Dicamba: Where it happened? How it happened? Why it happened?

Rich Zollinger NDSU Extension Weed Specialist Official Dicamba-related Injury Investigations as Reported by State Departments of Agriculture (*as of October 15, 2017)



Estimates of Dicamba-injured Soybean Acreage in the U.S. as Reported by State Extension Weed Scientists (*as of October 15, 2017)







7 Reasons WHY dicamba drifted in 2017?

Refer to page 29 in 2018 Weed Guide

Some reasons why off-site movement of dicamba drift occurred in 2017:

- Soybean can show phytotoxic symptoms from dicamba at rates as low as 0.0004 oz ae/A (0.028 g/ha). Very small amounts of dicamba from contaminated sprayers, particle drift, and volatility can cause injury symptoms on soybean. Extremely high sensitivity of soybean to dicamba influences all other discussion points.
- 2017 soybean acreage was approximately 8 m acres. The 25-30% adoption of dicamba tolerant (DT) soybean equals over 2 million soybean acres that dicamba was possibly applied.
- 3. Dicamba rate used in DT soybean is 8 oz ae/A compared to 0.5 to 2 oz ae/A used in wheat and corn. The higher rate of dicamba applied in DT soybean applied during a 3 week period in late June and early July resulted in very high release of dicamba into the environment, which could be a source for particle drift and volatility.
- 4. Higher temperatures occur in late June and early July. The vapor pressure of dicamba significantly increases as temperature increases.
- 5. Dicamba is normally applied in May and early June in wheat and corn. Dicamba in DT soybean allows application through R1 stage. Later applications are more prone to dicamba drift because temperatures are higher which allows greater dicamba volatility while soybeans are more advanced in growth to intercept dicamba, express injury symptoms, and possibly reduce yield.
- 6. Dicamba drift is more likely to cause yield loss the closer to and including reproductive stage. Summer solstice (June 21) is the reproductive trigger in soybean.
- 7. Precipitation normally decreases after late June. Dicamba is highly water soluble and rain events after application can "wash" the dicamba off plant leaves and on the soil surface into the soil to trap the dicamba and reduce off-target movement.

1. Soybean acreage: ND Soybean: 600,000 to 8 million acres

2. Dicamba rate:

0.5-1 oz ai in wheat and corn8 oz ai in DT soybean"Atmospheric loading"

2017 = 25% adoption 2018 = 50% adoption - 2x more loading

110

100

Air Temperature

3:44:AM

2:34:AM

6:04:AM 4:54:AM

7:14:AM

Ground Temperature

2:14:AM

:06:PN :56:PN

- 3. Application timing of dicamba on crops
 - EARLY timing on wheat or corn = 2 to 4-leaf
 - LATE timing on DT soybean = PRE through R1
 - June through mid-July

"Atmospheric Loading"





5. Dry summer

Soybean damage increases in drought stress conditions

<u>Herbicide</u>	H ₂ O solubility (ppm)
Prowl	0.33
Atrazine	35
Callisto	160
Harness/Surpass	282
Metolachlor	530
Glyphosate	10,500
Dicamba	250,000
Paraquat	620,000

6. The most underestimated factor.....

Soybean injury to dicamba and 2,4-D



Soybean is 100X more tolerant to 2,4-D

Platitude: A word or phrase used too often to be meaningful



Dicamba drift on sugarbeet and sunflower



Soybean response from dicamba and 2,4-D Bradley, U of MO

		•			Visihle	iniury	
				<u>2</u> W/	AT	4 WA	<u>NT</u>
He	rbicide	Rate		V3	R2	V3	R2
		oz ae/A			%		
2,4	-D	0.0004		2	0	1	0
		0.004		1	0	1	1
		0.04		1	0	0	0
		0.4		3	0	0	0
Ino							
o [∿] Dic	camba	0.0004	= 0.029 g/ha	21	15	10	17
Det		0.004	= 0.29 g/ha	28	17	9	16
and the second s		0.04		32	14	9	15
4 ⁰		0.4		44	18	12	14
LS	D			18	9	5	3

Table 2.2. Soybean injury combined across 2011 and 2012.

