WASHINGTON STATE UNIVERSITY
EXTENSION

Chemical and Environmental Influences for Off-Target Movement of Auxin Herbicide Droplets and Vapor

Allan Felsot

Department of Entomology

Washington State University

Agenda

- Dicamba Blues
- Application of environmental chemodynamic principles to understanding volatilization and atmospheric transport
  - ✓ The importance of physicochemical properties, phase transfer, and mass transfer
  - ✓ Importance of temperature and moisture conditions
  - ✓ Physics of spraying
- New herbicide formulation technologies and the issue of volatilization
- A quasi risk assessment approach to understanding dicamba issues

Once Upon a Time…

Monsanto Submits a Petition to the USDA APHIS for Non Regulated Status of Its New Dicamba Resistant Soybean Cultivar

MONSANTO™

Petition for the Determination of Nonregulated Status for Dicamba-Tolerant Soybean MON 87708

The undersigned submits this petition under 7 CFR §340.6 to request that the Administrator make a determination that the article should not be regulated under 7 CFR Part 340

July 6, 2010

(Revised on October 10, 2011, March 1, 2012 and March 26, 2012)

OECD Unique Identifier: MON-877Ø8-9

Monsanto Petition Number: 10-SY-210U

USDA Agrees (After ~4 Years of Hazard Assessment)

Determination of Nonregulated Status for Monsanto Company MON 87708 Soybean

In response to petition 10-188-01p from Monsanto Company (hereinafter referred to as Monsanto), the Animal and Plant Health Inspection Service (APHIS) of the United States Department of Agriculture (USDA) has determined that Monsanto dicamba herbicide-resistant MON 87708 soybean (hereinafter referred to as MON 87708 soybean) and progeny derived from it are not likely to pose a plant pest risk and are no longer to be considered regulated articles under APHIS' Biotechnology Regulations at Title 7 of the Code of Federal Regulations, part 340 (7 CFR part 340). Since APHIS has determined that MON 87708 soybean is unlikely to pose a plant pest risk, APHIS will approve the petition for nonregulated status of MON 87708 soybean. Therefore, APHIS approved permits or acknowledged notifications that were previously required for environmental release, interstate movement, or importation under these regulations will no longer be

M.J. Firko — 14 January 2015

Michael J. Firko, Ph.D. — Date

APHIS Deputy Administrator
Biotechnology Regulatory Services
Animal and Plant Health Inspection Service
U.S. Department of Agriculture

USDA **United States Department of Agriculture**
Animal and Plant Health Inspection Service

The Troubles Begin—2016

10 States Report Crop Damage From Illegal Dicamba Use on Monsanto's GMO Seeds

To the horror of farmers across America's farm belt, hundreds of thousands of crop acres have been adversely impacted by the apparent misuse of the drift-prone herbicide dicamba on Monsanto's Roundup Ready Xtend soybean and cotton plants.

Vapor Grip's Not Sticky Enough?

Crops in 25 States Damaged by Unintended Drift of Weed Killer

By ERIC LIPTON • NOV. 1, 2017

The New York Times

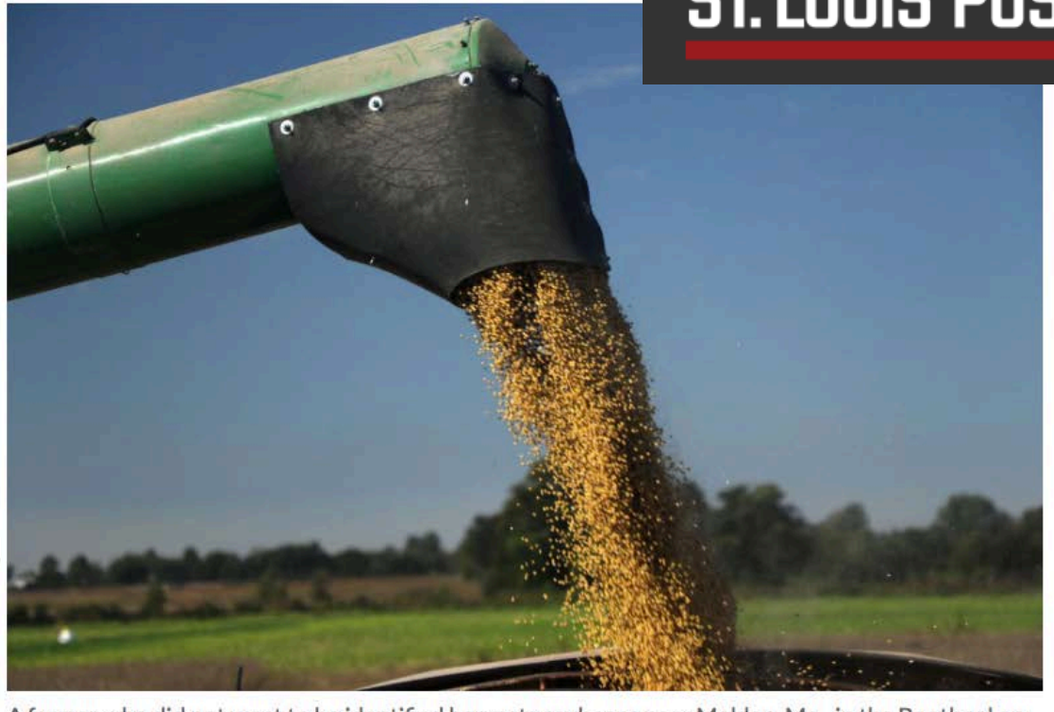
ybeans at his farm in Dell, Ark., which he said showed signs of
a. Karen Pulfer Focht/Reuters

ller called dicamba has damaged more than 3.6
s, or about 4 percent of all soybeans planted in the
Environmental Protection Agency said Wednesday in
response.

Dicamba damage is back — and possibly worse than before

By Bryce Gray St. Louis Post-Dispatch Jun 25, 2017 (5)

ST. LOUIS POST-DISPATCH



A farmer who did not want to be identified harvests soybeans near Malden, Mo., in the Bootheel on Tuesday, Oct. 11, 2016. The area has experienced diminished yields believed to be caused by illegal applications of the herbicide, dicamba. Photo by Bryce Gray

And You Thought Politics Was Divisive?

The Regulatory Systems Gets Retroactively Proactive

Missouri and Arkansas ban dicamba herbicide as complaints snowball

By Bryce Gray St. Louis Post-Dispatch Jul 7, 2017 (0)

Soybean plants grow in a growth chamber at the Monsanto Chesterfield Village facility in Chesterfield,

ST. LOUIS POST-DISPATCH

As complaints of damage from dicamba spiral ever higher across multiple states, officials in both Missouri and Arkansas enacted bans Friday on the herbicide blamed for vaporizing and injuring crops without genetically engineered resistance.

Play Nice, Guys

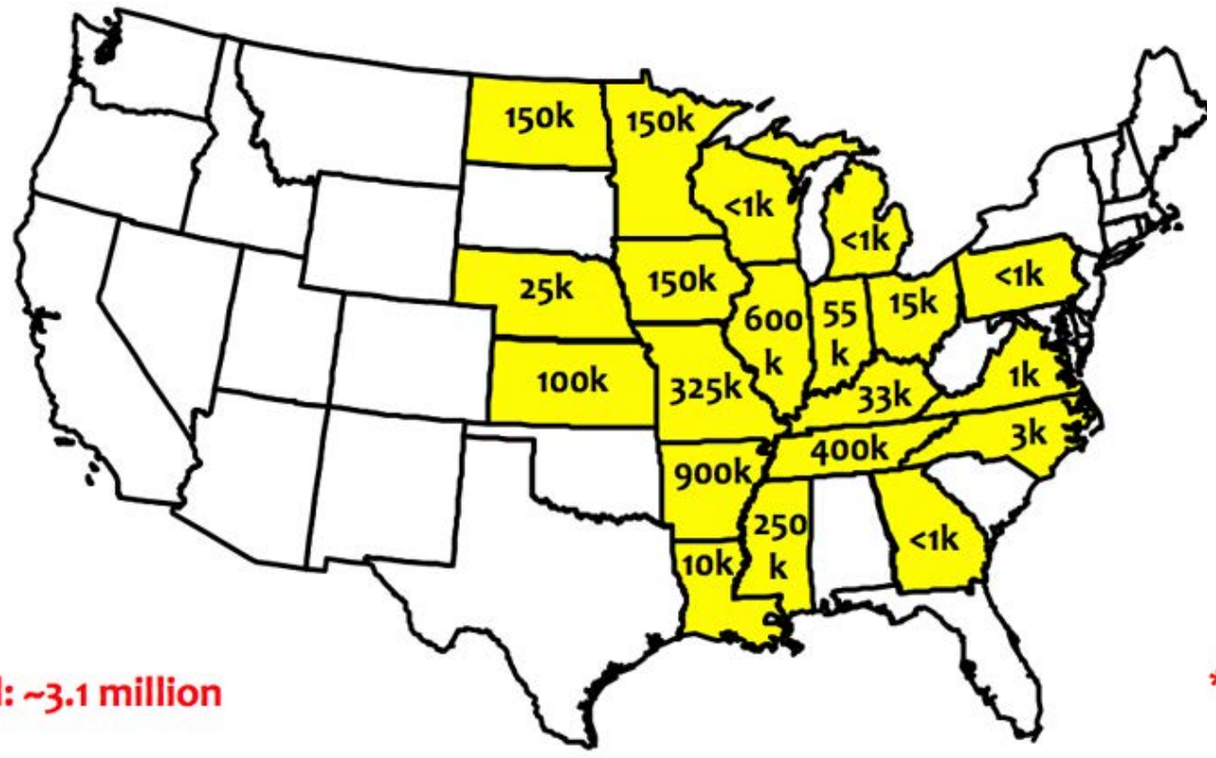
Monsanto Attacks Scientists After Studies Show Trouble For Weedkiller Dicamba

Dan Charles • October 26, 20174:57 AM ET

Bob Scott, a weed scientist at the University of Arkansas, says he wishes more testing could have been done on the new dicamba formulations, but "the product was not made available to us."

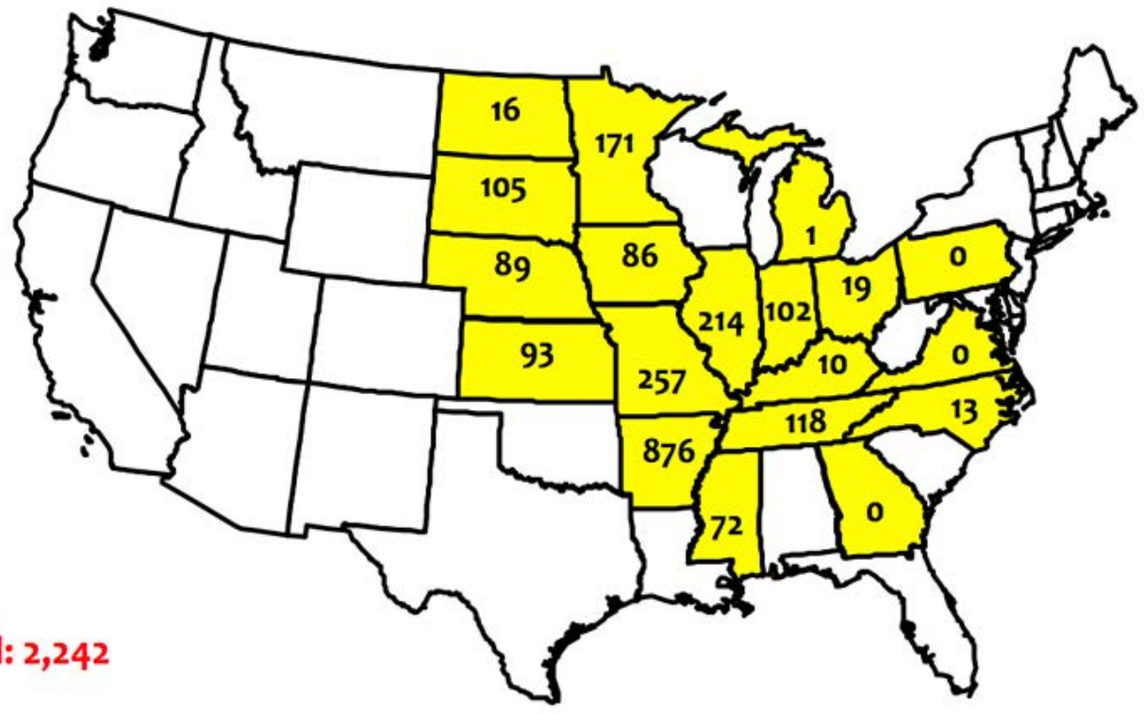
States Reporting Damage During 2017

Estimates from Weed Scientists



*Total: ~3.1 million

Documented Reports to State Agencies



*Total: 2,242

Credit: Prof Drew Lyon, WSU

What Up?

Same Old Story?

We’ve Been Here Before!

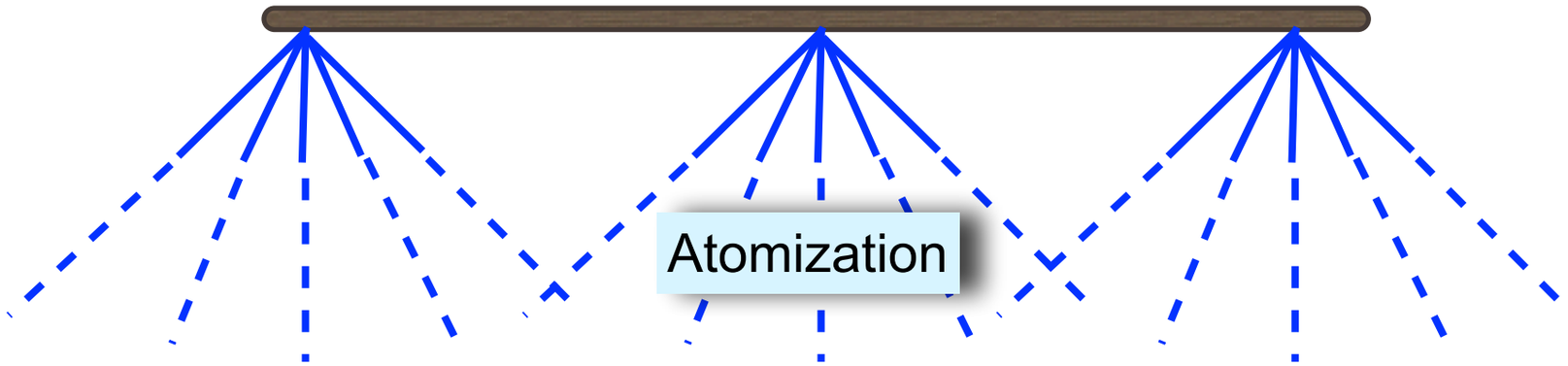
The Blame Game

Problems with Non-Target Phytotoxicity Presumed to be Caused by…

- Spray drift
  - ✓ Thus, farmers' fault
- Volatilization post drift
  - ✓ Thus Monsanto's fault

Time to Look Under the Hood for a New Perspective—A Physcial Chemists Understanding of How Chemicals Behave in the Environment: Environmental Chemodynamics

- Environmental Chemodynamics
  - ✓ Interdisciplinary study of the relationship between physicochemical properties and environmental behavior
  - ✓ **Objective: Predict exposure by studying distribution of pesticide residues in the environment**
- Focus Areas
  - ✓ Physicochemical properties
  - ✓ Partitioning (Phase transfers)
  - ✓ Attenuation
  - ✓ Transport
  - ✓ Modeling



Atomization

Drift Losses

Transport to Target

Evaporation

Impaction on Target

Reflection
(Bounce-Off)

Retention

Spreading

Drying

Deposit Formation

Movement in/on Plant

Diffusion into Animal

Biological Effect

Soil

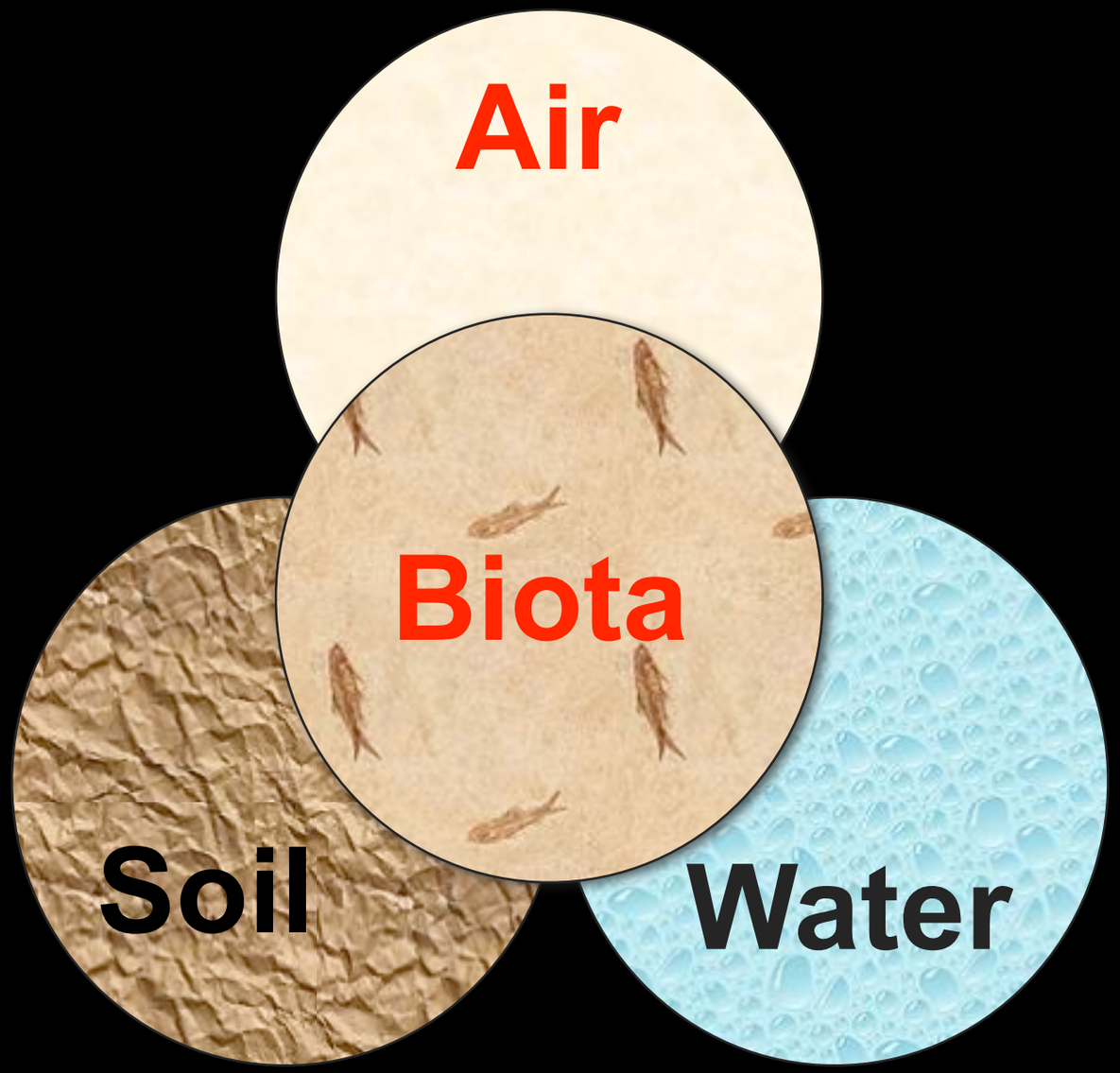
Washoff
Photodegradation
Metabolism
Root Exudation

Volatilization

Runoff
Leaching

Holistic Perspective

Environment is perceived as
interfacing compartments or phases



Fundamentals of Chemical Behavior

- All molecules are governed by

  ✓ **Thermodynamics** (energy relationships in a system)

    ✳ Molecules naturally arrange themselves so that the total energy in a system is at the lowest possible level (maximum entropy)

    ✳ All systems tend toward equilibrium (the lowest energy state)

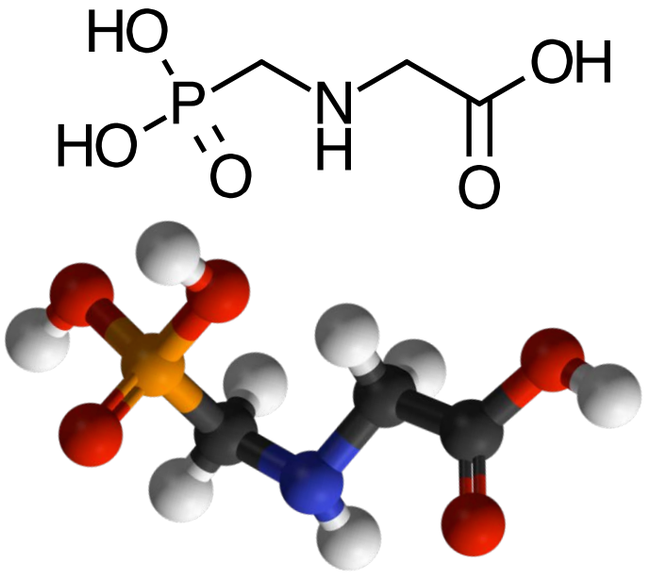
  ✓ **Kinetics** (reactivity of system components)

    ✳ How fast are chemical reactions?

    ✳ What kinds of reactions are possible?

