higher than DGA + VR volatility, demonstrating that the use of glyphosate in the mixture may increase the volatilization of dicamba. Nevertheless, a VR is an efficient tool in reducing volatilization, and the largest differences occurred mainly at high temperatures (above 30 °C). At temperatures of approximately 15 °C, the levels were very low (concentrations below 5% of those observed above 30 °C). The mixture of glyphosate to the dicamba decreased the pH of the spray solution and increased the concentrations of dicamba in the air and the addition of glyphosate to the dicamba salt of DGA + VR increased the detectable concentrations of dicamba in the air from 2.9 to 9.3 times in all temperature ranges examined.

Carbonari et al. (2022) evaluated the volatilization of the application of dicamba DGA alone or with different formulations (salts) of glyphosate and observed that the mixture with glyphosate increased the volatilization. Despite this, the author showed that VR was efficient in reducing volatility for dicamba alone and in combination with all glyphosate salts. The combination of DGA dicamba salt with potassium salt of glyphosate and a volatility reducer was the blend with the lowest volatility and is the most suitable combination to recommend to farmers (Carbonari et al., 2022).

The different glyphosate formulations may have different pH values because the solubility of these salts is different and the pH of the glyphosate solutions increases with dilution (Dill et al., 2010; Mueller, Steckel, 2019b). However, there is no consensus on the direct relationship between the decrease in pH and the increase in dicamba volatility (Sharkey et al., 2020) since this is apparently not the only variable influencing the volatilization of dicamba. Despite that, the inclusion of this type of information in packages insert ensures greater transparency and safety in terms of the use by farmers. Glyphosate potassium salt is the safest option to combine with the dicamba DGA and BAPMA salts.

Bish et al. (2019) quantified dicamba in the air after application of the dicamba formulations DGA + VR and

BAPMA with and without glyphosate and under different weather conditions. The authors observed that the DGA + VR and BAPMA salt were quantified at similar levels over time when applied simultaneously. The highest concentrations for each formulation occurred from 0.5 to 8 hours after application, and the concentrations of DGA + VR and BAPMA were 22.6 and 25.8 ng m^{-3}, respectively. Both dicamba formulations had similarly rapid dissipation in air, with dicamba concentrations decreasing from > 20 ng m^{-3} in 0.5 to 8 hours after application (HAA) to <7 ng m^{-3} between 8 and 16 HAA and 24 and 48 HAA. The dicamba concentrations were <2 ng m^{-3} and remained at this level until 72 HAA. The air dicamba levels were higher when glyphosate was used.

In the USA, ammonium sulfate is regularly used in mixture with glyphosate, especially under hard water conditions (Jordan et al., 1997). Carvalho et al. (2009) reported that an increase in glyphosate concentration promoted acidification of the spray solution, which stabilized at pH 4.5. Ammonium sulfate caused a small acidification of the herbicide solution (Mueller, Steckel, 2019b). In addition, in the USA, the package inserts of the dicamba DGA salt and BAPMA salt herbicides include the notification that these products have the potential to volatilize in lower pH mixtures and that the process of mixing them in a tank with ammonium sulfate products is not recommended as it can significantly increase the volatility potential of dicamba. Thus, avoiding mixing any adjuvants that will acidify the spray solution is recommended. In addition, pH levels lower than 5.0 may increase the dicamba volatility potential, and using pH modifiers approved by the US Environmental Protection Agency (EPA) to increase the pH of the solution is recommended. (Carbonari et al., 2020) found that even with the addition of potassium salt to a dicamba solution, volatilization did not increase for some surfaces, such as glass and wet soil. Sharkey et al. (2020) also found that the association of glyphosate to a dicamba solution significantly decreased the pH value; however, volatilization did not increase significantly, indicating that even with lower pH values, there may be no increases in volatilization.