Soybean susceptibility to dicamba

Lowest rate response:	Labeled rate	% of rate
Dicamba on soybean	0.5 lb ae/A	0.005%
Glyphosate on corn	0.75 lb ae/A	1%
Glyphosate on soybean	0.75 lb ae/A	10%

Soybean is 2,000X more susceptible to dicamba than glyphosate



Soybean flat dose response to dicamba



What does this mean regarding dicamba? Zero tolerance for soybean!

- Particle drift
- Contaminated sprayers
- Temperature inversions
- Run-off water
- Volatilization (vapor drift)







BASF data using Engenia Herbicide (0.5 lb ae/A) + Roundup WeatherMax (1 lb ae/A) and 04 orifice size at 40 PSI.



BASF data using Engenia Herbicide (0.5 lb ae/A) + Roundup WeatherMax (1 lb ae/A) and 04 orifice size at 40 PSI.





Crop susceptibility to dicamba Southern states

Visual Sensitivity: Example Dicamba

Lower	Moderate	Severe	Extreme
Broccoli Cabbage Kale Mustard Pecan Turnip	Cantaloupe Cucumber Peach Peanut Squash	Cotton Pepper Tomato Watermelon	Grapes* Lima Bean Southern Pea Snap Bean Soybean Tobacco*
>1/75X	1/75-1/300X	1/300-1/800X	< 1/800X
Herbici	de Rate of <u>Vis</u>	ually Detectable	e Injury

Crop susceptibility to dicamba NDSU

None/Low

- Wheat
- Barley
- Corn
- Canola
- Flax

NORTH DAKOTA STATE UNIVERSITY

Moderate/Severe

- Alfalfa
- Potato
- Safflower
- Sunflower
- Tomato

<u>Severe</u>

- Chickpea
- Dry bean
- Field pea
- Lentil
- Soybean
- Sugarbeet

*Classification is visually detectable injury; North Dakota crops

Crop susceptibility to dicamba NDSU



<u>Moderate</u>

- Alfalfa
- Potato
- Safflower
- Sunflower
- Tomato

Severe

- Chickpea
- Dry bean
- Field pea
- Lentil
- Sugarbeet

Extreme/ Canary in the coal mine

Soybean

*Classification is visually detectable injury; North Dakota crops

1 last point about DRIFT!

Just cause you didn't see injury..... doesn't mean drift does not happen.

Example: dicamba ~30% (adoption) of 100 m soybean acres x 0.5 lb ai = <u>15 m lbs</u> of dicamba applied in U.S.

Example: glyphosate ~200 m acres RR corn and soy x 0.75 lb ae = <u>150 m lbs</u> glyphosate applied in U.S.

15 m lbs dicamba vs. 150 m lbs glyphosate

(Not include: preplant, higher rates, multiple applications, and other RR crops)



Parable of the 5 blind men and elephant

Trunk = snake Leg = pillar/tree-trunk Side = wall Tail = rope Tusk = spear.



Dr. Don Penner Michigan State University

"Most aspects of science and life can be explained through chemistry"



Dr. John Nalewaja Michigan State University

"Tell science as a story"

Dicamba drift on soybean:

- 1. Injury across entire fields (1/4 section)
- 2. Injury occurred 3 to weeks after application
- 3. Injury occurred 2 to 3 times across same field

How is vapor drift different than particle drift?