Physicochemical Properties

- Intrinsic directly or indirectly measurable characteristics of molecules that vary with the environment they are measured in



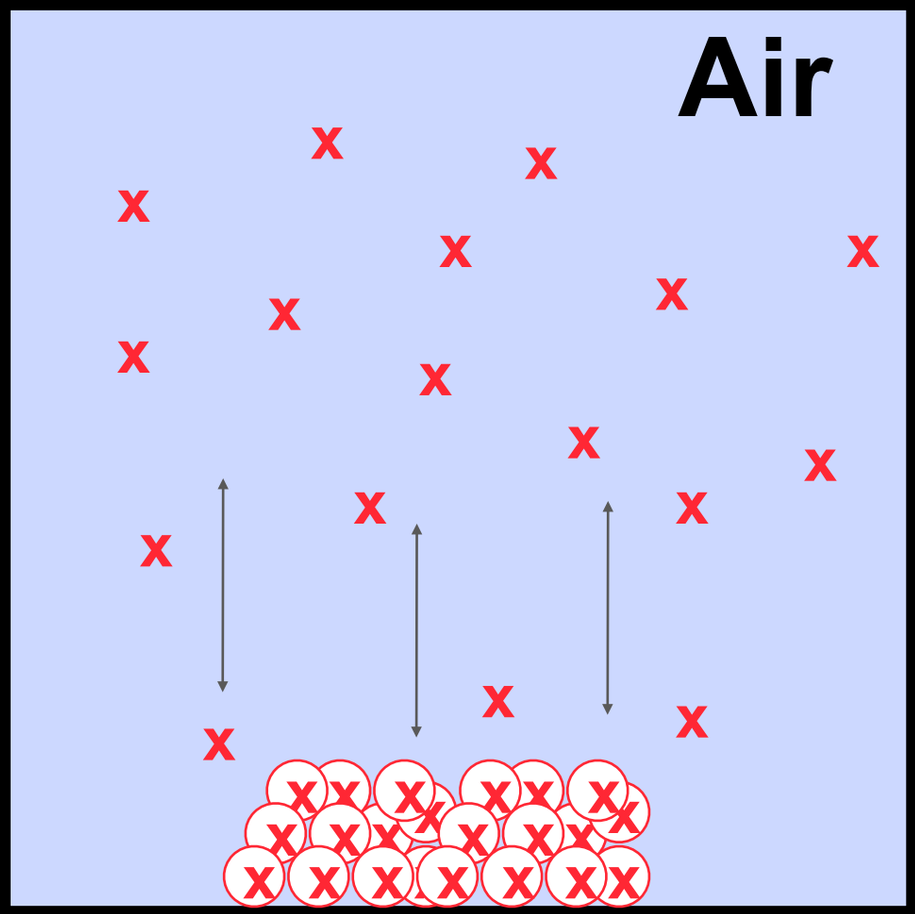
✓ Magnitude of properties results from the specific chemical structure (i.e., the 2-D & 3-D arrangement of the atoms)

✓ These unique characteristics are the driving forces for distribution in the environment, allowing us to make predictions of behavior

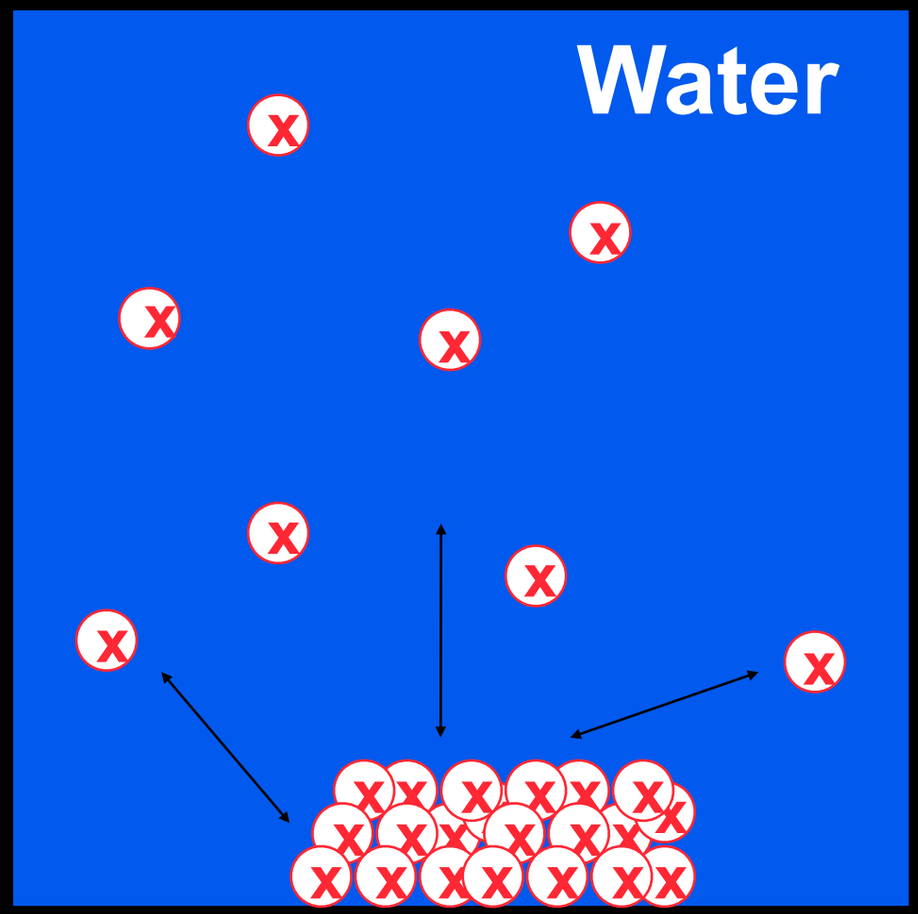
✓ Properties are dynamic depending upon the conditions under which they are measured

Physicochemical Properties

Vapor Pressure



Water Solubility



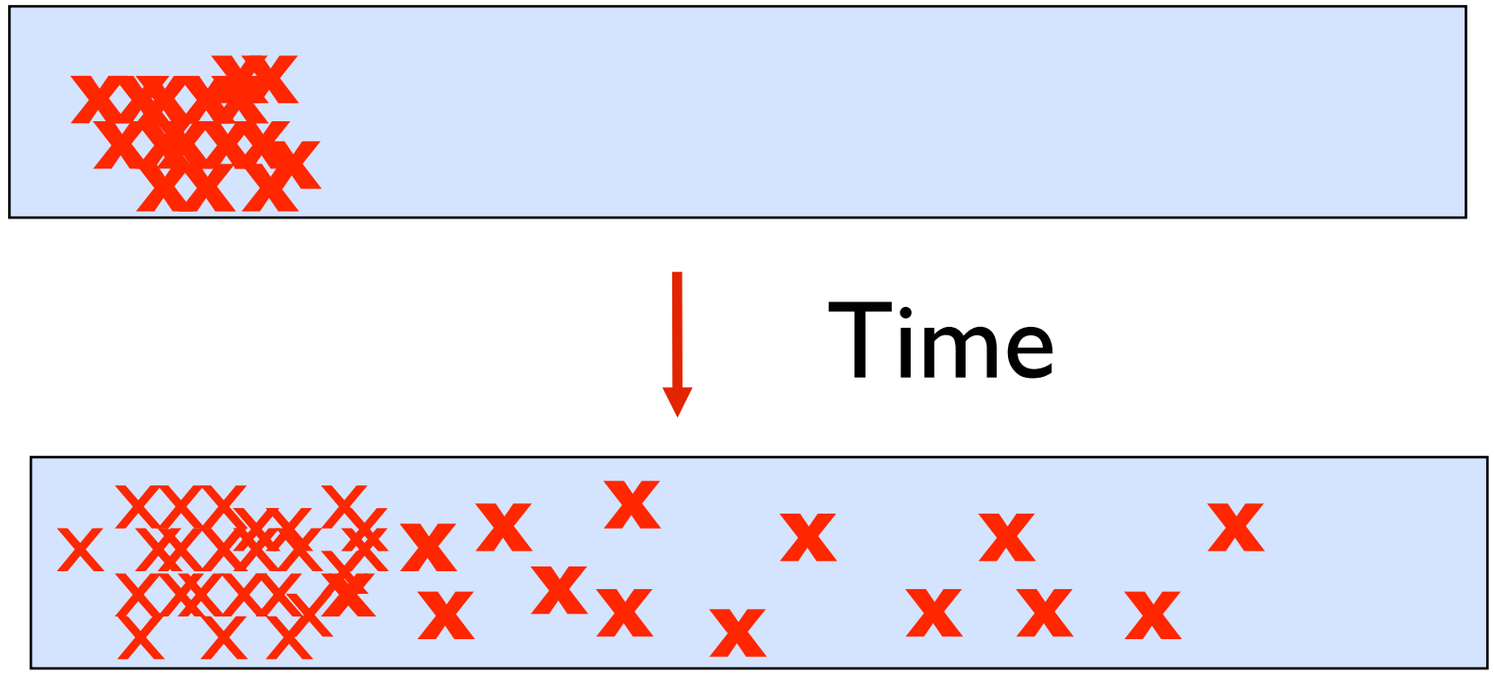
Molecules of ***pure substances*** escape (disperse) from one another and recondense with each other until equilibrium is reached. At equilibrium there is no net movement & energy of the system is at lowest level.

Phase Transfer Processes

- Reversible partitionings of dilute concentrations of a compound between two phases (for ex., soil & water; water & air)
- Expressed by the partition coefficient
  - ✓ Ratio of the concentration of the chemical in one phase (air, soil, biological tissue, organic solvent) relative to the concentration in water
  - ✓ Can be thought of as the ratio of the fugacity (escaping tendency) between two phases
- Phase transfers occur through diffusion, the molecular scale movement of molecules

Fundamental Driver: Diffusion

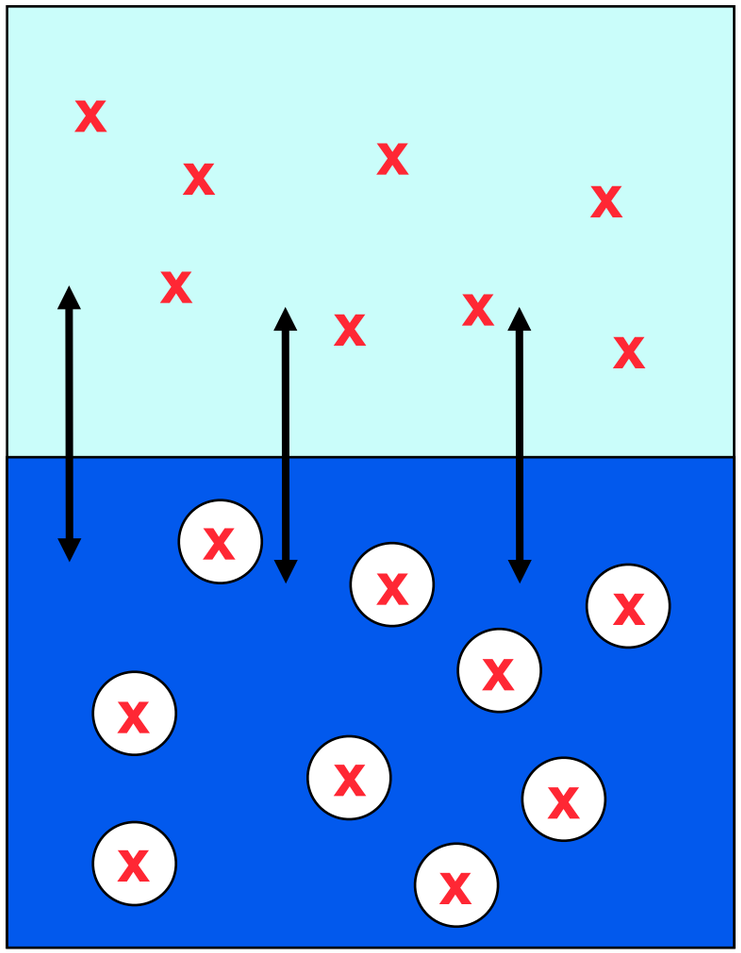
- Tendency of molecules to move within a medium (phase) from high concentration to low concentration



Phase Transfer (Partitioning)

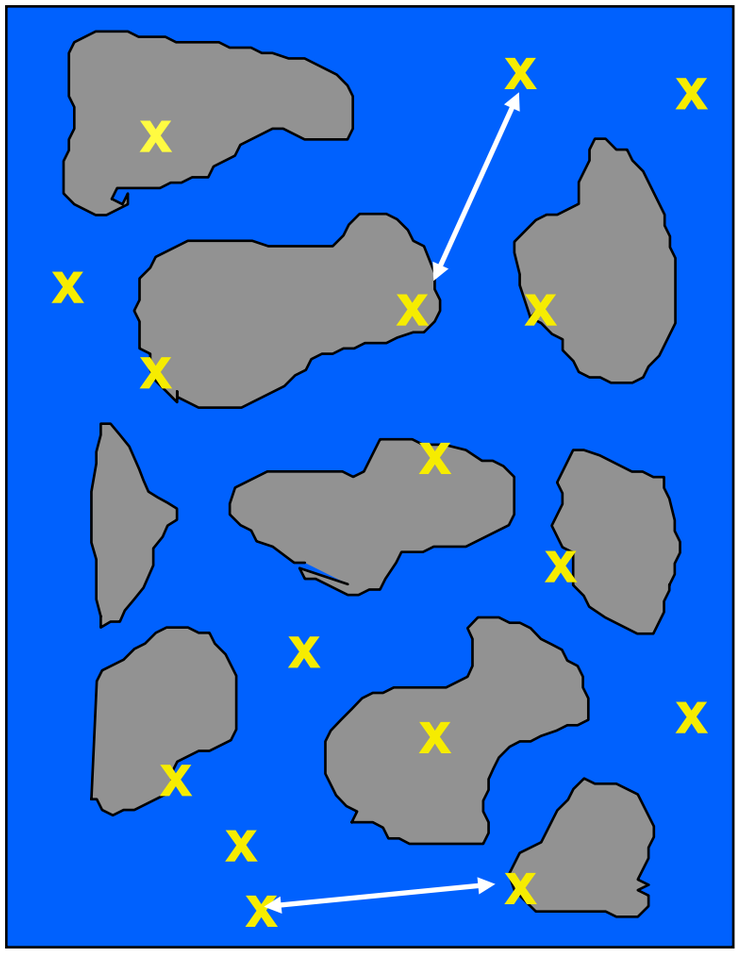
Tendency of molecules to escape from one medium (air, water, soil, organism) into another medium

Air:Water



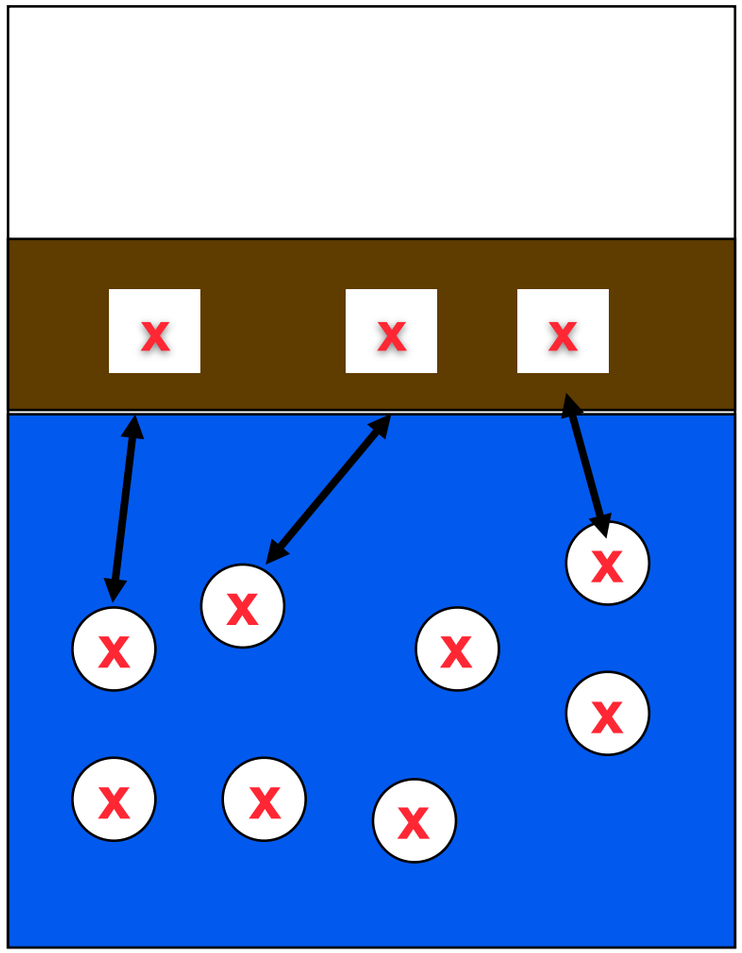
Henry's Law Constant
(K_H)

Soil:Water



Soil Sorption Coeff.
(K_{oc})

Oil:Water

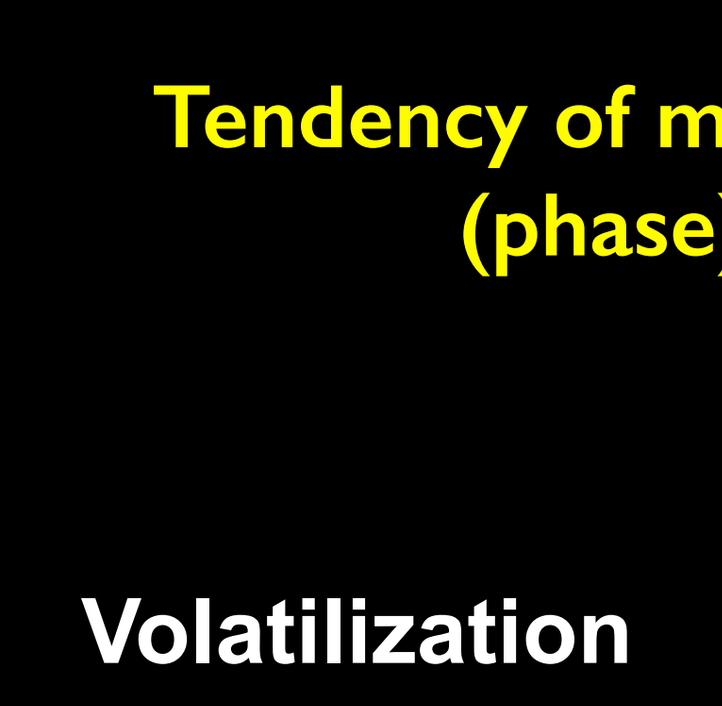


Octanol-Water Partition Coeff.
(K_{ow})

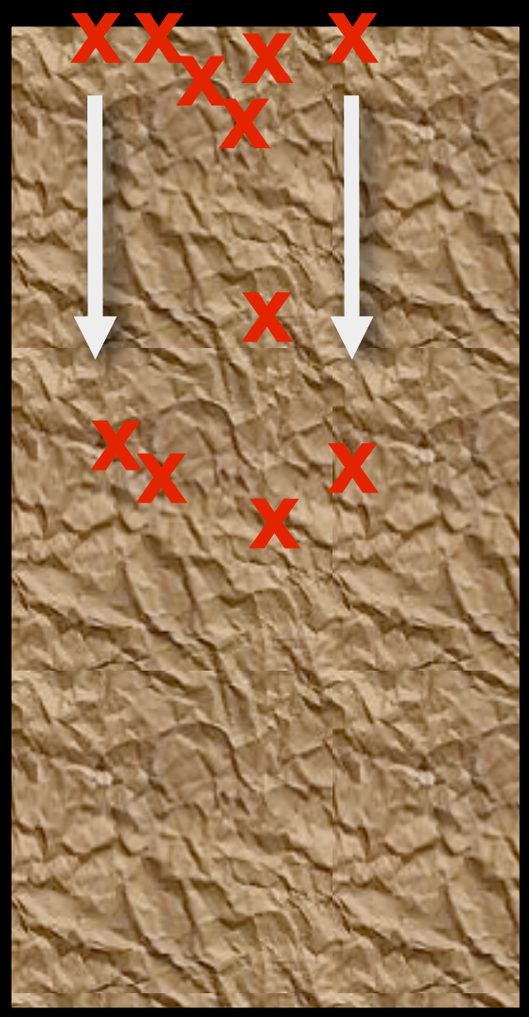
Transport Processes = Mass Transfer

Tendency of molecules to be carried by a medium (phase) from one place to another