The characteristics of the different surfaces on which dicamba spray solution is deposited after application directly influence volatilization (Hartzler, 2017). The DMA dicamba deposited on corn and soybean increased dicamba volatilization by 35% compared to dicamba deposited to clayey soil (Behrens, Lueschen, 1979). In Brazil, with the greater adoption of the no-tillage system in soybean, corn and cotton and the double-crop system in the Cerrado region (soybean/corn), a significant amount of the dicamba will be deposited in straw after spraying. The no-tillage system in Brazil is implemented on approximately 33 million hectares and continues to be expanded (Instituto Brasileiro de Geografia e Estatistica, 2017), and the relation of the dicamba with the mulch surface is different from that with the soil or plant leaf surface (Carbonari et al., 2020). In this study, for all treatments and surfaces tested, the addition of a VR significantly reduced volatilization, highlighting the importance of its use in dicamba applications. However, application on wet soil increased volatilization in relation to dry soil or straw (Carbonari et al., 2020). This may have occurred due to the high-water solubility of dicamba together with its low affinity with the solid soil phase (Kerle et al., 2007).

Oseland et al. (2020) evaluated the effect of different soil pH values (ranging from 4.3 to 8.3) in the field and observed a significant increase in soybean volatility and injury when dicamba was sprayed the soil with a lower pH of all formulations of dicamba tested (DGA, DGA + Vapor Grip® as A VR, BAPMA and choline salt).

6. Main methods of studying the volatility of herbicides with an emphasis on dicamba

Different methods have been used to evaluate and compare the volatilization of dicamba in several countries worldwide, including Brazil. Brazil has used or adapted methods widely used worldwide and recommended by the US EPA at different scales: 1 – under controlled laboratory conditions in closed systems; 2 – under semicontrolled field or greenhouse conditions (hoop-house), which consist of application to targets stored in plastic tunnels in the field; and 3–large-scale field studies. Below are related studies available in the international literature and similar studies conducted in Brazil.

Behrens and Lueschen (1979) applied dicamba DMA salt (0.28 kg ha^{-1}) in corn crop to test volatilization (using pots with sensitive plants – bioassays). They use potted soybean plants placed in seven locations at 0, 3 and 30 m (or 20, 40 and 60 m in same replicates) from the application area one hour after application. The plants injury was evaluated 14 days after dicamba applied field exposition, and the greatest damage (injury index = 68) was observed at the shortest distances (0 m). Some symptoms were observed at distances up to 60 m downwind of the application area. It is important to note that this study was performed more than 4 decades ago with the formulation of DMA salt and, therefore, without incorporating all the advances that have occurred in terms of formulations and safe dicamba salts. Behrens and Lueschen (1979) also observed that rain (3 and 9 mm of precipitation), which occurred 12 and 14 hours after the application reduced significatively the dicamba volatilization.

Egan and Mortensen (2012) used bioassay techniques to study volatilization after the application of dicamba and observed that dicamba was detected at a concentration of 0.56 g acid equivalent (ae) ha^{-1}, or 0.1% of the applied dose, at 21 m from the application area.

Mueller and Steckel (2019a) described a method to evaluate the volatilization of dicamba in a closed system with cumulative air flow in different periods under room temperature conditions. The authors called this system the "humidome", which consists of an air sampler connected to a soil tray treated with a lid and connected to a 10 cm diameter plastic tube that was attached to the sampling device, in which a filter (puff) collects the dicamba vapor. Each sampler had an exhaust port connected to a hose that was ventilated out of the oven. This is a method that allows the quantification with precision and in controlled conditions of the volatilized dicamba, allowing to simulate different situations that occur in the field, as well as to compare different treatments in the same condition. In the same way, with the same advantages, (Carbonari et al., 2020) developed a method for evaluating volatilization from a vapor sampled system composed of a PVC tube with inlets to hold 24 cartridges and an outlet containing a connection (3 mm) to a vacuum pump (30 mL min $^{-1}$). This system was placed inside a precision chamber to maintain a constant temperature at 40 °C. The cartridges, where the applied targets were placed, were 19.2 cm in length and 132 cm^3 in volume. These cartridges were closed with a lid containing an opening of 3 mm in diameter to ensure the passage of air through the system, and at the opposite end of the cartridge, two filters (PVDF 0.20 μm - 25 mm) were used to sample the dicamba vapor. The filters were arranged in series to ensure high vapor collection efficiency in each cartridge.