Application Education Summary

36

12	HERBICIDE	6	WEED HEIGHT
NOW CTA APPROVED FOR IN-CROP USE	Low volatility XtendiMax [®] herbicide with VaporGrip [®] Technology	<4"	Spray weeds that are less than 4 inches tall
Apris	AMMONIUM SULFATE Ammonium sulfate and ammonium-based additives are prohibited in applications that include XtendiMax" with VaporGrip" Technology	3-10 mph	WIND SPEED Apply when wind speed is between 3 and 10 mph
22 flozik	APPLICATION RATES Apply 22 fluid ounces per acre for any single, in-crop application		DOWNWIND BUFFER Maintain the required label buffer to protect sensitive areas
	SPRAY VOLUME Apply in a minimum of 40 gallons of spray solution per acre		SUSCEPTIBLE CROPS Do not apply when wind is blowing toward adjacent susceptible crops
8	NOZZLES To minimize drift, use nozzles approved on the herbicide product label and operating pressures to minimize driftable fines	e 15 mph	GROUND SPEED Do not exceed 15 mph ground speed
I (24)	SPRAY BOOM HEIGHT Do not exceed a boom height of an inches abuve target get or cron canony. Excession	3	TRIPLE RINSE

Some things a grower can control. Once the droplet leaves the nozzle then no control

Very important question

1. What happens to bapma salt and Vapor Grip after droplet is released from nozzle?

Deposit formation after water evap.
Pool of H⁺ on leaf surface and soil
Effect dew and small rain events

Very important question

As water evaporates in droplet:

- protons (H+) accumulate
- pH decreases = lower acidity
- acidity increase protonation (pKa)
- protonated dicamba = dicamba acid
- dicamba acid = volatile form

How does that affect the Vapor Grip?

Monsanto/BASF Academic Summit – Fall 2017

- 1. Under what conditions do dicamba anion and acid form?
- 2. Does the salt dissociate and bind again in an equilibrium?
- 3. Do other cations compete with binding sites of dicamba?
- 4. How does high surface temperatures influence dissociation?
- 5. What is the fate of dicamba under drought?
- 6. Does dew solubilize dicamba deposits and cause volatility?
- 7. How does dicamba cause symptoms 30 days after exposure?
- 8. How does dicamba injury soy multiple times on same field?
- 9. Explain effect of other ammonia sources?
- 10. Why was physical properties of dicamba not discussed?

Anonymous letter to AR Plant Board – Sept 2017

Dear Arkansas State Plant Board:

As a career agricultural formulation chemist, I have viewed the development of genetically modified crops to allow post emergent application of dicamba with skepticism regarding any formulation technology that could effectively keep dicamba from volatilizing after application.

The Facts about Dicamba

Acidity and Dissociation Constant

Dicamba is considered a strong acid having an acid dissociation constant (pKa) of 1.87. The pKa value indicates a compound's ability to dissociate from its salt when dissolved in water. The pKa value is also an indication of a compound's acidic strength.

Simply put, the lower the value the stronger the acid. When compared to 2,4-D, which has a pKa value of 2.8, dicamba is nearly 10 times more acidic than 2,4-D and is more

Due to the sensitive nature and the emotion this issue has generated, I am submitting these comments anonymously. Hope the plant board understands.

ability to associate with any stronger basic ion, a cation, that might also be present in

Questions:

How much dicamba is FREE?
What is the fate of dicamba?
In what form is free dicamba?

Herbicide Absorption

How much glyphosate is absorption?

Herbicide Absorption

•How much glyphosate is absorption? = ~33%

•How much dicamba is absorbed?

Dicamba Absorption Data

- Wheat = 80% (Cessna Weed Sci 41:682-686)
- Leafy spurge = 60% (Lym et al. Weed Tech 19:329-341)
- Kochia = 35% (Cranston et al. Weed Sci 49:164-170)
- Apple leaf cuticles No adjuvant = 15%

6 adjuvants at 2 rates = 25 to 30%

(Adams and Zollinger, 2016 – absorption studies conducted in Germany in collaboration with Clariant)
- Wheat = 80% (Cessna Weed Sci 41:682-686)
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6 adjuvants at 2 rates = 25 to 30%

(Adams and Zollinger, 2016 – absorption studies conducted in Germany in collaboration with Clariant)

• Dicamba absorption in waterhemp = ?

• Dicamba absorption in soybean = ?

• Soybean = (-) surfactant = 38%

(+) surfactant = ~75%





Soybean exude 66% of absorbed dicamba through roots!!!