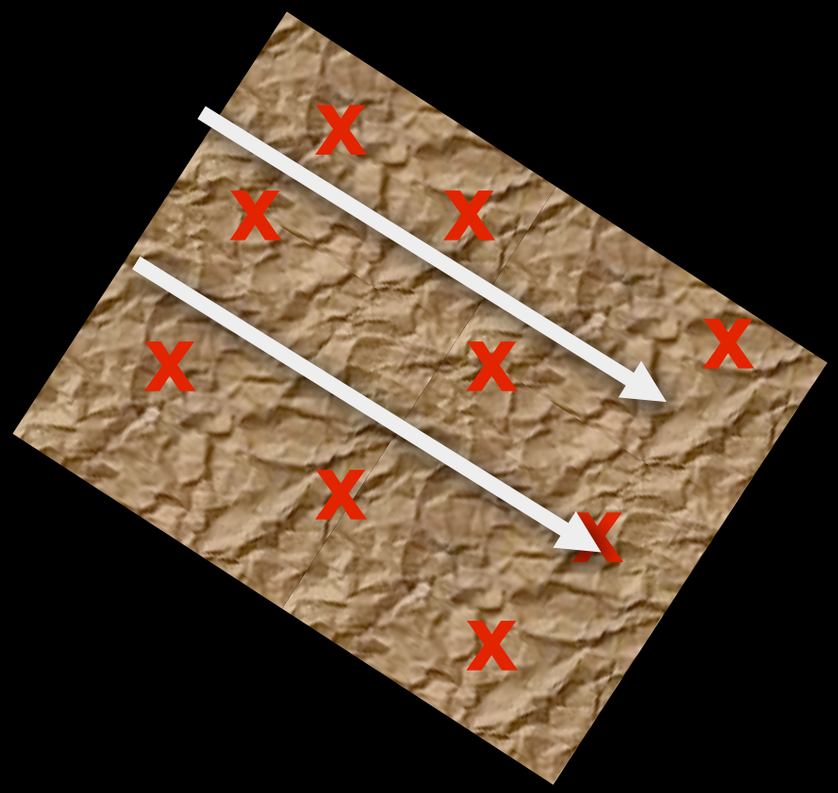
Volatilization



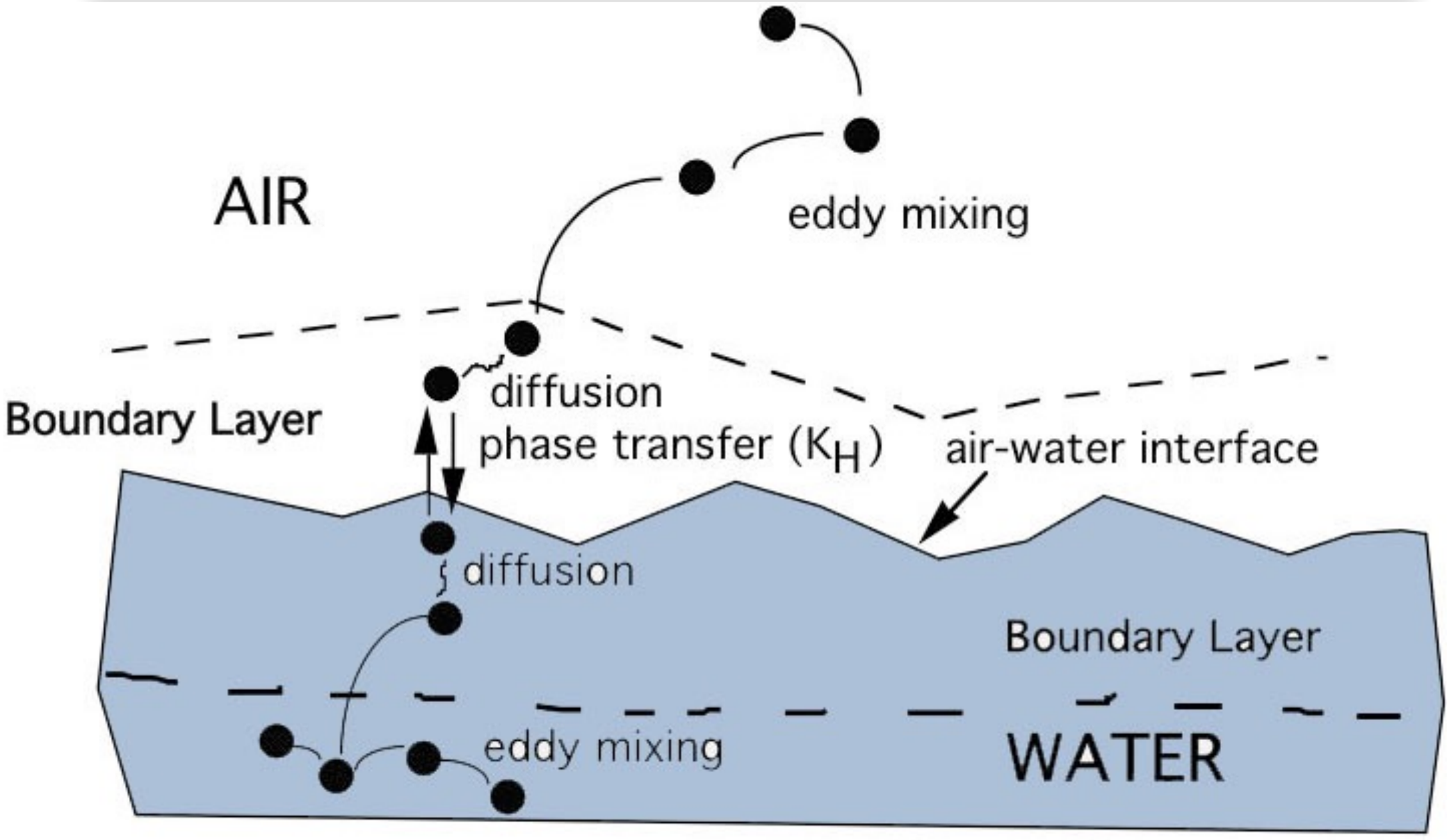
Leaching



Runoff

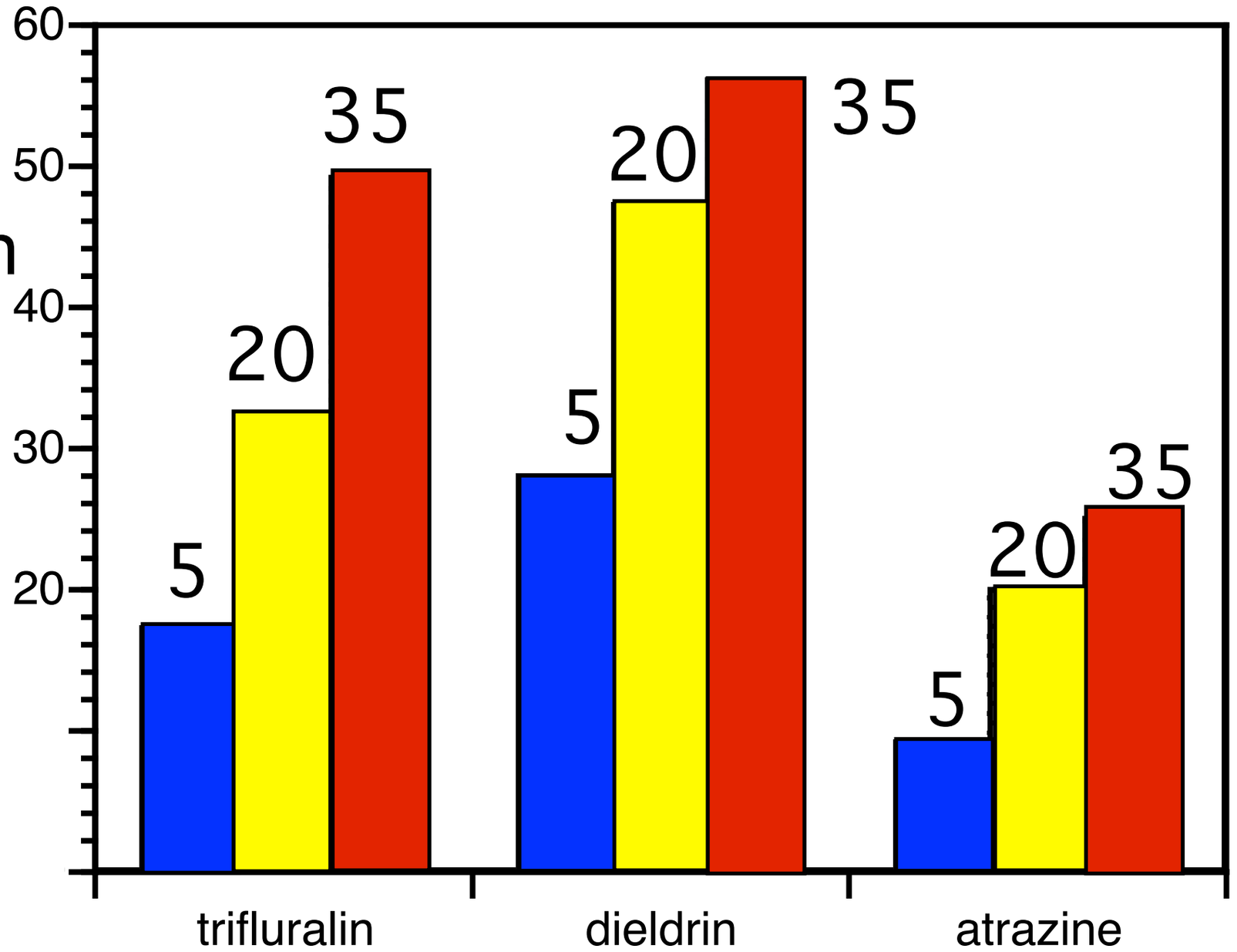


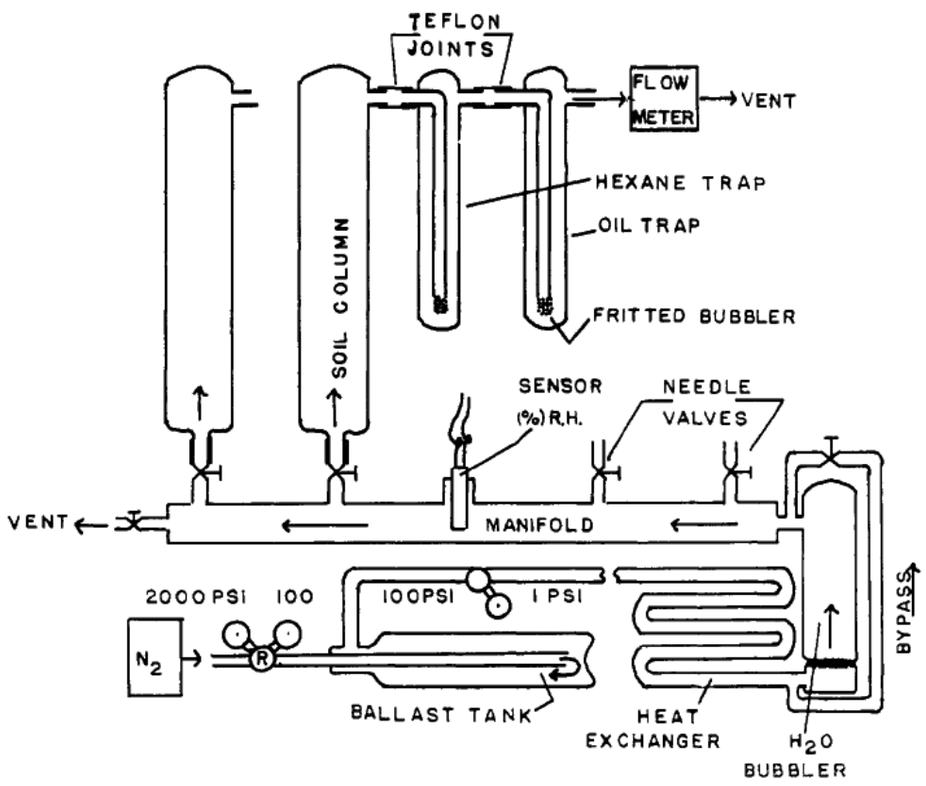
So, What Is Really Happening During Volatilization



Volatilization is actually a multi-step process consisting of molecular diffusion into a boundary layer followed by movement into a turbulent layer where the concentration of the chemical is continually reduced by eddy diffusion

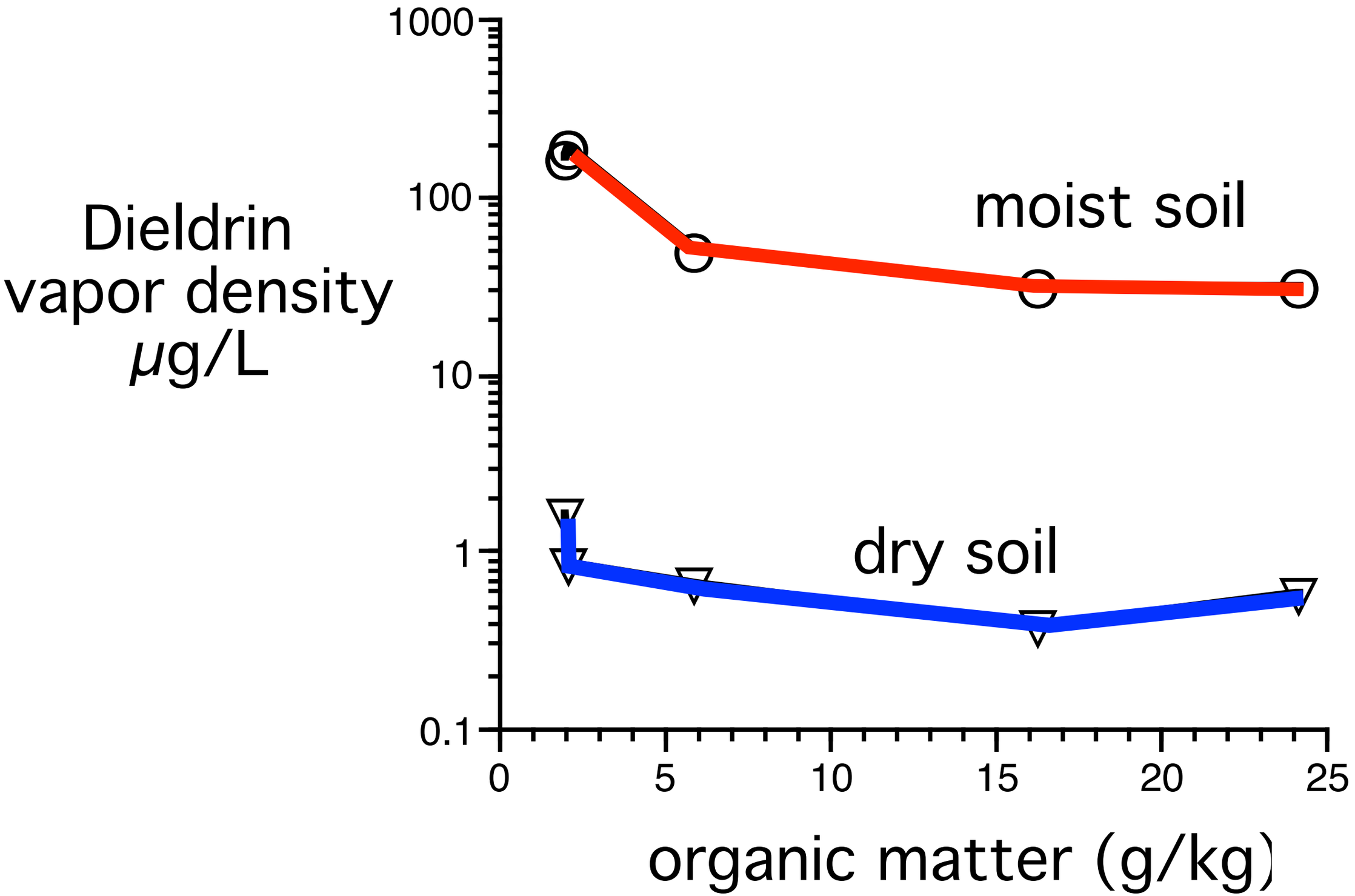
Volatilization Is Influenced by Temperature





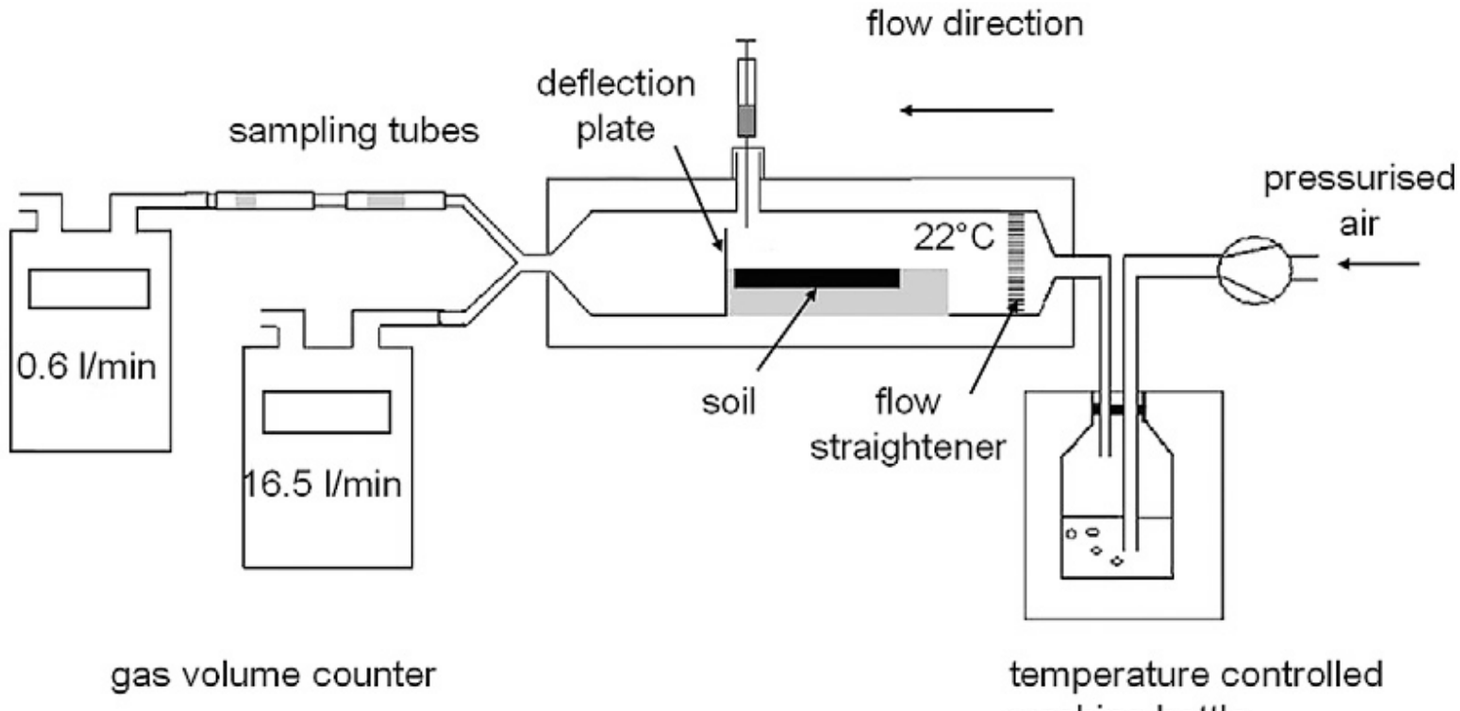
Spencer et al. (Univ CA-Riverside)

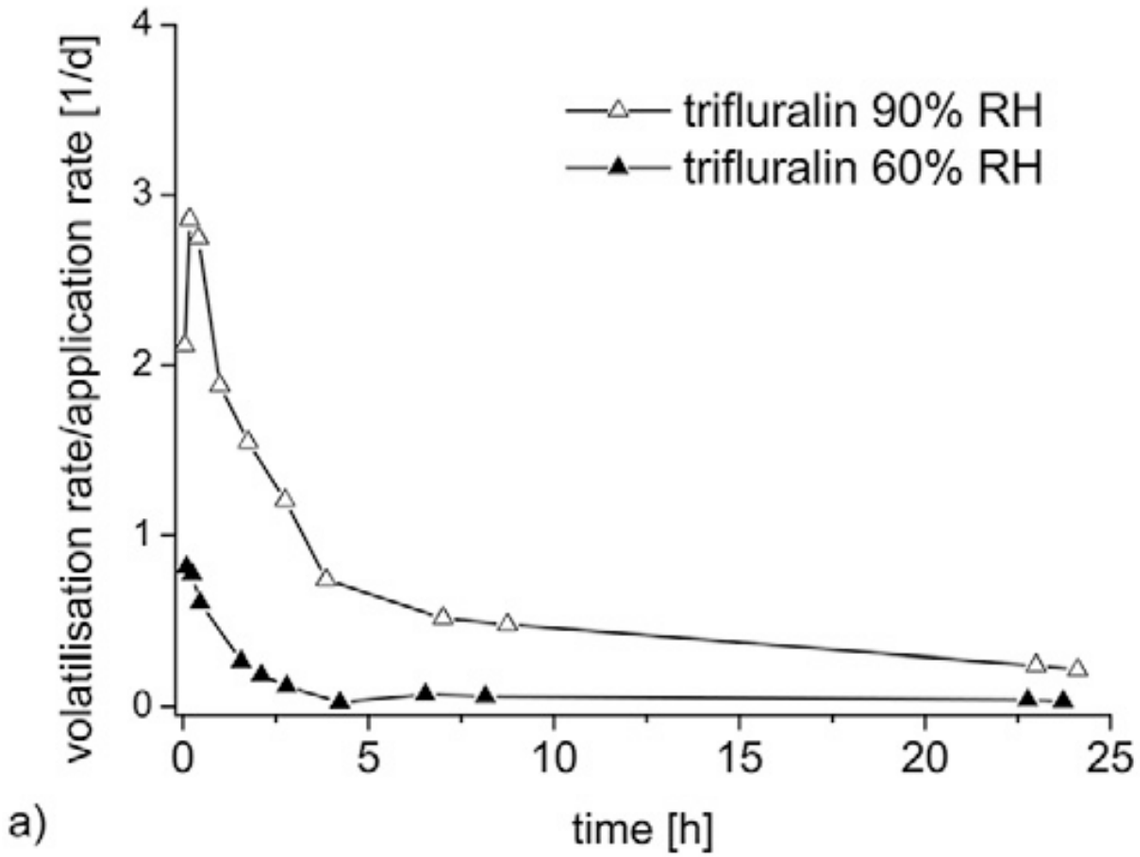
Volatilization Is Influenced by Soil moisture and Organic Carbon

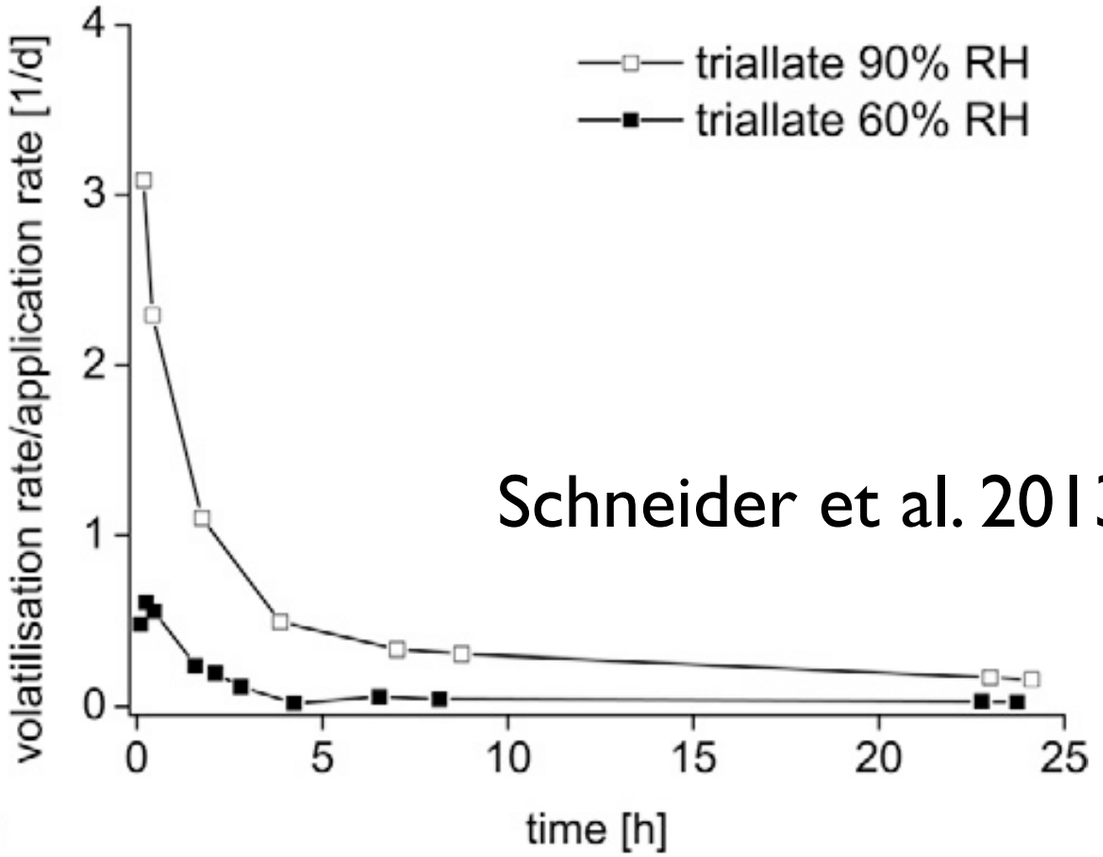


Increased Relative Humidity Enhances Pesticide Volatilization from Soil

- RH in soil controlled at 60% or 90% in an experimental device
- Trifluralin and triallate volatilization increased with greater RH