There are also many reports of the use of field experiments, called low tunnel or hoop house experiments. In these experiments, a tray with soil that received the application of dicamba is place in a plot with the herbicide-sensitive crop and this plot is covered with a plastic tunnel to confine the vapors produced, with a subsequent evaluation of the effects on the plants at different distances from the tray with the herbicide (Weed Science Society of America, 2018; Young, 2019).

The transport of herbicide vapor outside the target area can be determined with atmospheric dispersion models to evaluate the transport and dispersion of vapors from the application area (Sall et al., 2020), as well as to define the potential need for or the size of any protection buffers zone to ensure that exposures outside the applied area are at safe levels.

A quantitative evaluation of the volatility of herbicides applied in the field requires very careful and planned sampling logistics, robust analytical methods, and sophisticated data modeling techniques. Sall et al. (2020) conducted a field experiment in two plots to show the usefulness of these methods under regular agricultural conditions. The volatile flow profile was variable over time and showed that less than 0.2 ± 0.05% of the dicamba applied was volatilized during the sampling period of 3 days.

Waite et al. (2005) evaluated the atmospheric concentrations of dicamba and the air samples collected from May to June had higher dicamba concentrations than those collected at other times. The air samples were collected at heights of 1, 10 and 30 m, and the highest dicamba concentration was 0.47 ng m^{-3}. No significant differences were identified for the different sampling heights. In a similar experiment, Yao et al. (2006), evaluated the atmospheric concentrations of dicamba at 1, 10 and 30 m aboveground and the dicamba concentrations ranged from 0.01–0.187 ng m^{-3}.

Twenty-three field experiments were carried out in six locations in the US to estimate of dicamba volatility after the application of 0.56 or 1.12 kg per hectare (Sall et al., 2020). The volatilization quantified in these experiments for all formulations and conditions tested ranged from 0.023% to 0.302% of the total dicamba applied, and volatilization peaks occurred in the first 24 hours after application.

Direct air sampling followed by chromatography/mass spectrometry is a method with high analytical precision and sensitivity for differentiating the volatility levels of different formulations and application conditions. Under controlled conditions, it is even possible to quantify the fraction of the applied dose that volatilized from the target where the dicamba was deposited.

According to Riter et al. (2021), the methods that allow quantification, usually by chromatography and mass spectrometry, require high sensitivity, criteria in the validation of the limit of quantification (LOQ) and great care to avoid contamination in the handling of samples during collections. The concentrations found in these studies are very low and requires to characterize the contamination using field blanks, laboratory blanks and injection blanks. Although these methods have points in common, each has important differences to consider in experimental design.

The use of bioassays is simpler and cheaper but less accurate in detecting the volatility of different compounds. Care must be taken when performing assessments based only on the bioassay method, which does not allow accurate quantification of volatilization and should not be used as an isolated tool for this purpose. Therefore, it is strongly recommended to evaluate volatilization with by sampling and quantifying the fraction of volatilized dicamba from the deposition at the target, and this method can be combined with bioassays.

7. Conclusions

The movement of dicamba out of the target area by physical drift and/or volatilization is cause for concern due to potential injuries to susceptible plants. The volatility of a herbicide is a controllable factor and not a characteristic exclusively inherent to the active ingredient. It is possible to mitigate volatility with appropriate formulations and/or with the use of VR products. In recent years, there has been a significant evolution within the industry in terms of adapting new salts and adjuvants to reduce dicamba volatility.

There are different methods for evaluating the volatility of herbicides, and this literature review presented results detailing each of them. The quantification of volatilized dicamba in laboratory or field studies has been shown to be fast and consistent and can test different surfaces, weather conditions and technologies to reduce volatilization. Nevertheless, it is desirable under some conditions to combine this method with bioassays and/or quantify dicamba deposited from volatilization in biological targets.

From the information presented, it is concluded that there are safer formulations of dicamba and adjuvants (VRs), which are effective in mitigating volatilization and may allow the prioritization of safe technologies for the use of dicamba in Brazil. The DMA formulation has high volatilization risks and should be avoided.

Author's contributions

All authors read and agreed to the published version of the manuscript. CAC, and EV: conceptualization of the manuscript. CAC, RNC, and BFG: writing the original draft of the manuscript. CAC, and EDV: writing, review and editing.

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