* Implication on soybean toxicity

* Influence tissue residue tests

(Peterson, Haderlie, Hoefer, McAllister, Weed Sci 33:717-720)

Dicamba Absorption Data Average absorption Soybean = 38-75% Leafy spurge = 60%Kochia = 35% Apple cuticles - 15% - 30% ~50% absorbed ~50 unabsorbed! 0.25 lb of dicamba on leaf + soil surface 7.5 m lbs of dicamba FREE!

Questions:

How much dicamba is FREE?
 What is the fate of dicamba?
 In what form is free dicamba?

What does dicamba look like after water is gone?

Herbicide deposit on leaf surface

What does dicamba look like after water is gone?

Herbicide deposit on leaf surface





Glyphosate deposit

2,4-D ester

Dicamba crystallization on leaf surface

Deposit of dicamba crystals after water evaporation from droplet.

Mag 1000x

BOP2830 V4

SE

Scanning electron microscope

Adams and Zollinger- NDSU

What is the fate of dicamba?

- Dissociated or acid?
- Wetting from dew?
- Wetting from light rain?
- Re-crystallized?

Universal principle of chemistry =

ADSORPTION



How much dicamba is adsorbed to soil?

Soil adsorption coefficient (Kd) = amount of chemical adsorbed to soil per amount of water.

- Kd = Concentration of chemical in soil/water
- Koc = (Kd * 100)/ % Organic carbon Concentration of chemical in OM/water
 What are the values of dicamba?
 Kd range = 0 to 600
 Koc range = 0 to 10,000

Dicamba Physical Properties				
	Koc (mg/L)	Kd (mg/L)		
Acetamides	100-600	1.1-2.7		
DNAs	3000-9000	-		
EPTC	136-264	0.77-3		
Sulfentrazone	43	1		
Glyphosate	24,000	324-600		
2,4-D	20-136	0.17-1.27		
Clopyralid	~60	_		
Fluroxypyr	40-71	0.78-1.34		
Picloram	17-160	0.5		
Dicamba	?	?		

Dicamba Physical Properties				
	Koc (mg/L)	Kd (mg/L)		
Acetamides	100-600	1.1-2.7		
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2,4-D	20-136	0.17-1.27		
Clopyralid	~60	_		
Fluroxypyr	40-71	0.78-1.34		
Picloram	17-160	0.5		
Dicamba	2	0.05-0.13 – Not adsorbed!		

What main environmental factor affects volatile herbicides on soil?

Herbicide vapor pressure				
		mm Hg (mercury	<u>()</u>	
Liber	ty	0.00000000009	$(x10^{-12})$ b	
Para	quat	0.00000001	(x10 ⁻⁹) ²	
Glypł	nosate	0.0000002	(x10 ⁻⁸)	
Trefla	an	0.0002	(x10 ⁻⁴)	
2,4-D	salt	"Not volatile"	1.4 x 10 ⁻⁷	
	ester	0.0004	(x10 ⁻⁴) 4	
	acid	0.4 (insoluble in	water)	
Dicar	nba salt	0.000002	(x10 ⁻⁶)	
	acid	0.00002	(x10 ⁻⁵) at 75F	
	acid	0.004	(x10 ⁻³) at 100F	
Eptar	n	0.03	(x10 ⁻²)	
Wate	r	24		

Temperature and vapor pressure of dicamba



Questions:

How much dicamba is FREE?
 What is the fate of dicamba?
 In what form is free dicamba?

Why Engenia[™] Herbicide? A stepwise improvement on reduced volatility



Relative Volatility vs. Form of Dicamba¹



¹Volatility ratings using five different measurement techniques: Field testing, Humidome, TGA, C¹⁴, Incubator





Engenia – Molecular Weight Theory

What is wrong with this picture?

BAPMA salt reduces volatility risk



Banvel[®] Herbicide DMA Dicamba

Clarity[®] Herbicide DGA Dicamba

MUUUU

Dissociation – fundamental principle of chemistry

Salt compounds dissociate in water!