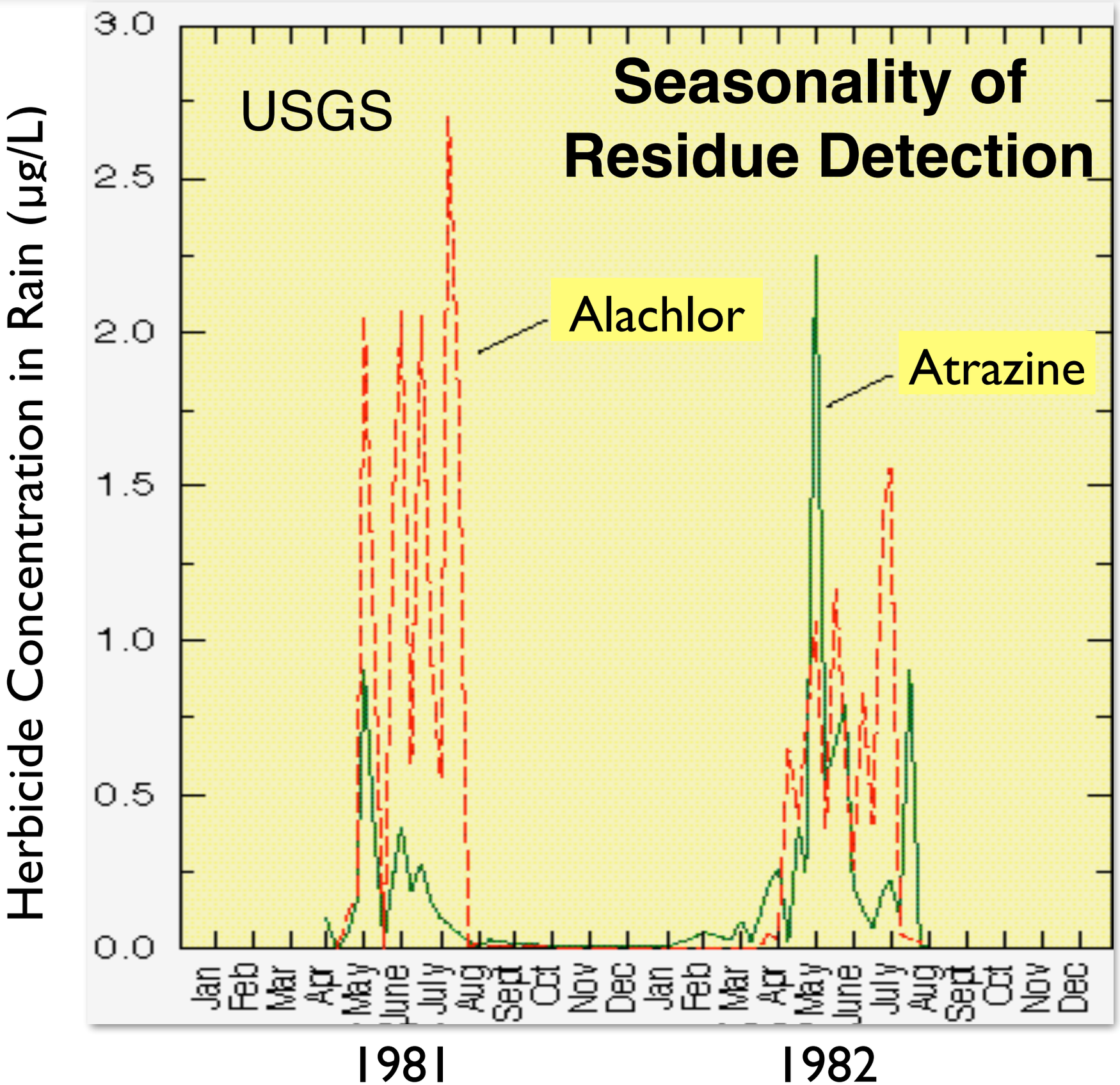
Schneider et al. 2013

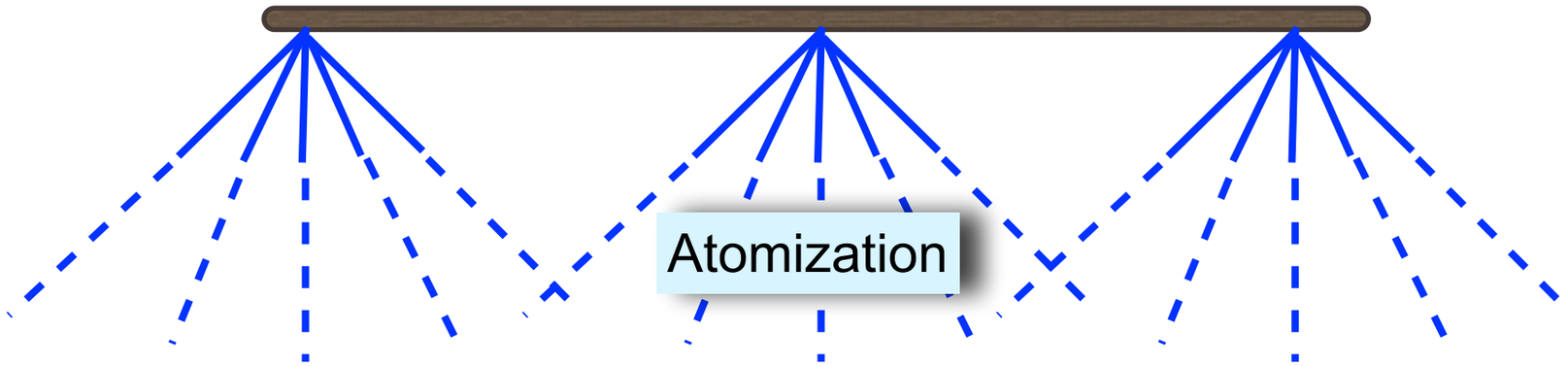
Any Pesticide Is Subject to Volatilization to Some Extent

Pesticide	% Volatilized from Soil in 24 Hours	Cropping System
simazine	0.05	fallow
atrazine	0.1	fallow
alachlor	1.1	fallow
2,4-D	4.2	alfalfa
EPTC	33.6	wheat
trifluralin	41.4	fallow (moist)
trifluralin	11.9	fallow (dry)

Spencer 1990

The Result of Mass Transfer





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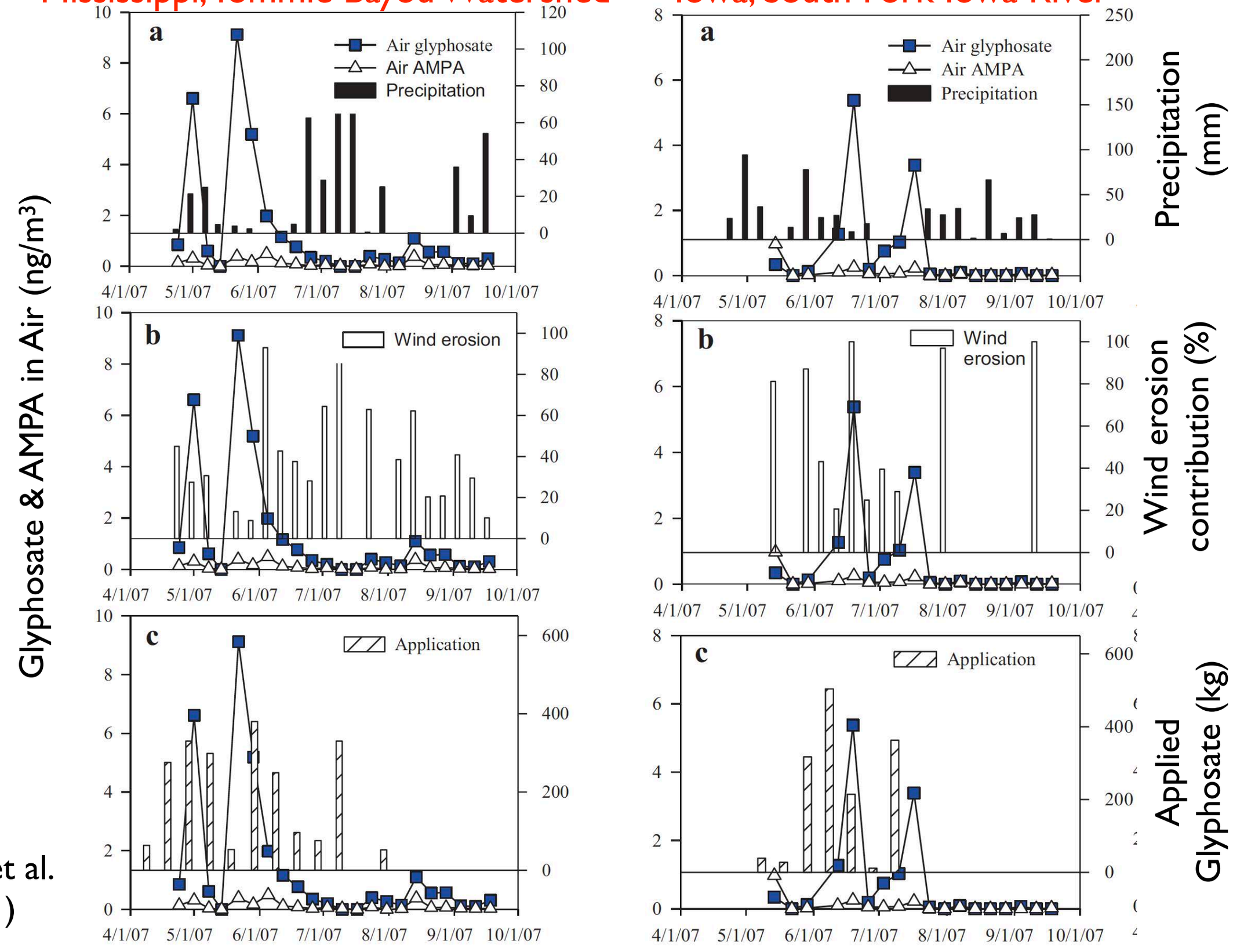
Glyphosate & AMPA in Air Follow Seasonal Application Patterns But Are Washed Out by Rain

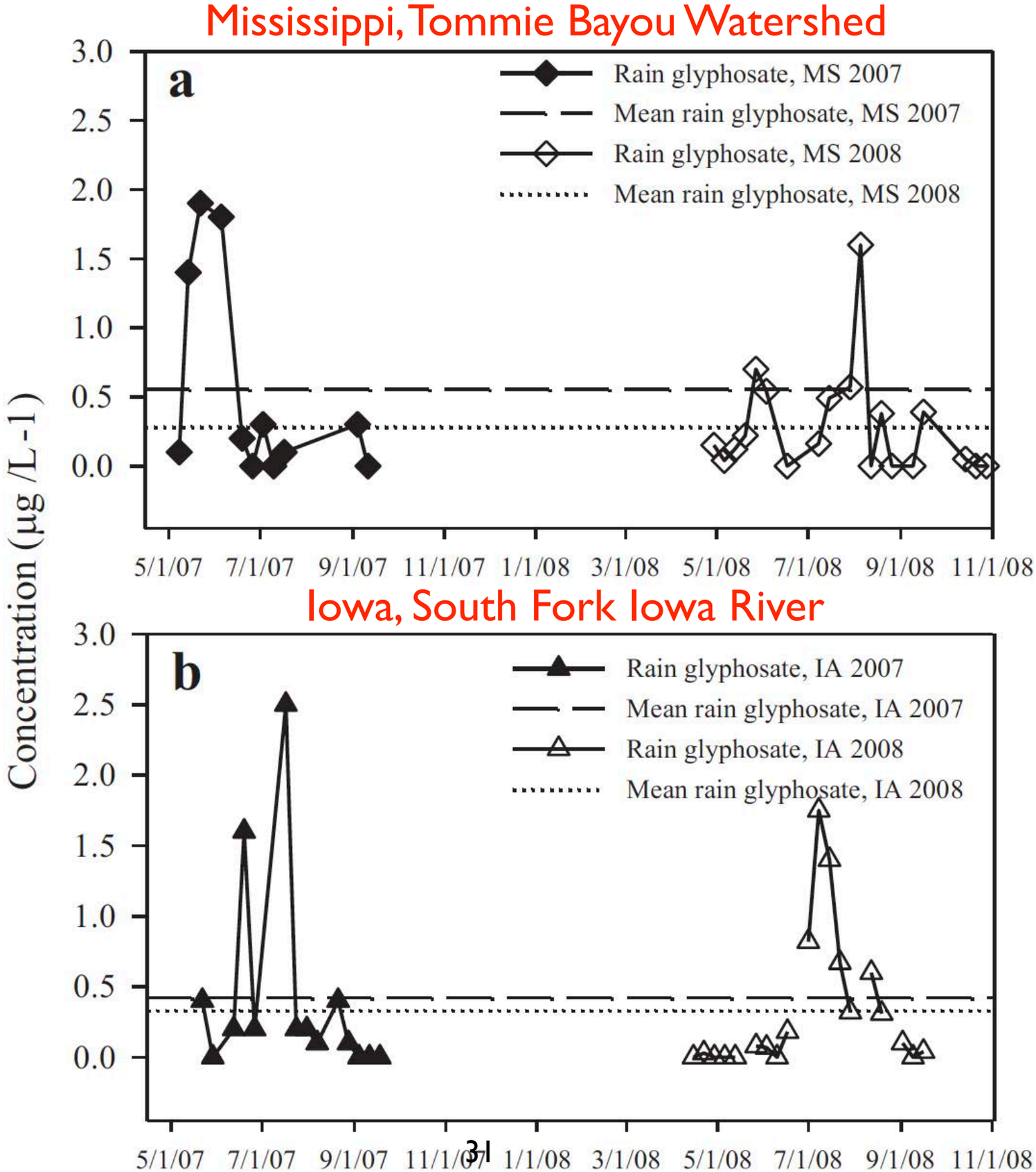
Mississippi, Tommie Bayou Watershed

Iowa, South Fork Iowa River



Chang et al. (2011)

Time Series Concentrations of Glyphosate in Rain



Chang et al. (2011)

Presence of Pesticides in Air/Rain & Timing Suggests Three Sources

- Volatilization
  - ✓ Nonpoint source contamination
    - ✳ Vapor Phase
  - ✓ Chronic, but influenced by seasonal application timing
- Drift
  - ✓ Point source contamination
    - ✳ Discrete aerosols
  - ✓ Acute
- Volatilization of carrier from smallest aerosols during spraying, generating airborne residues that do not deposit until impacting a surface or washing out in rain

IUPAC (International Union of Pure & Applied Chemistry)—Definition of Spray Drift

- "Downwind movement of airborne spray droplets beyond the intended area of application originating from aerial or ground-based spraying operations"

- Does not include volatilization

  ✓ Volatilization is a mass transfer phenomenon that occurs due to atmospheric turbulence and movement of chemical residues away from a source following water-air partitioning according to Henry's Law

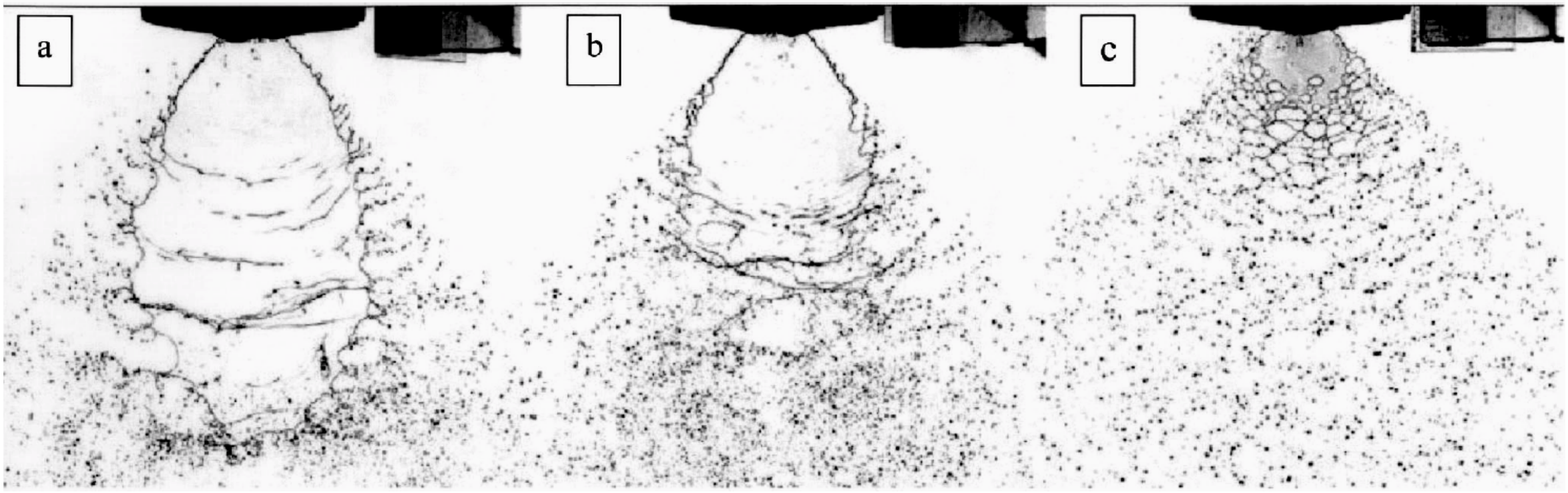
Pesticide Drift:
A Direct Route to the Atmosphere

- Movement of spray droplets during application of pesticides

  ✓ Phenomenon can be applied to any application of any chemical in which a liquid is sheared under pressure and released into the environment

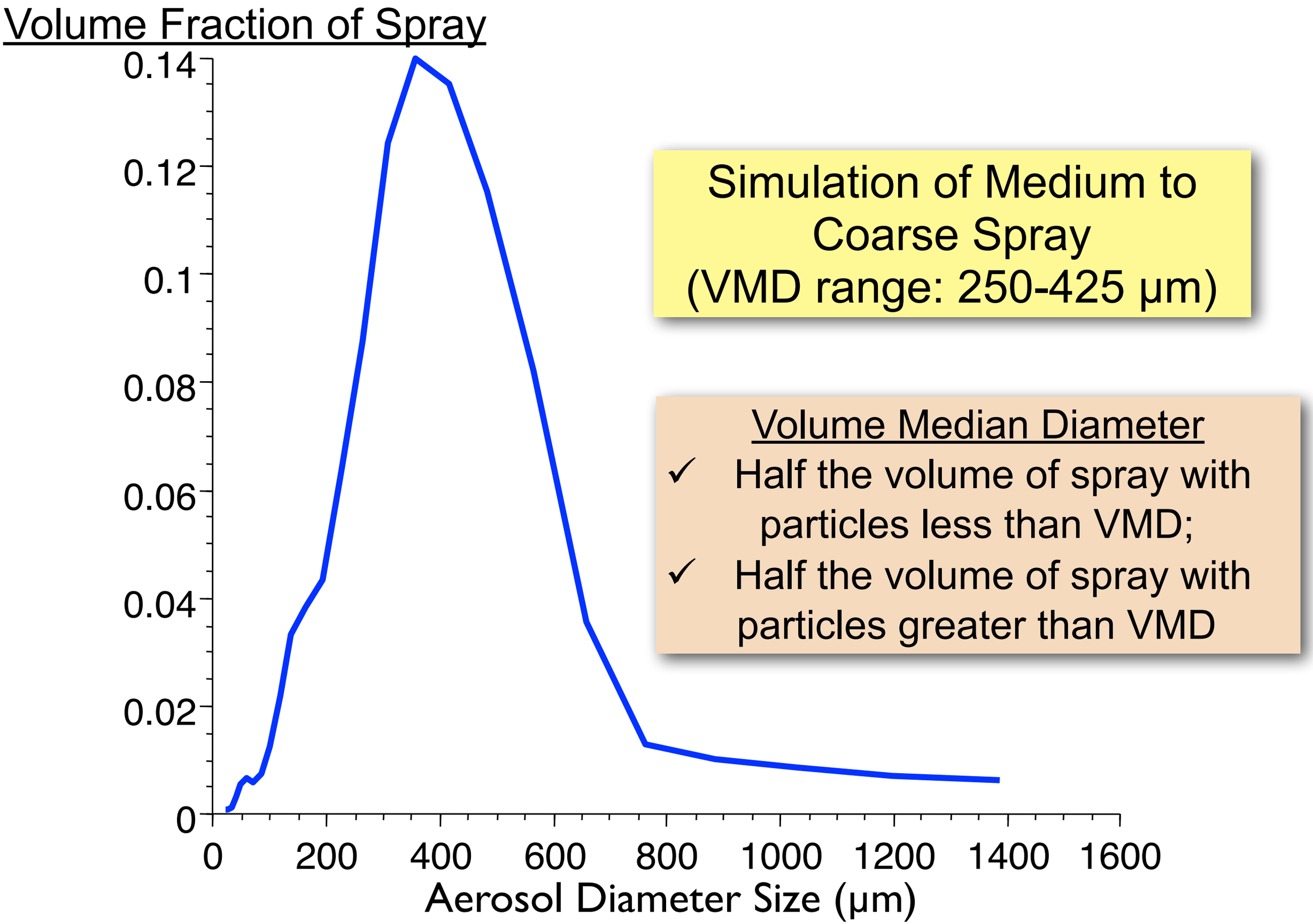
Creating Spray Droplets

- When forced under pressure through sprayer nozzles, liquids emerge as thin elongated sheets with edge instabilities that break up into small aerosols or particles having nearly a thousand fold range in spherical diameters



- The active pesticidal ingredient does not influence breakup of liquid sheets; however, formulation ingredients (solvents, emulsifiers, etc.) and physical parameters like pressure have a big influence

Be Aware of the Full Particle Size Distribution



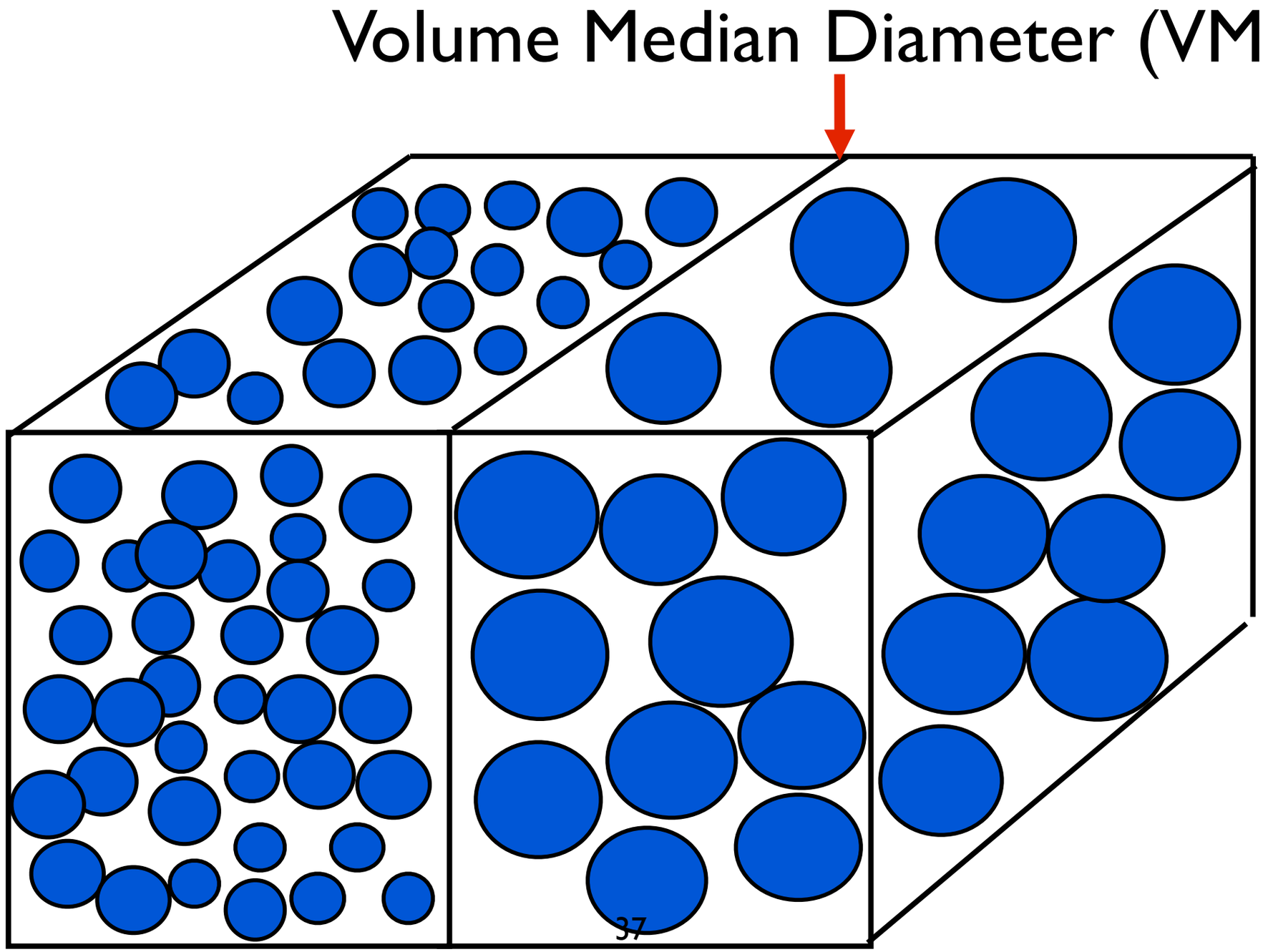
Simulation of Medium to Coarse Spray (VMD range: 250-425 μm)