С С Dicamba-bapma or -dga or -dma

Cl

O



Anonymous letter to Arkansas Plant Board

Susie Nichols Arkansas State Plant Board P.O Box 1069 Little Rock, AR 72203

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Simply put, the lower the value the stronger the acid. When compared to 2,4-D, which has a pKa value of 2.8, dicamba is nearly 10 times more acidic than 2,4-D and is more acidic than glyphosate, which has 3 pKa values of 2.6, 5.6, and 10.3 due to glyphosate being a polyprotic acid.

Engenia[™] Herbicide Why will AMS be restricted?

We create chemistry



Spray Water Quality



very little absorption

Does the same thing happen to dicamba?

Water Conditioner



Glyphosate-NH₄

Vapor Grip – The Great Inigma

XtendiMax with "Vapor Grip"? 90% lower volatility than Clarity

What is Vapor Grip? Monsanto Academic Summit – Sept 27, 2018 "Polymerized carboxylic acids"???

What is the mode of action of Vapor Grip? "Do not add acidifiers" "Do not add AMS"

Dicamba Physical Properties

pKa = the pH value at which equal concentrations of the acid and conjugate base forms of a substance.

- At pKa:
 - -1/2 molecules lose their protons = anion

-1/2 molecules retain protons = neutral

Dicamba pKa =

50% molecules = anion = No volatility 50% molecules = acid = High volaitility

Dicamba Physical Properties

	рКа
Paraquat	
Glyphosate	2.6, 5.6, 10.3
2,4-D	2.73
Aminopyralid	2.56 - dissociated and (-) charge
Clopyralid	2.3 - dissociated and (-) charge
Fluroxypyr	3
Picloram	2.3
Dicamba	1.87

Dicamba Physical Properties

4. XtendiMax with "Vapor Grip"? pH < 5.5 = dicamba-dga $\xrightarrow{H^+}$ dicamba-acid

 $pH > 5.5 = dicamba-dga \longrightarrow dicamba-anion$

Dicamba pKa = ~2 dissociation constant
Low H+
$$pH 6 = 99.99 : 0.01$$
 ratio of anionic : acid molecules
 $pH 5 = 99.9 : 0.1$ "
 $pH 4 = 99:1$ "
 $pH 3 = 90:10$ "
High H+ $pH 2 = 50:50$ "



VaporGrip[™] Technology

DMA Dicamba

(Not Approved for use in the Roundup Ready® Xtend Crop System)



In the tank there is the potential for dicamba acid (DCH) to form in solution and create off-target movement of dicamba through volatility after spraying

9

Low-Volatility Dicamba with VaporGrip™ Technology



In the tank, VaporGrip™ Technology prevents the formation of dicamba acid (DCH) in solution, minimizing potential off-target movement of dicamba through volatility after spraying

THIS PRESENTATION ON APPLICATION REQUIREMENTS IS NOT A SUBSTITUTE FOR THE PRODUCT LABELING ALWAYS READ AND FOLLOW ALL PRODUCT LABELING. V1 – 11/2016

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MONSANTO

What is Vapor Grip?



BAPMA: H₂N





Dicamba-anion

Many other anions can compete with binding sites.

Engenia[™] Herbicide Why will AMS be restricted?



Engenia – 560 g/ha AMS – 0.5% w/v

Time: 1 day (24 hr), Air flow: 0.5 l/min using 2.5 l tank, Relative Humidity: 5%, Substrate: glass We create chemistry



Ammonia loss from soil, ND



2015, Franzen, NDSU


Ammonia exchange from corn foliage during reproductive growth. Francis, Schepers, and Sims Agron J 89:941-94(1997)

Table 3. Concentration of NH₃-N and atom % ¹⁵N in air drawn over various corn leaves at the R2-R3 growth stage in greenhouse and field.