Volume Median Diameter

- ✓ Half the volume of spray with particles less than VMD;
- ✓ Half the volume of spray with particles greater than VMD

Expressing Particle Sizes as a Unitary Parameter

- One half of the volume of spray is occupied by particles with spherical diameters larger than the VMD, and one-half of the volume has particles smaller than the VMD



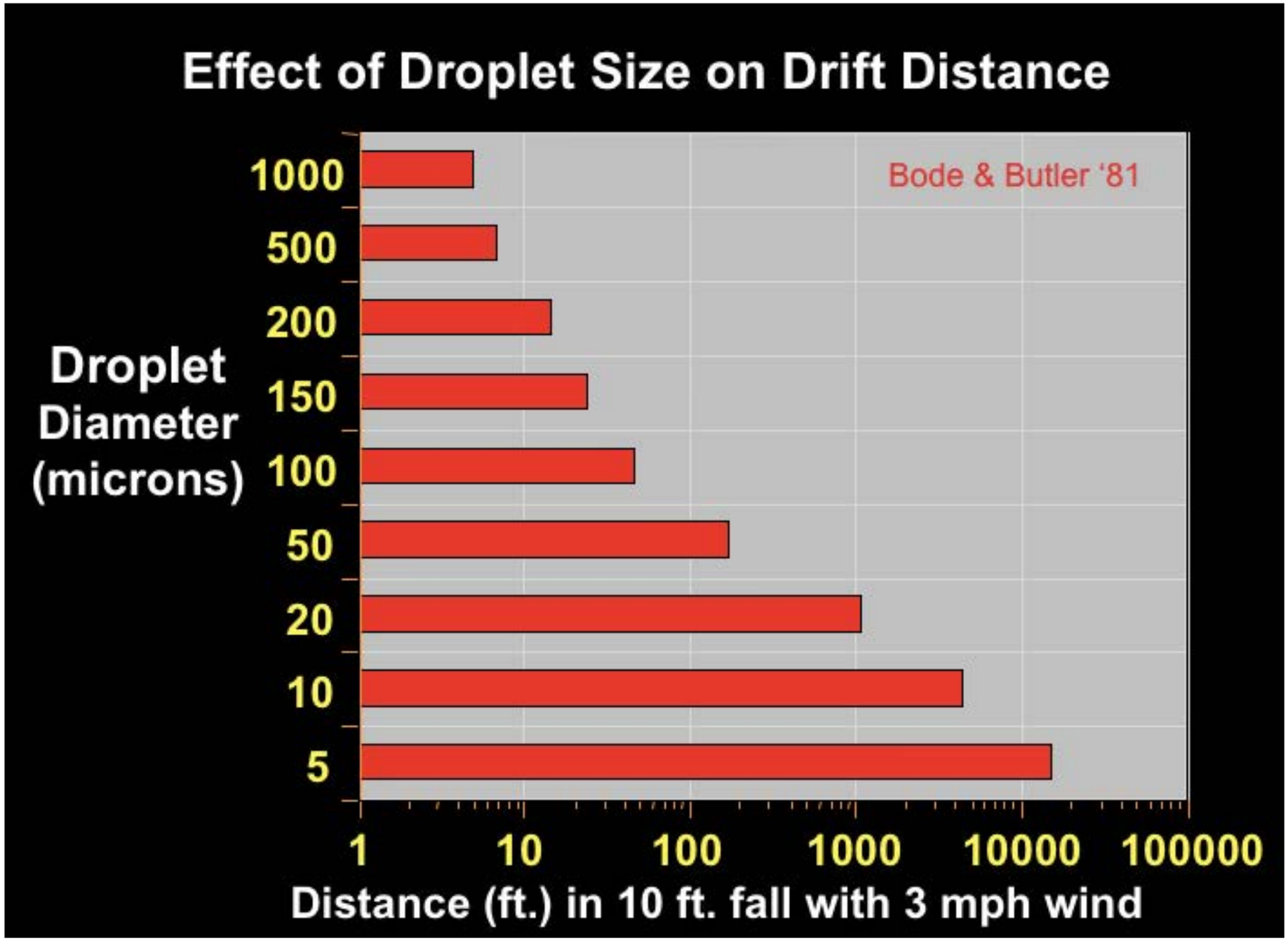
So, What Is the Problem with Small Particles

- Owing to gravitational forces and the viscosity of air, the rate of fall to ground can be predicted by Stokes Law and is proportional to the radius of the particles

Diameter (μm)	Appearance	Time to Fall 10 Feet in Still Air
1	Fog	28 hours
10	Fog	17 minutes
100	Mist	11 seconds
200	Fine Spray	4 seconds
400	Coarse Spray	2 seconds
1000	Coarse Spray	1 second

Smaller Particles Have More Potential for Translocation

- The rate of fall before a particle hits the ground (or conversely how long it takes a particle in air to fall a given distance) is modified by entrainment in a mobile air mass. Rate of fall of a spray particle will also be influenced by the rate of evaporation of the liquid constituting the aerosol.



Predicting Drift Potential As Influenced by Physical Parameters

About AgDRIFT

AgDRIFT®

Spray Drift Task Force Spray Software

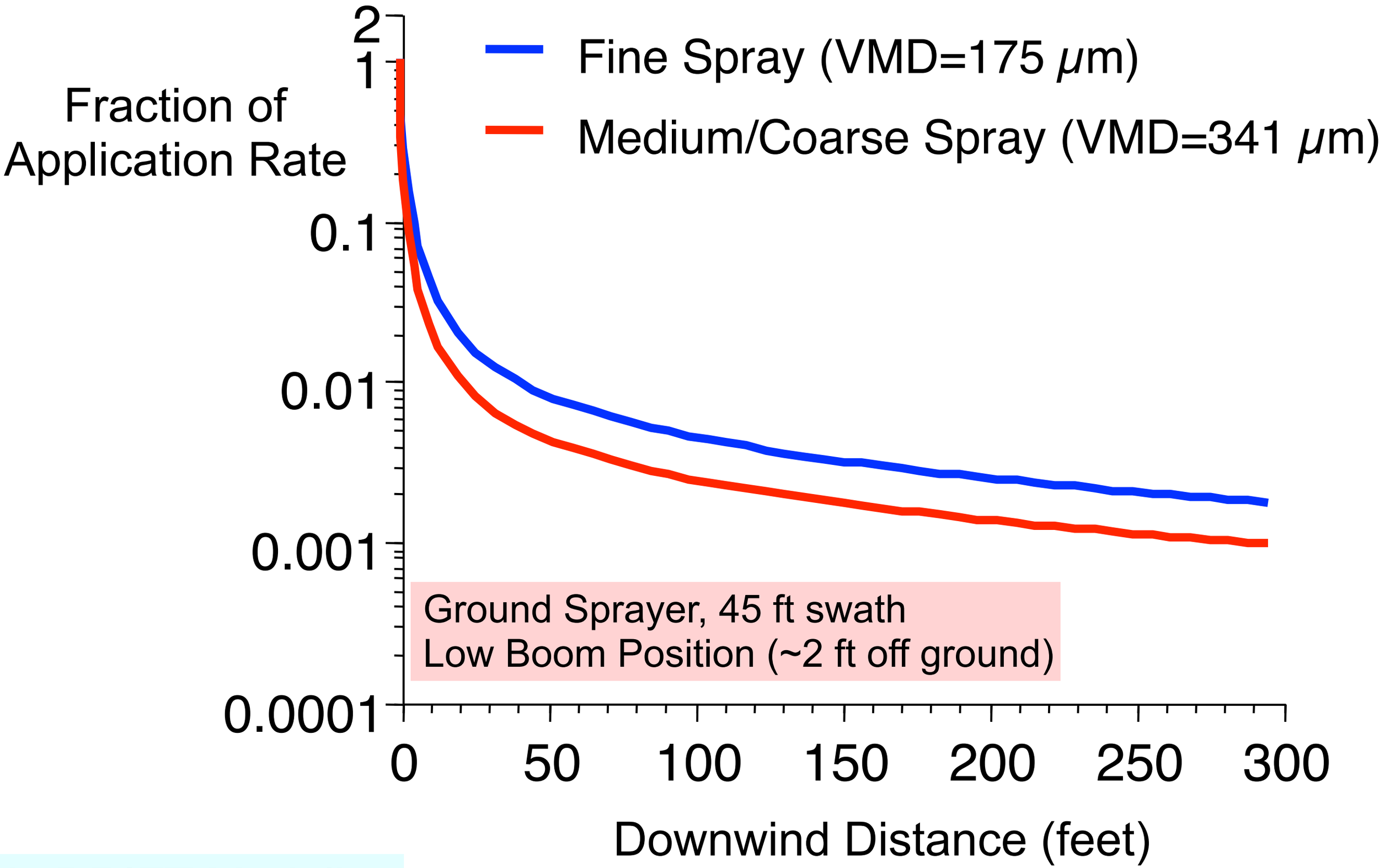
Version 2.03

The computer model AgDRIFT® and its companion drop size distribution model DropKick® describe a proposed overall method for evaluating off-site deposition of pesticides applied by aerial, ground, and orchard airblast spraying means, and for evaluating the potential of buffer zones to protect sensitive aquatic and terrestrial habitats from undesired exposures.

These models are provided to the U. S. Environmental Protection Agency's (EPA) Office of Pesticide Programs (OPP) as a product of the Cooperative Research and Development Agreement (CRADA) between the EPA's Office of Research and Development, USDA Agricultural Research Service (ARS), USDA Forest Service, and the Spray Drift Task Force (SDTF), a coalition of 39 pesticide registrants formed to develop a comprehensive database of off-target drift information in support of pesticide registration requirements. The protective assessment methodology represents the joint work of industry and EPA researchers working under this agreement as the modeling subcommittee of the SDTF.

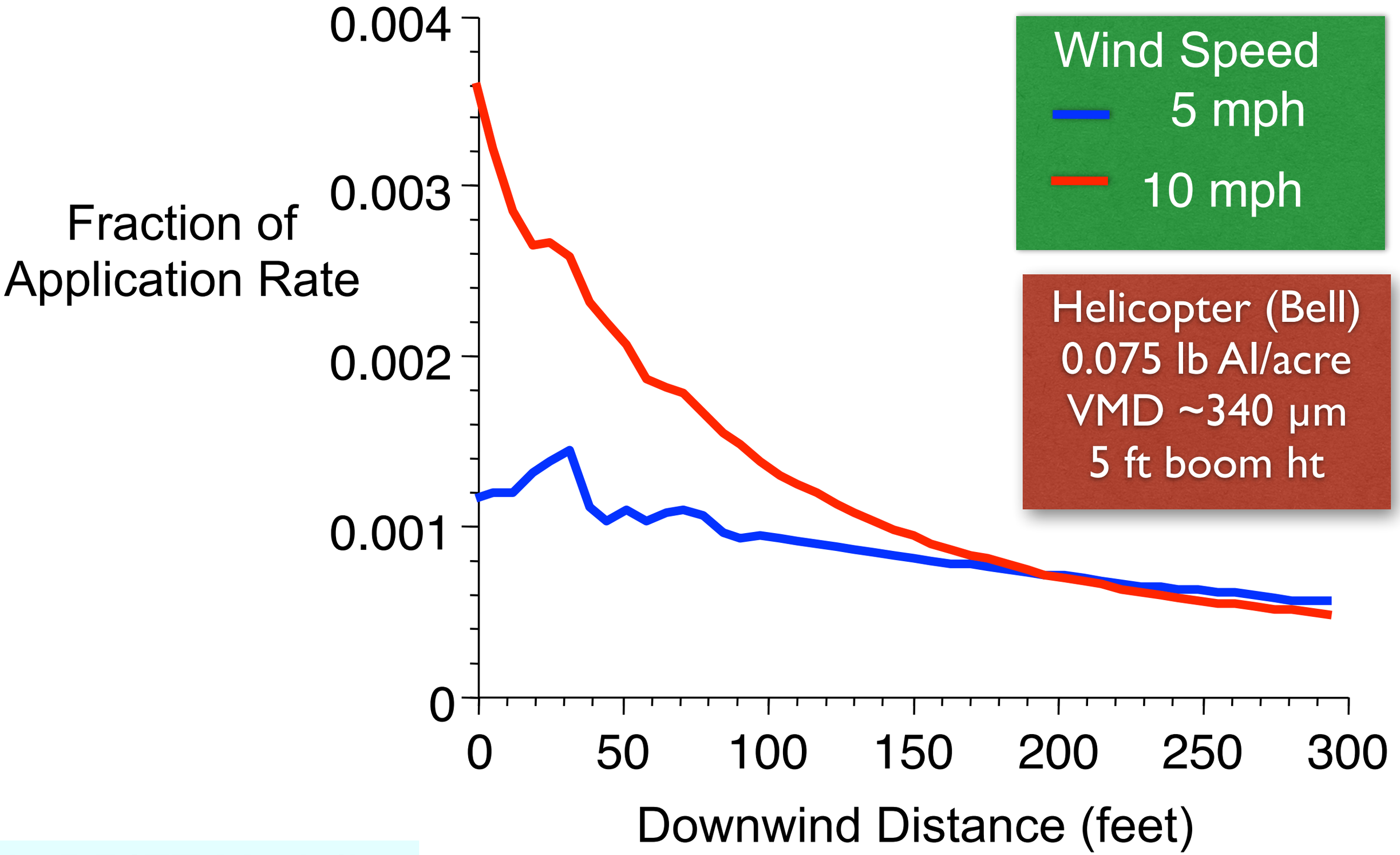
OK

Effect of Spray Quality on Downwind Drift Deposition



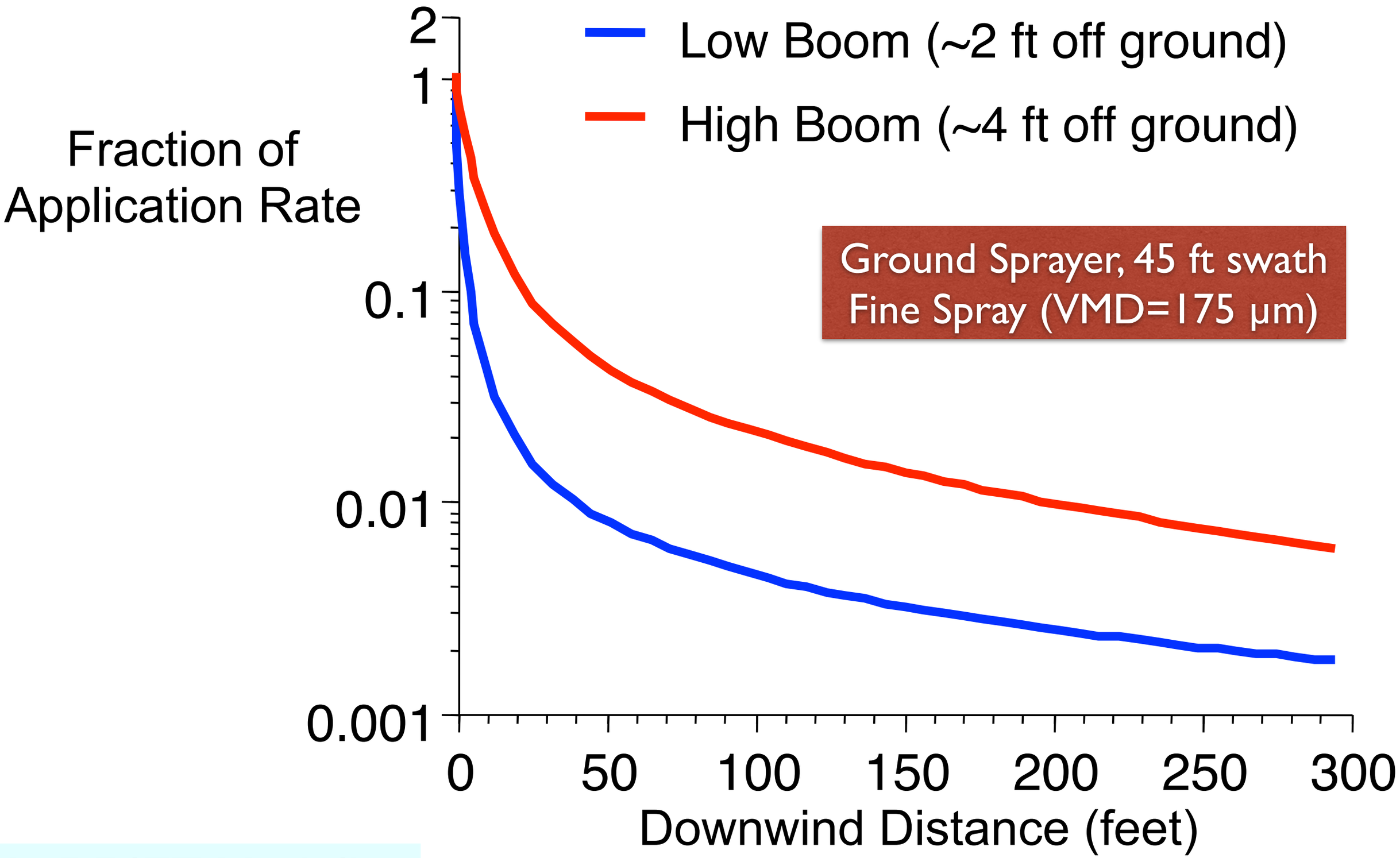
AgDRIFT Modeling

Effect of Wind Speed on Downwind Drift Deposition



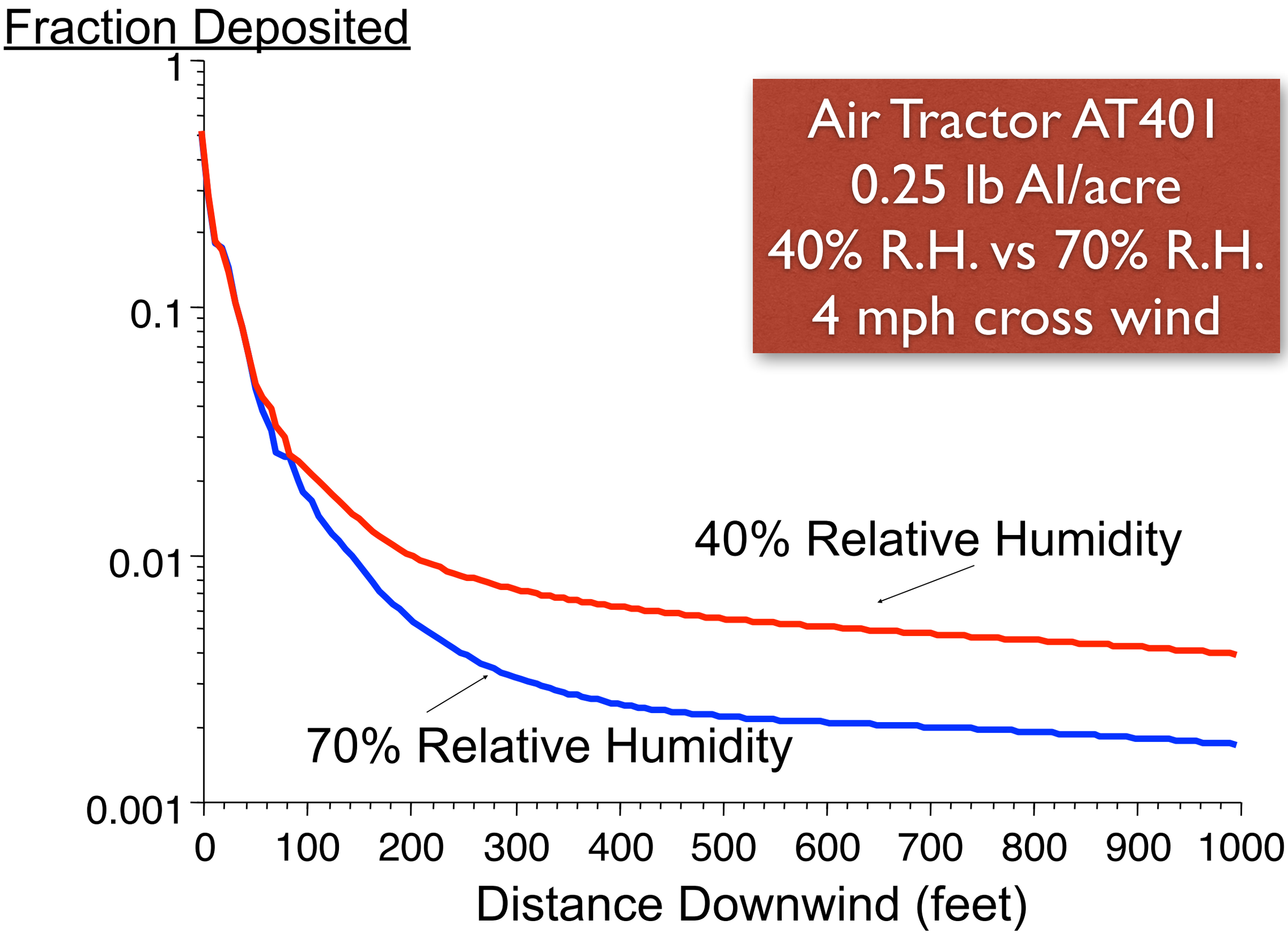
AgDRIFT Modeling

Effect of Boom Height on Downwind Drift Deposition



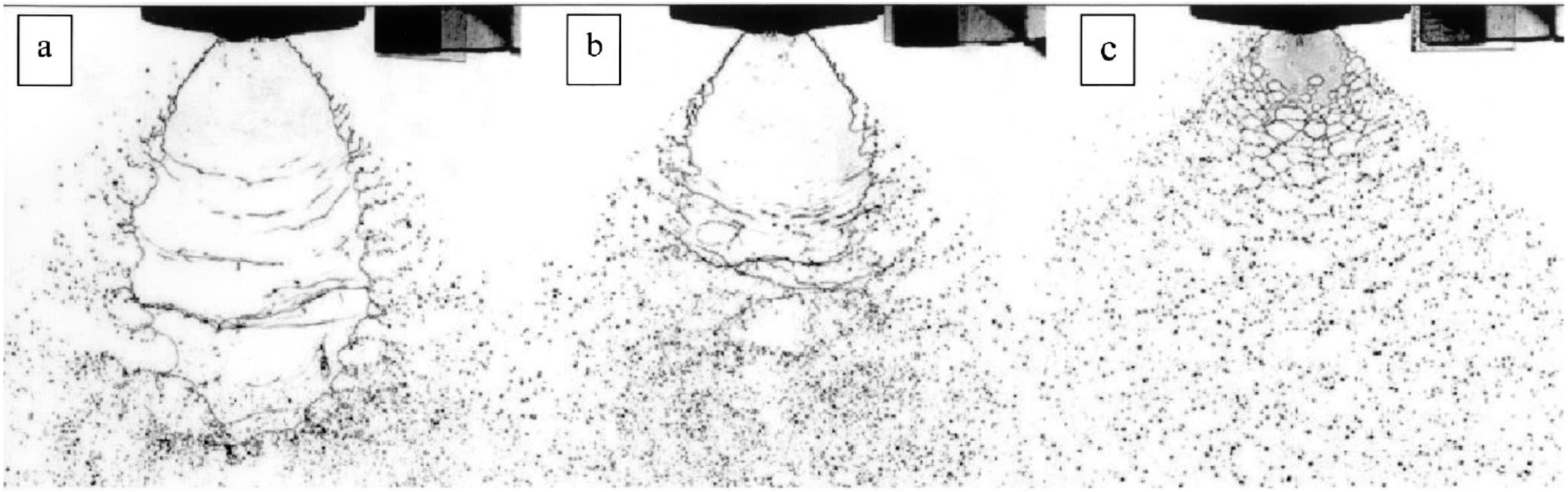
AgDRIFT Modeling

Effect of Humidity on Drift from an Aerial Fixed Wing Application



Air Tractor AT401
0.25 lb AI/acre
40% R.H. vs 70% R.H.
4 mph cross wind

Adjuvants Can Influence the Geometry & Stability of the Laminar Sheet Emitted from a Nozzle



0.5% Tallow amine Surfactant

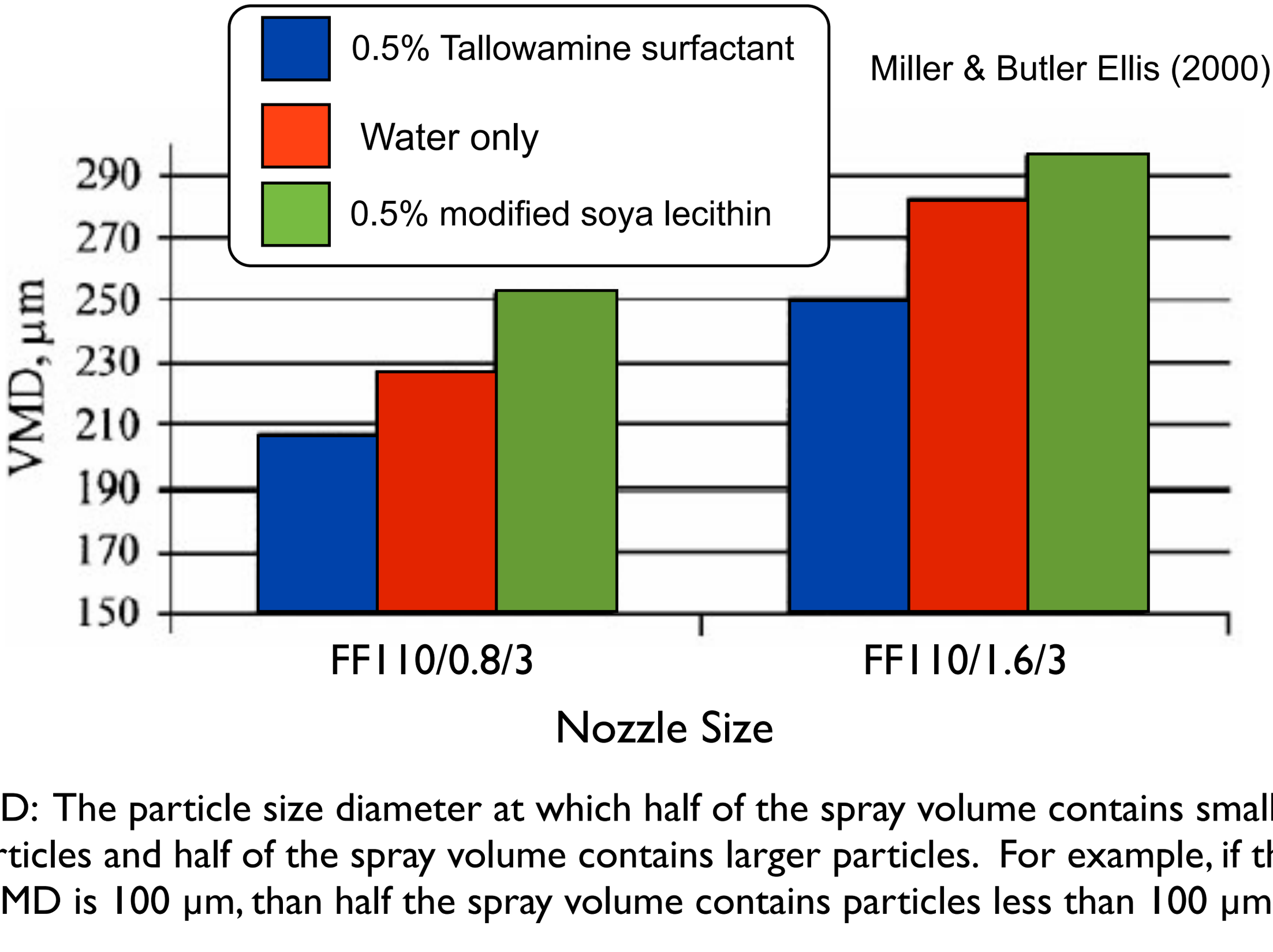
Water Only

1% Vegetable Oil Adjuvant

Result: In addition to the usual effects known from the interaction of nozzle type, hydraulic pressure, sprayer speed, boom height, etc., adjuvants can change the distribution of aerosol diameters

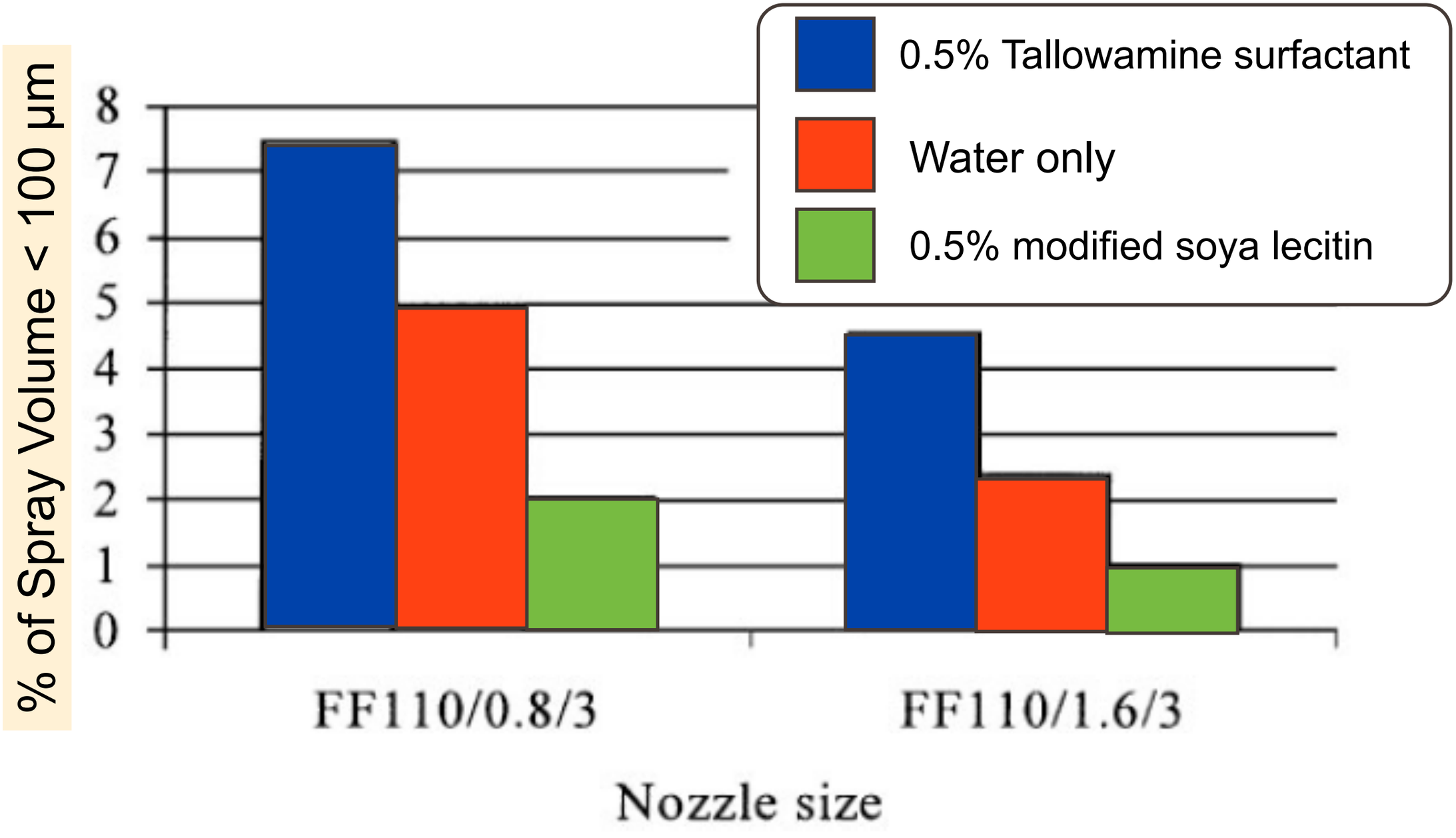
Miller & Butler Ellis (2000)

Effect of Adjuvant on Volume Median Diameter (VMD, µm)



VMD: The particle size diameter at which half of the spray volume contains smaller particles and half of the spray volume contains larger particles. For example, if the VMD is 100 µm, than half the spray volume contains particles less than 100 µm.

Percentage of Spray Volume in Spray Particles Less Than 100 µm



Miller & Butler Ellis (2000)

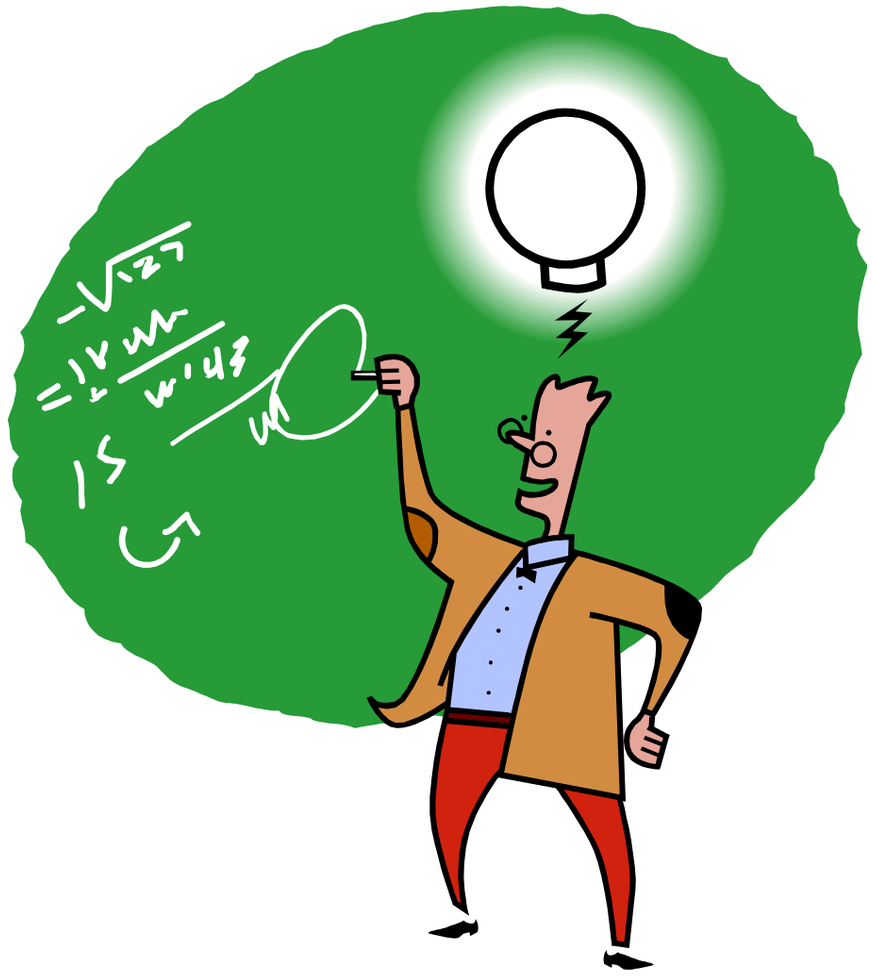
Thus, all Pesticide Sprays Will Drift to Some Extent

- The longer the aerosol remains in air before falling to ground (or alternatively striking an object above ground) the greater the opportunity to be carried away from its intended target (e.g., crop canopy)

- In general, all size classes of spray particles are capable of movement off-target, but the smallest particles will move the farthest before depositing on the ground or striking an object above ground

- Sprays naturally drift within the crop canopy itself during an application swath, serving to increase the potentially bioavailable residues on foliage

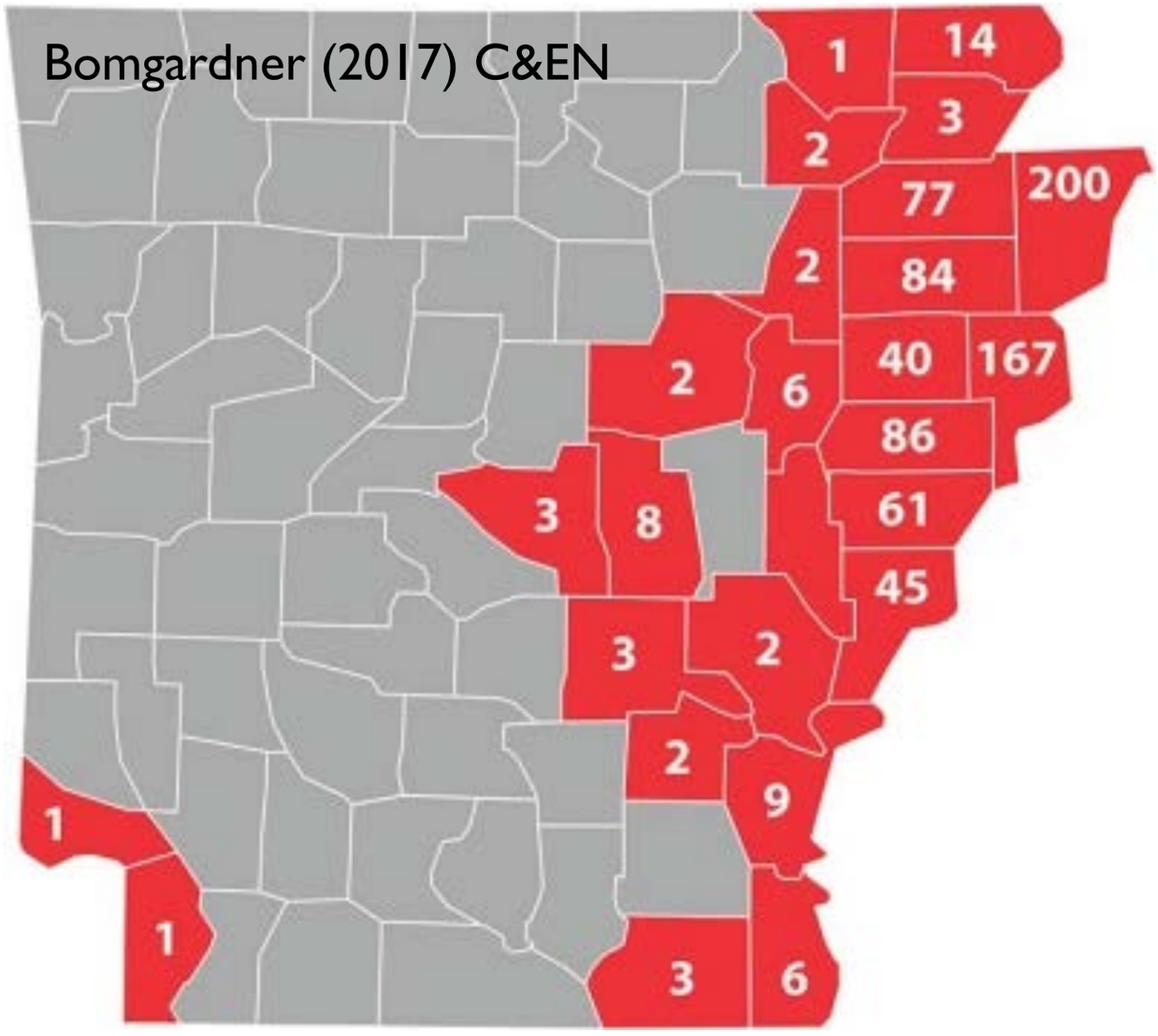
It's All About Physics of Particles



- Off-target or out-of-field drift during application may produce a high concentration of residues that potentially has an immediate or acute effect on non-target receptors

Always Test for Inversions

Can Spray Drift Explain the Widespread Extent of Soybean Injury Seen from Dicamba?



The Arkansas Plant Board received more than 800 dicamba injury complaints in 2017

AgDrift Simulation of Dicamba Deposition (g/ha) from a Ground Sprayer in Relation to the Lowest Observable Adverse Effect Level (g/ha) for Soybean

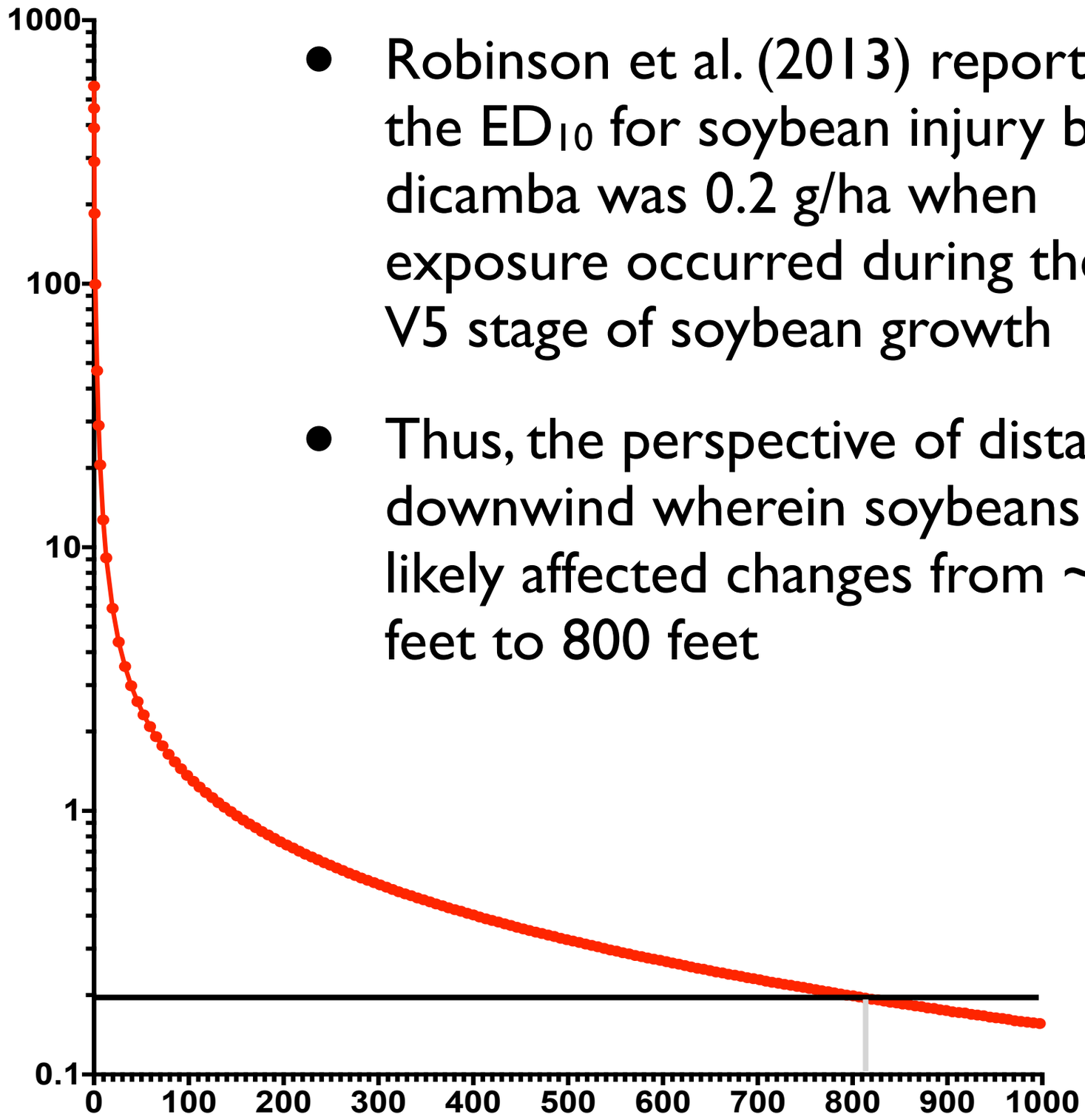
Phytotoxicity endpoints from Griffin et al (2013)

Exposure at V3/V4 Stage

Exposure at R1 Stage

Downwind Distance (ft) from Field Edge

Perspective of Downwind Injury Changes as Toxicological Endpoint Changes



- Robinson et al. (2013) reported that the ED_{10} for soybean injury by dicamba was 0.2 g/ha when exposure occurred during the V2 or V5 stage of soybean growth
- Thus, the perspective of distance downwind wherein soybeans are likely affected changes from ~120 feet to 800 feet

Expected Injury Pattern In Fields Affected by Drift During Application

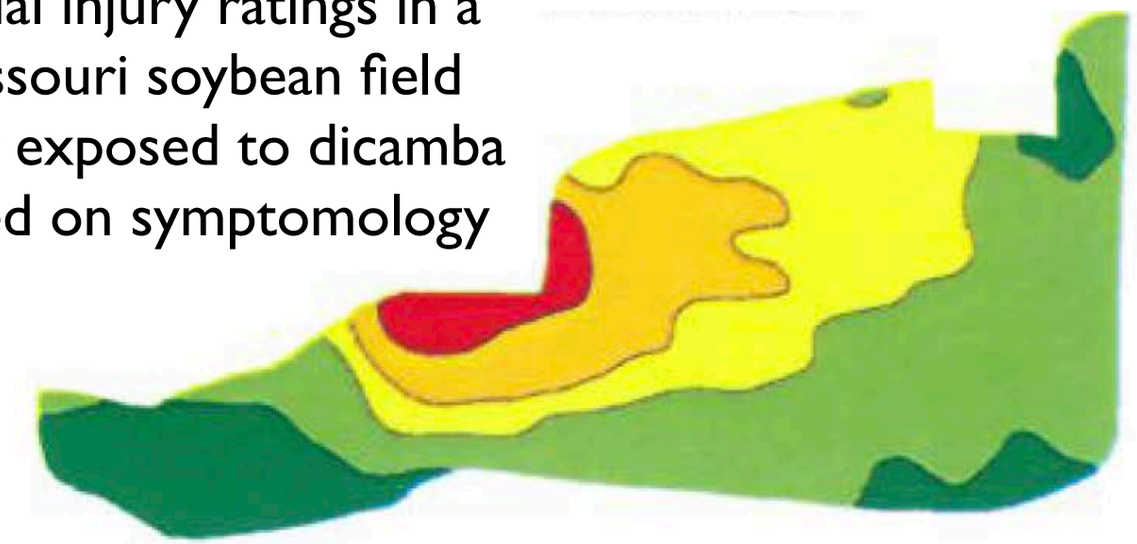
- When exposure to drift is suspected of causing foliar injury, then a pattern of decreasing intensity should be observed moving downfield from the source

- The heat maps were produced by visual injury ratings taken in Missouri (Dintelmann et al. 2017)