Plant component	NH ₃ -N concentration	¹⁵ N concentration	
	μg N m ⁻³	atom % ¹⁵ N	
Field plots, 16 Aug.			
Ambient air	3.7 ± 0.1	0.3682 ± 0.0038	
3rd leaf above ear	3.9 ± 0.3	0.4567 ± 0.0166	
Ear leaf	5.1 ± 0.6	0.5890 ± 0.0465	
3rd leaf below ear	4.2 ± 0.1	0.4395 ± 0.0204	
LSD (0.05)	0.7	0.0502	

Ammonia exchange from corn foliage during reproductive growth. Francis, Schepers, and Sims Agron J 89:941-94(1997)

- Nitrogen in plant foliage can be lost by volatilization (Farquhar et al., 1980)
- Loss of NH3 was found to occur during all sampling periods
- Highest volatilization rates occurred during reproductive growth (Harper et al., 1987; Holtan-Hartwig and Bockman, 1994)
- Agricultural crops (i.e. corn) grown under high N fertility levels will loose high levels of NH3 (Holtan-Hartwig and Bockman, 1994)
- Large number of plant communities dispersed across the land suggests that, in aggregate, vegetation is a significant source for atmospheric NH3.

- The field study found that 15% of the applied N was lost as ammonia.

Ammonia binding to anions

Ammonia/Ammonium is a:

- flirtatious ion moving from partner to partner
- binds with anions with the most attraction
- breaks up the marriage of dicamba and DGA salt
- DGA finds solace with calcium or sodium
- or disappears into the foliage and consumed for its N
- can on a whim then leave the anion alone as free acid
- when the ammonium cation has moved on, the lonely sulfates left behind acidify the soil.

Soybean injury from dicamba vapors:1. What gas do plants absorb from atmosphere2. What gas do plants release into atmosphere3. Would dicamba "gas/vapor" be any different?

Dicamba Summary:

- 1. Unprecedented soybean susceptibility
- 2. Atmospheric loading
- 3. Low foliar absorption
- 4. No soil adsorption
- 5. High air and soil temperatures
- 6. Dissociation of salt
- 7. Fate as salt or acid
- 8. Pools of ammonia from soil and plants



Factors to reduce dicamba drift:

ND Weed Guide page 29

- 1. PRE only and maybe EPOST
- 2. Temperatures below 85
- 3. Sufficient rain to deposit dicamba in soil



Herbicide water solubility

<u>Herbicide</u>	<u>H₂O solubility</u>		
	_ ppm)		
Atrazine	35		
Callisto	160		
Harness/Surpass	282		
Metolachlor	530		
Prowl	0.33		
Glyphosate	10,500		
Dicamba	250,000		
Paraquat	620,000		

Factors to reduce dicamba drift:

1. PRE only and maybe EPOST

2. Temperatures below 85





Table 1: Soybean Injury and subsequent yield Columbia, MO 2016

Sovhea	Herbicide Rate		% Injury	Yield	
n stage	dicamba rate*	Amount compared to labeled rate	14 Days After Treatment	Bushel/acre	
V3	0.05 lb/a	1/10th	80	32	
V3	0.005 lb/a	1/100th	70	54	
V3	0.0005 lb/a	1/1000th	50	54	- Q II:
V3	0.00005 lb/a	1/10,000th	45	52	The second
V3	Glyphosate only		0	56	A.
R1	0.05 lb/a	1/10th	80	6	Det y
R1	0.005 lb/a	1/100th	60	40	and the
R1	0.0005 lb/a	1/1000th	50	49	1
R1	0.00005 lb/a	1/10,000th	20	55	
R1	Glyphosate only		0	59	

Soybean injury increases as plant age increase

Summary of dicamba yield studies





Xtend and Enlist Systems

	Dicamba		2,4-D
Soybean	Susc	eptible	~Tolerant
Acid	Vola	tile	Not volatile
AMS/NH ₃	Vola	tile	Not volatile
Rate	0.5 l	b ai	0.7-0.95 lb ai
Soil residue	2-3 \	weeks	None
Kochia	+		_
Waterhemp) = 9	size dep	endent