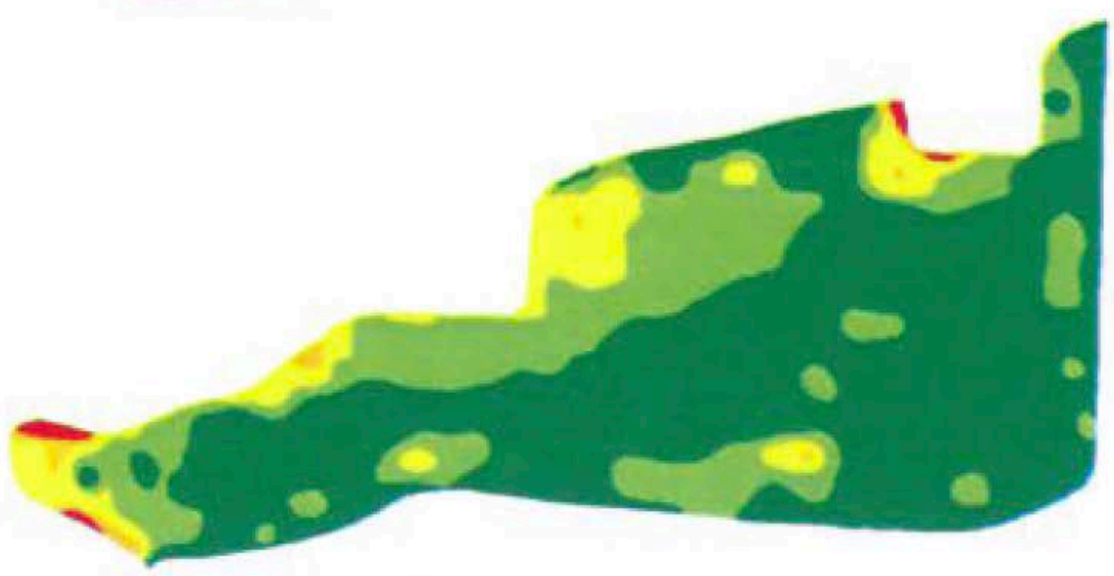
✓ Note that the injury is high on one end of a field and decreases in a likely downwind direction

✓ Furthermore, visual injury is not directly related to yield loss until a certain threshold of injury is reached

Visual injury ratings in a Missouri soybean field likely exposed to dicamba based on symptomology

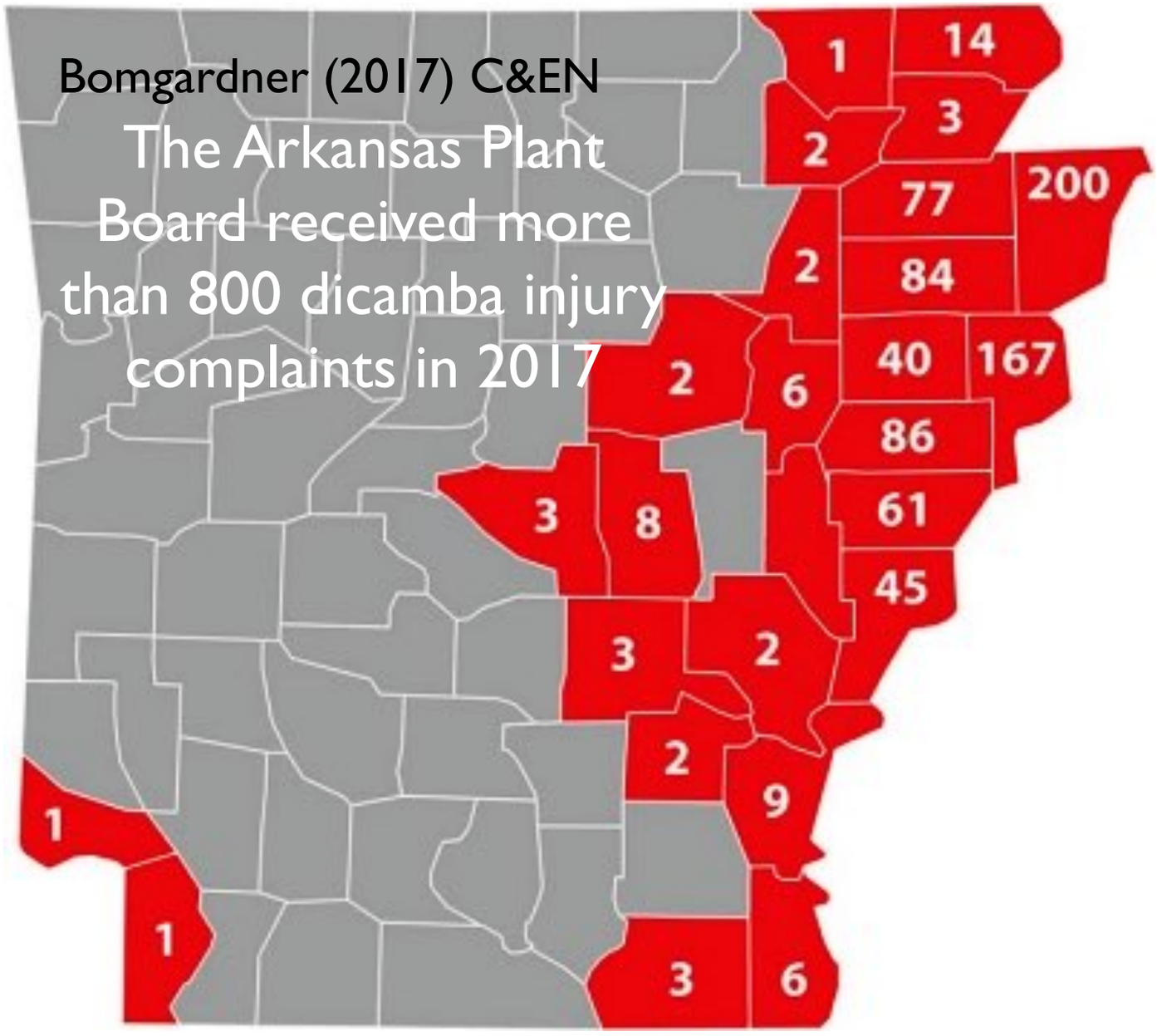


B



Legend for Figure 2A and 2B		
Color Scheme	% Visual Injury Ranges (A)	% Yield of Field Average (B)
	0	≥100
	1-20	99-90
	21-40	89-80
	41-60	79-70
	61-80	≤ 70

Can Post-Application Volatilization Explain the Widespread Injury of Non-Resistant Soybeans from Dicamba Use

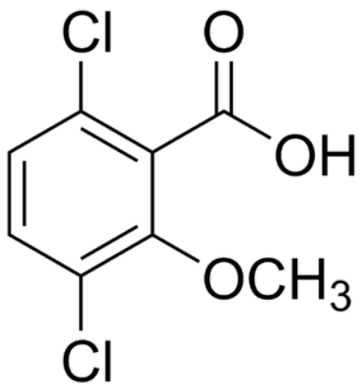


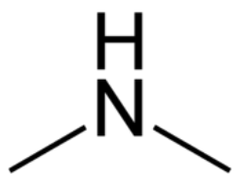
Bomgardner (2017) C&EN

The Arkansas Plant Board received more than 800 dicamba injury complaints in 2017

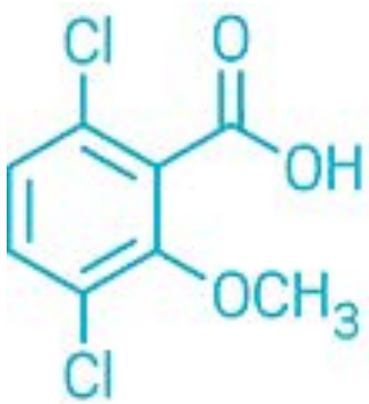
A reasonable case can be made that the widespread injury in 2016 may have been due to use of the old volatile formulation of dicamba containing the dimethyl amine salt

Dicamba Derivatives Alter the AI Volatility

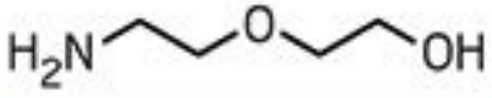




Dicamba dimethylamine

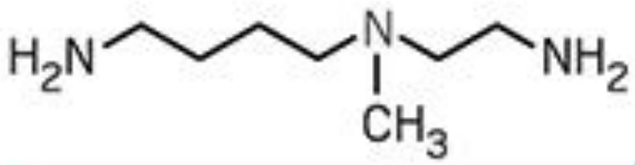


Dicamba



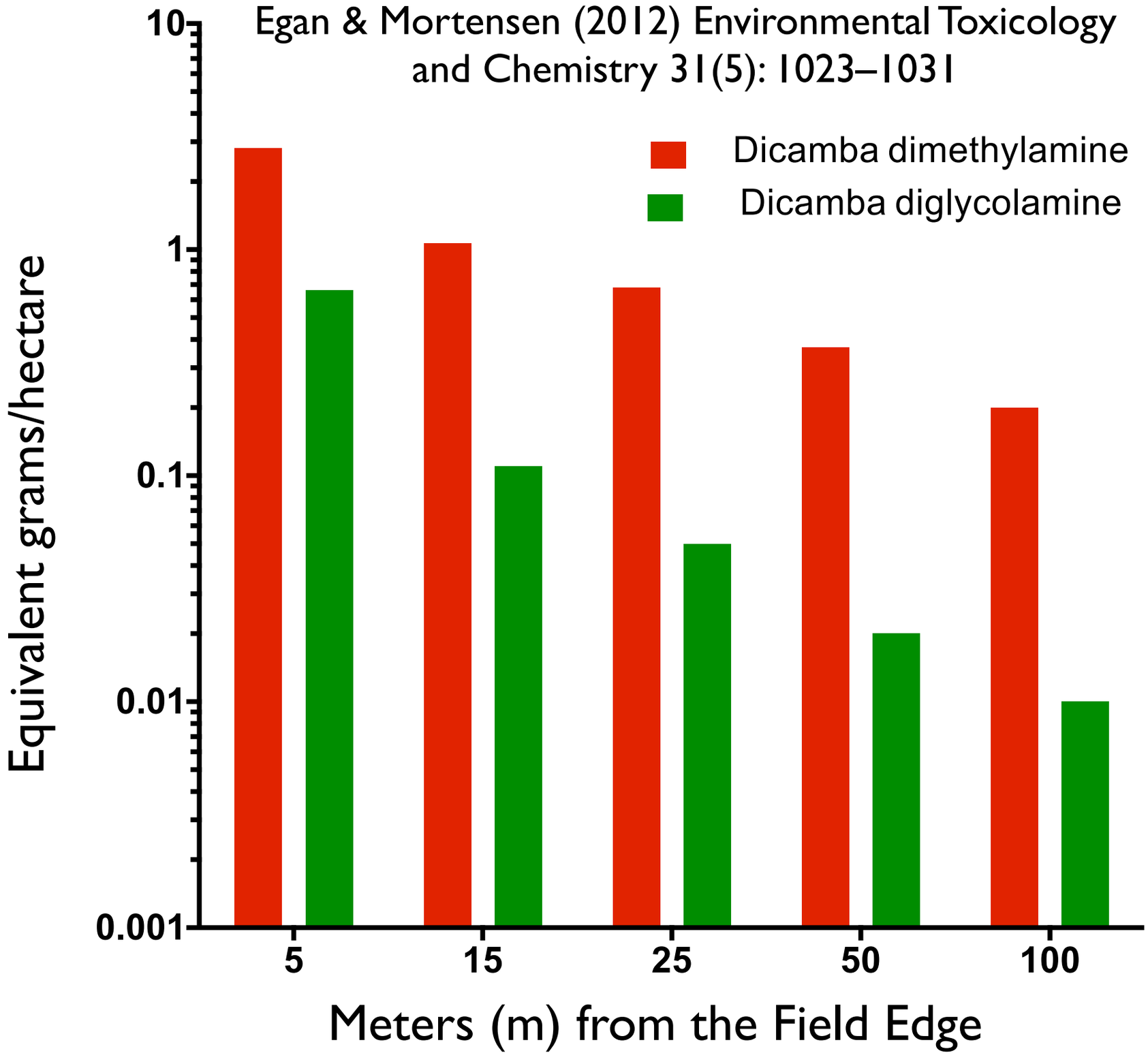
XtendiMax: Dicamba diglycolamine

Low-volatile salts



Engenia: Dicamba *N*,*N*-bis(3-aminopropyl)methylamine

Bioassays to Test Formulation Volatilization Show Significant Reductions in Movement of DGA Compared to the DMA



Begging the Question…

- Is the phenomenon of extensive non-HR soybean injury from dicamba use on HR soybean due to drift, volatilization, a combination of both?

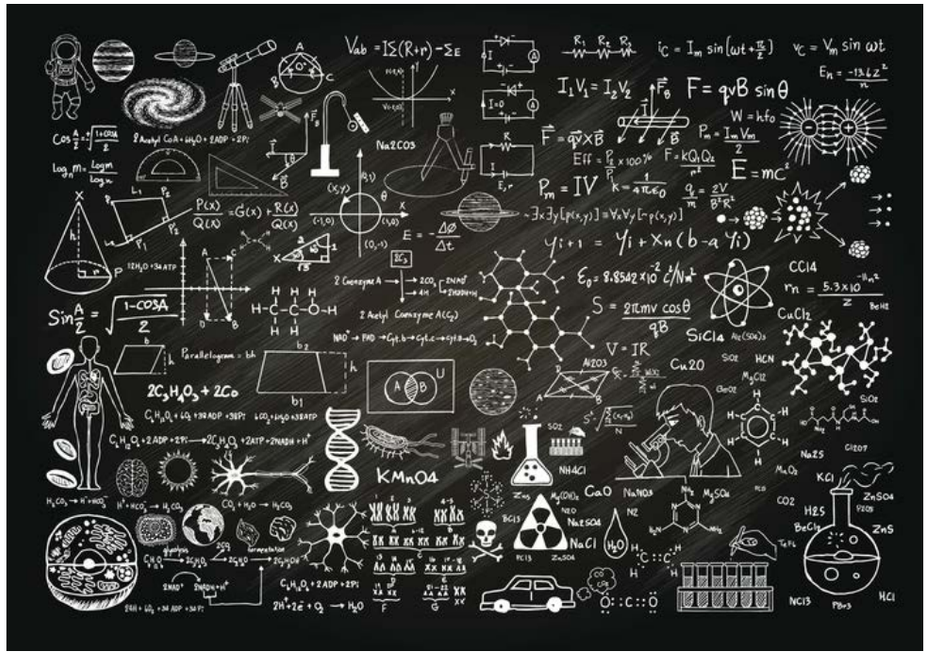
  ✓ Unless clear patterns of injury showing a "drift" gradient occur, drift does not explain widespread injury symptoms

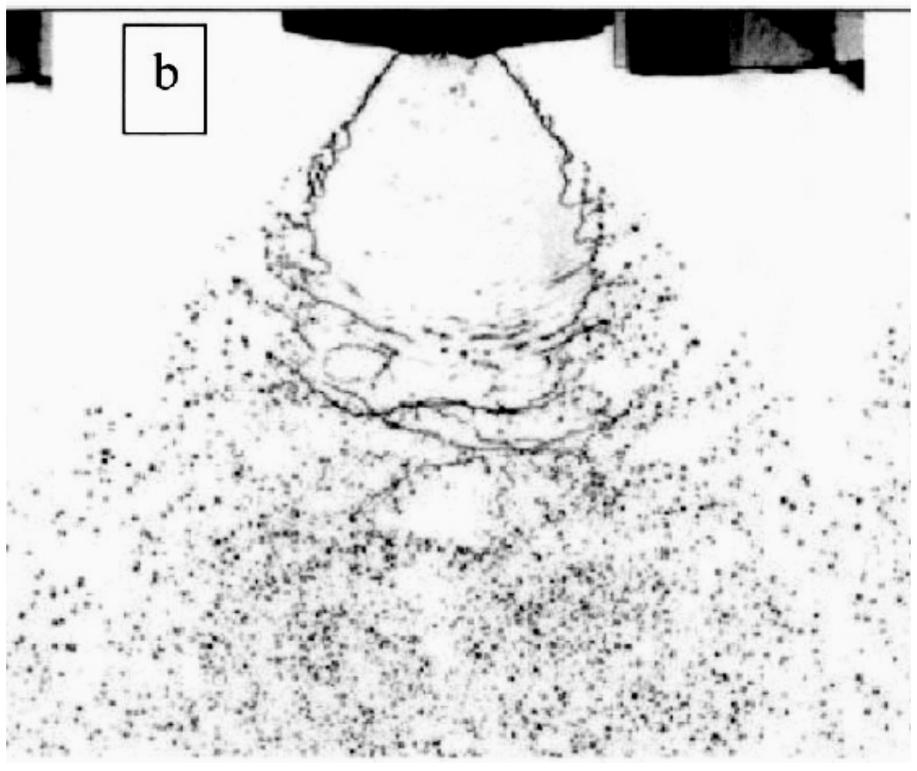
  ✓ The low volatility formulations of dicamba are at least 10-50 times less volatile over distances of 100 meters

- Or…Is the phenomenon to be expected owing to the interaction of "spraying physics", planting over large landscapes of crops with mixed susceptibilities, and natural occurring (i.e., expected) atmospheric deposition processes (a.k.a. non-point source pollution)

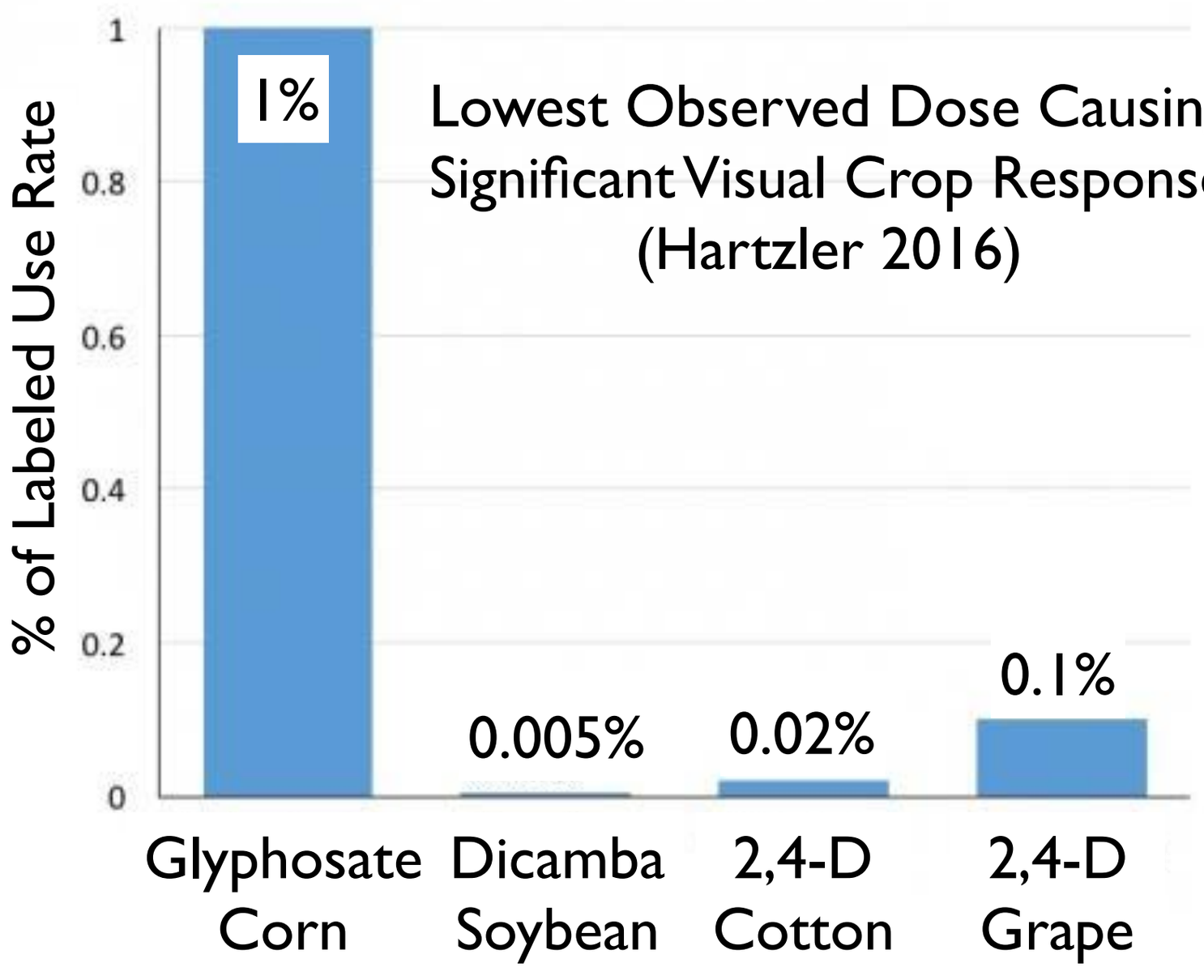
Basically, Two Factors at Work…

Spray Physics





Mixed landscape consisting of susceptible and resistant crops



Lowest Observed Dose Causing Significant Visual Crop Response (Hartzler 2016)

We've Seen this Phenomenon Before (Ever Since the Invention of 2,4-D)

- ~25 years ago, the Badger Canyon, a topographical feature in south central WA created by an earthquake that changed the course of the Yakima River, was embroiled in herbicide drift complaints that had been set off from an errant application of diquat to potatoes a few years earlier

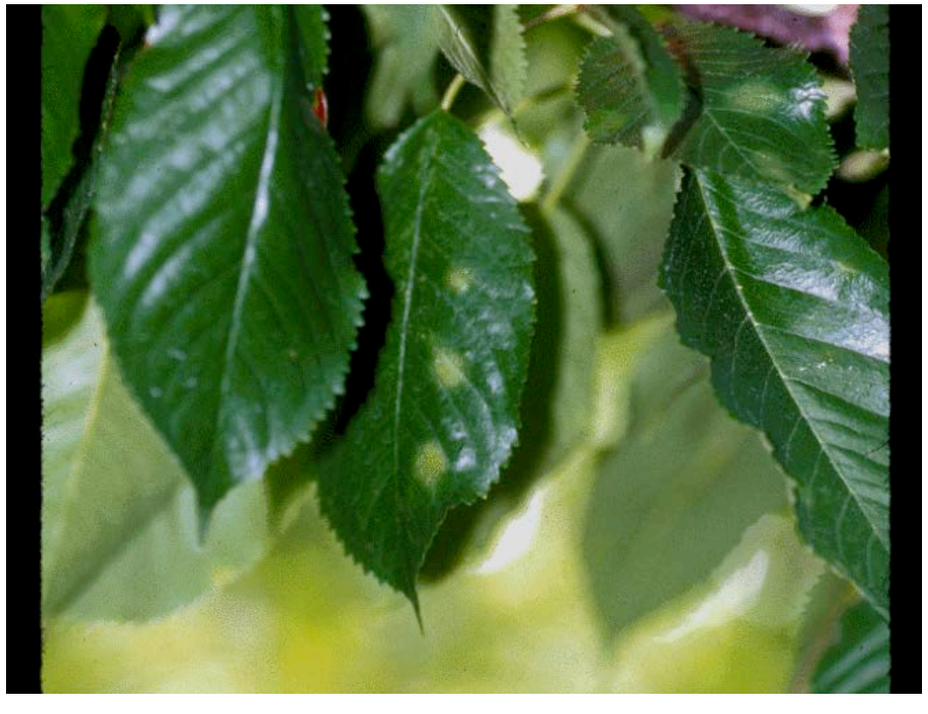
- Canyon growers of crops sensitive to 2,4-D (e.g., grapes) and sulfonylurea herbicides (e.g., cherries) affected at the time hypothesized that the herbicide applications in Horse Heaven Hills wheat were drifting into the canyon

- After tramping around the region, setting up a sentinel plant biomonitoring network in an attempt to detect this drift, I decided that different processes were going on…namely, deposition of residues associated with the natural tendency of chemicals to volatilize

- However, I decided that there is a third process of chemical impact on plants that results from rapid volatilization of carrier from the smallest spray aerosols, driving residues airborne that eventually partition into rain or impact sensitive plants

Personal Early Observations

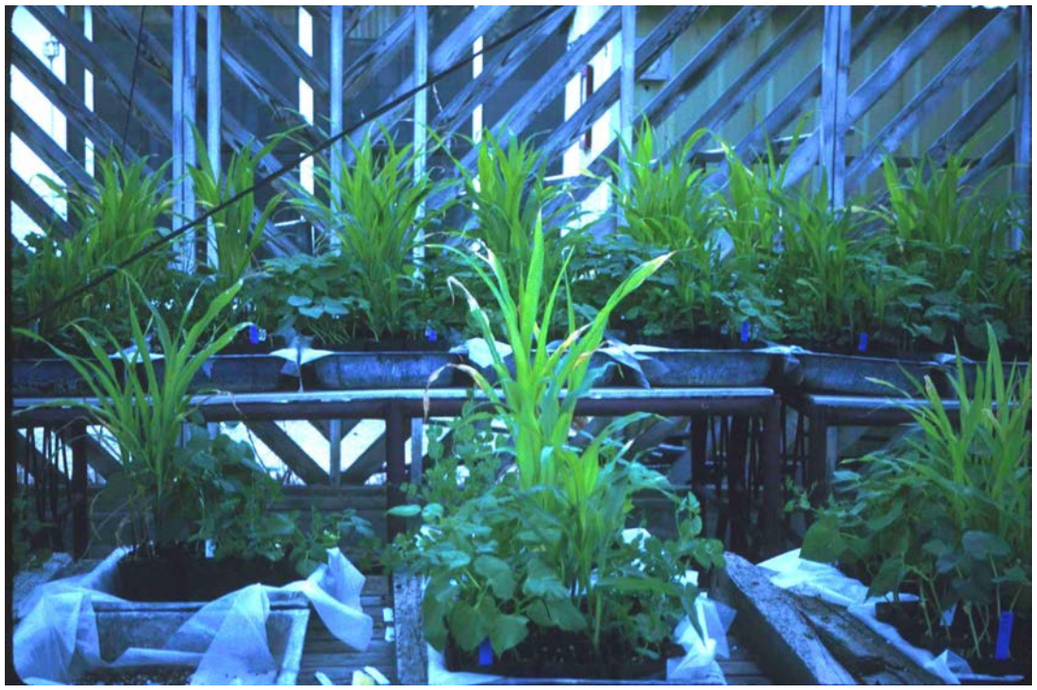
- Grapes and cherries were often the most responsive to impact of herbicide movement
- Observations on cherry leaves ranged from isolated chlorotic spots to widespread coalescing of yellow spots
- Observations on grapes were more often leaf morphological distortions with anastomizing veins, loss of apical dominance, fringing at the edges of leaves



Why Drift (During Application or Secondary) Was Insufficient to Explain Observations

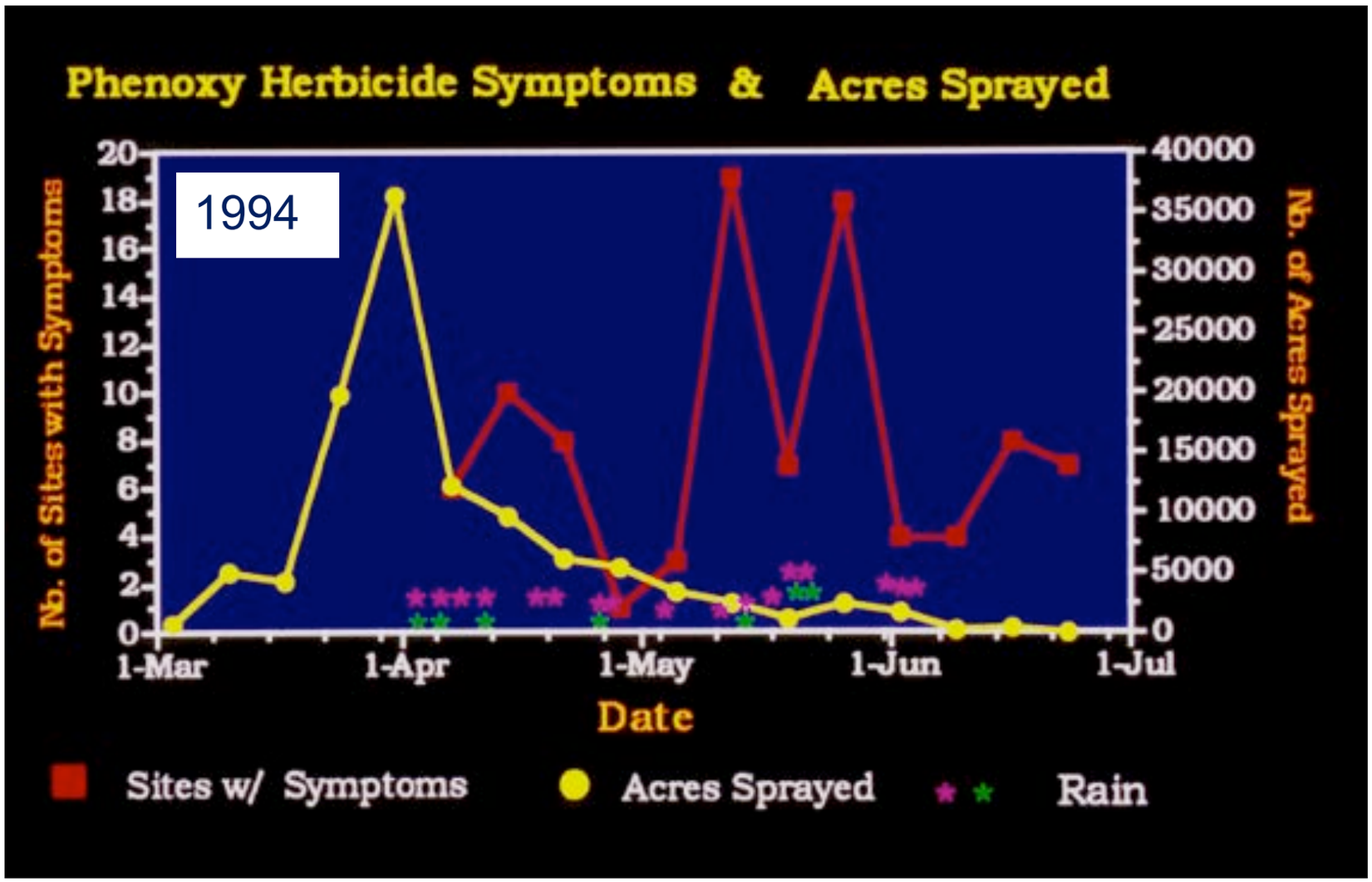
- **Drift** was indicated if severe leaf injury occurred in many plants near a field border with gradient of lesser effects as field was traversed

- **Non-point source deposition** was indicated if random patterns of leaf injury including isolated chlorotic or necrotic spots and morphological abnormalities in newer growth; no apparent gradient of effect with symptoms occurring throughout a field



- The use of sentinel plants showed probable herbicide responses, but appearance of the morphological symptomology did not correspond well with timing of applications

Sentinel Plant Monitoring Network Was Setup to Detect Timing of Herbicide Deposition via Bioassays and Timing of Applications



Symptomology characteristic of phenoxy herbicide exposure seemed to coincide more with drizzle precipitation events than with actual applications

Badger Canyon & Horse Heaven Hills Biomonitoring Using Sulfonylurea-Induced Chlorotic Spotting

BIOMONITORING WITH SENTINEL PLANTS TO ASSESS EXPOSURE OF NONTARGET CROPS TO ATMOSPHERIC DEPOSITION OF HERBICIDE RESIDUES

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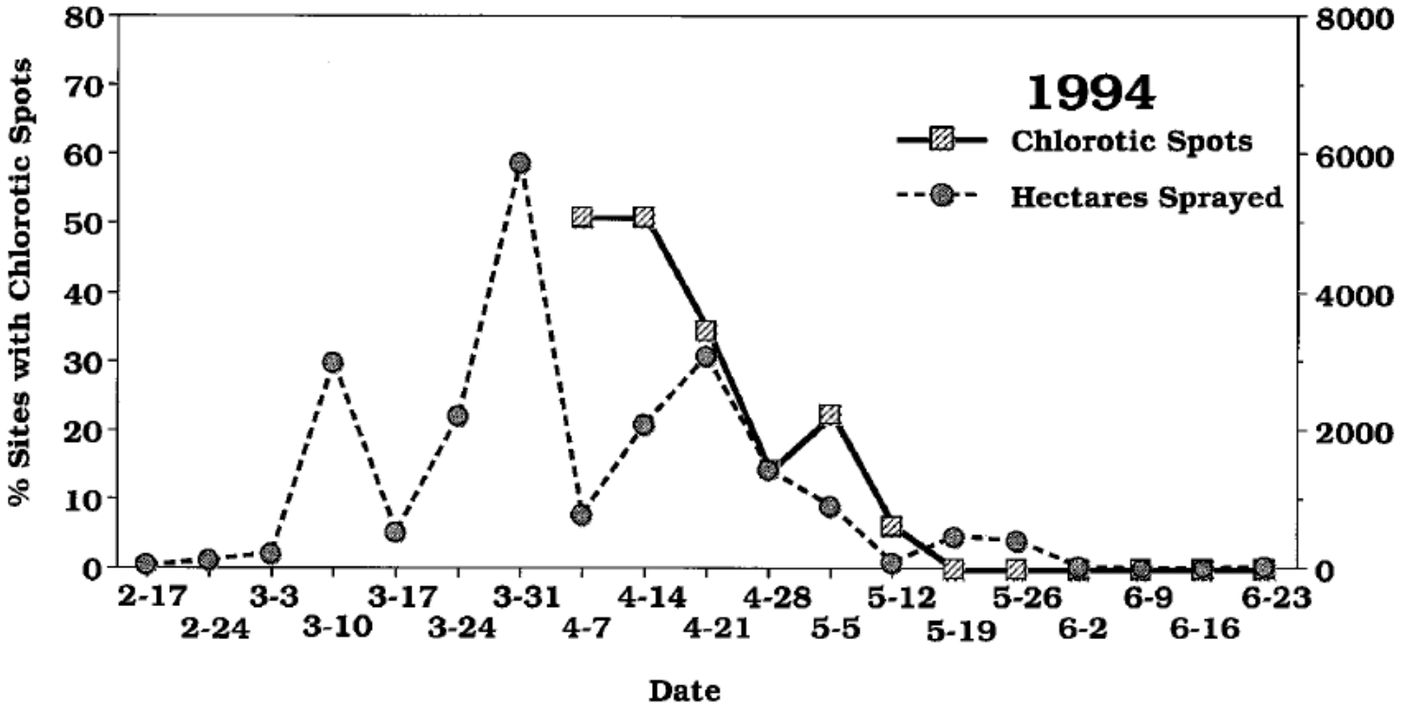
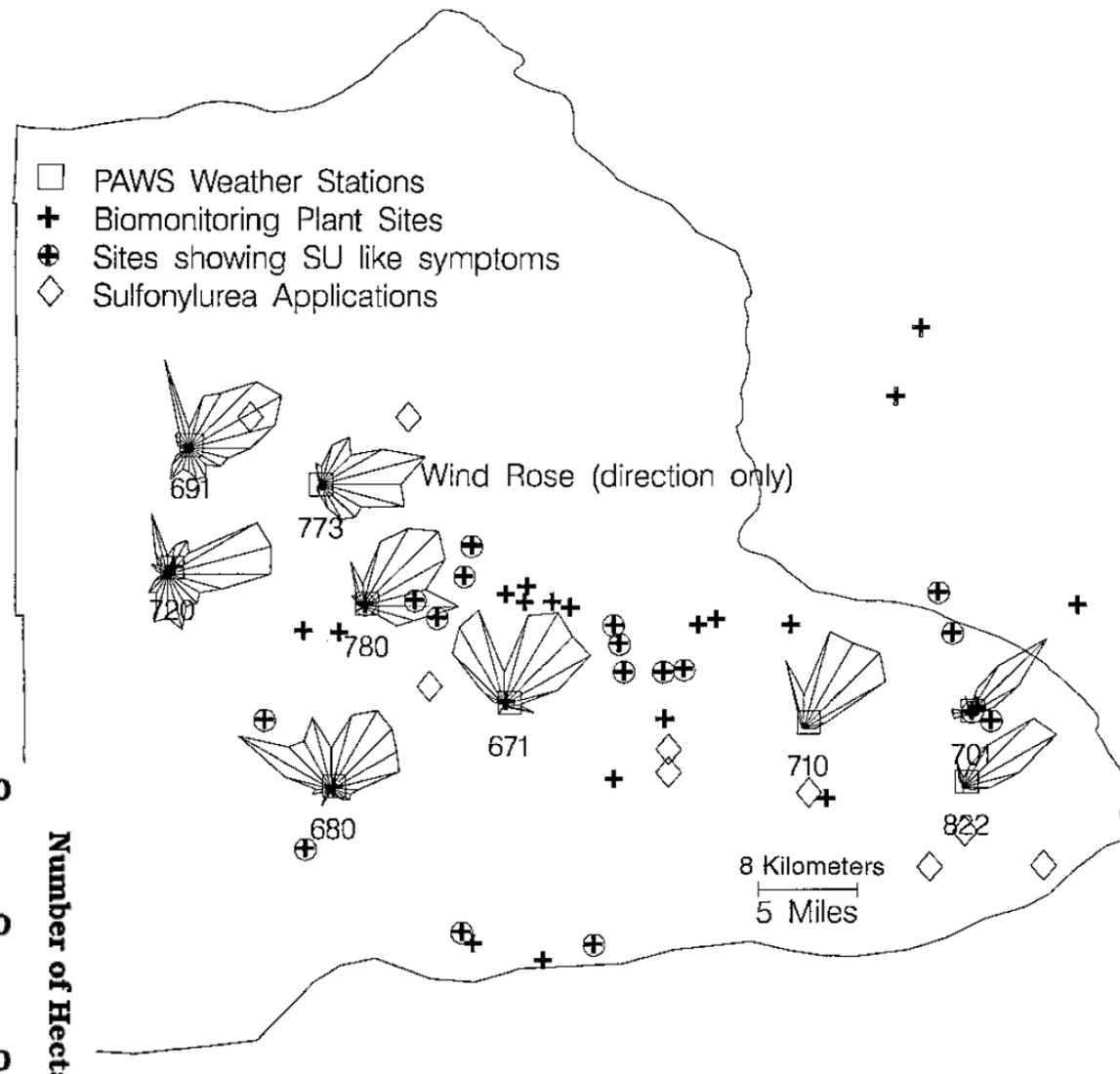
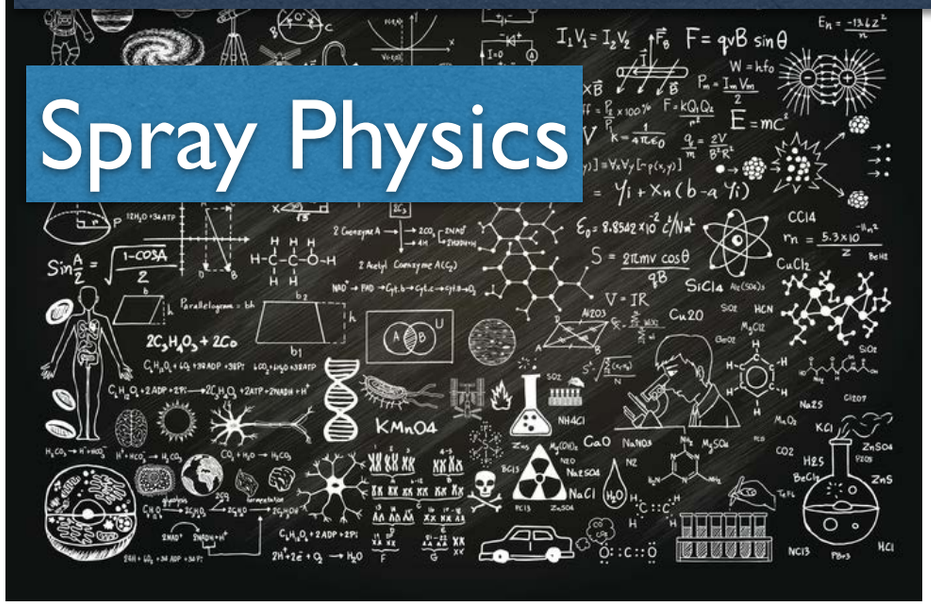
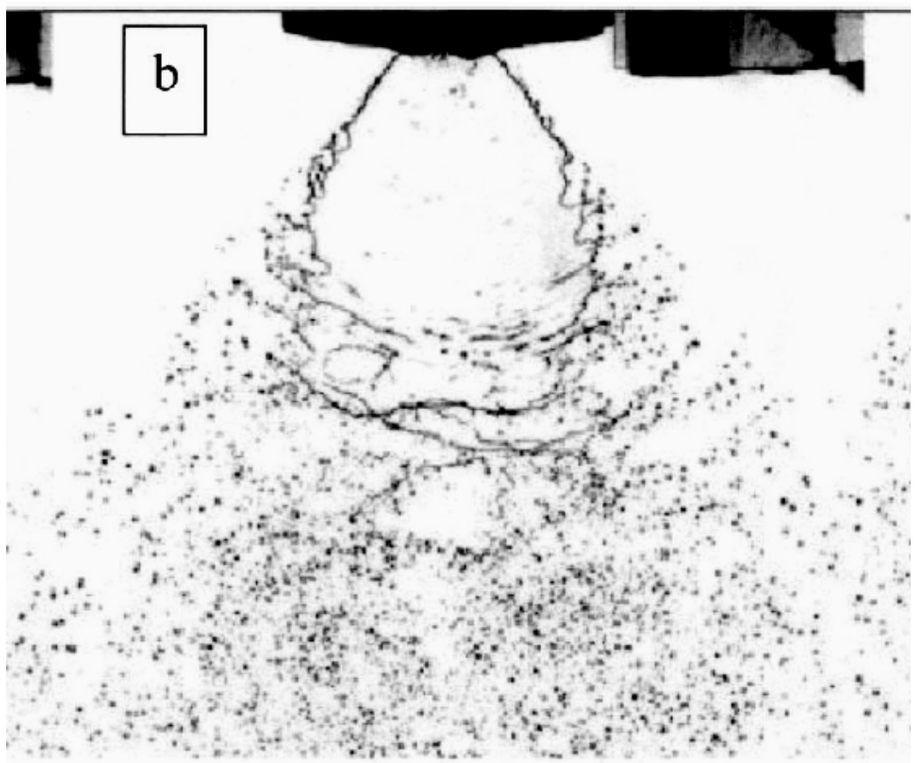




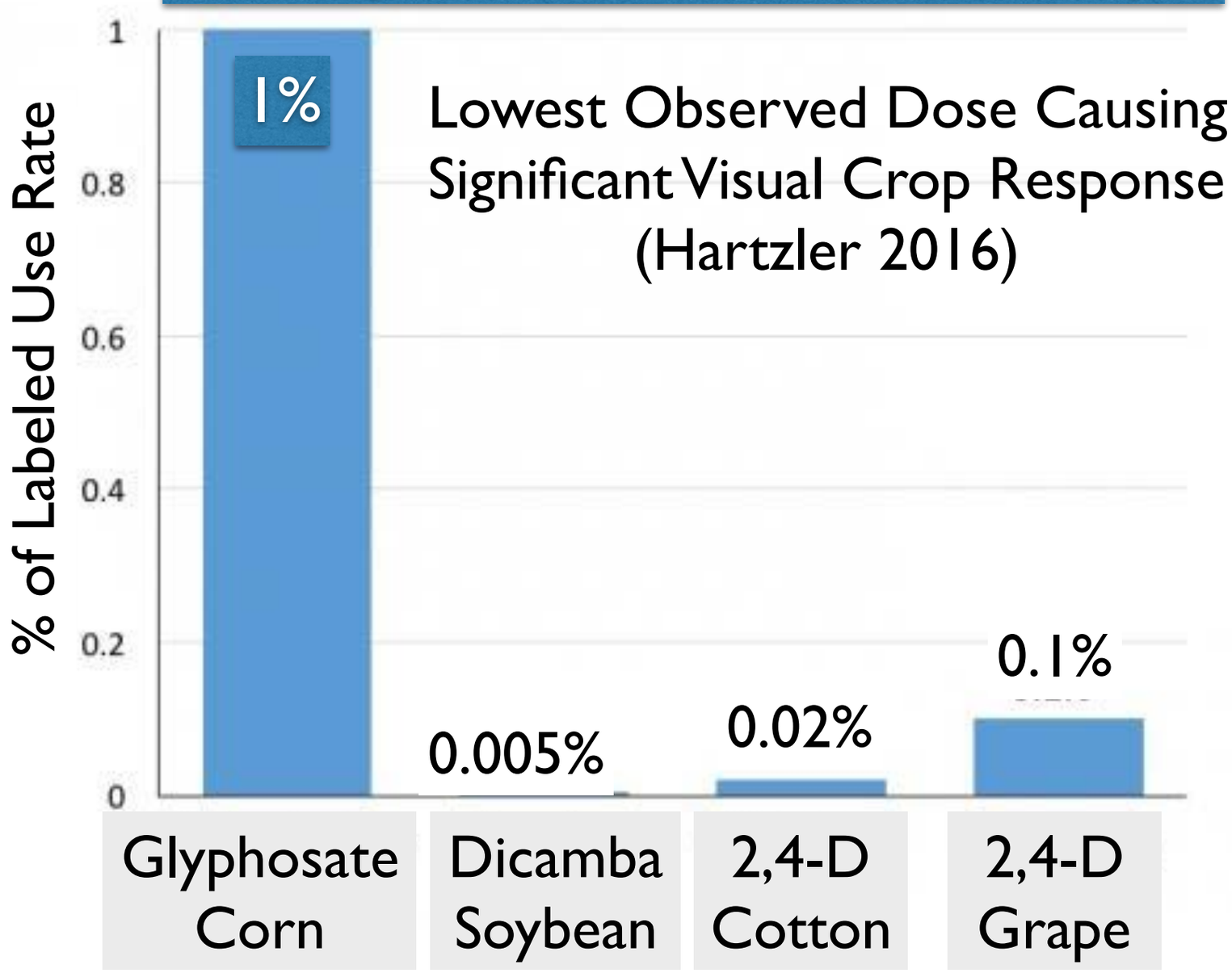
So, If What Has Been Happening in the Southern Soybean Belt Is Not Due to Drift, and Volatility of Currently Registered Low Vol Dicamba Formulations Reduces Volatilization….then What's Happening?

Basically, Two Factors at Work…





Mixed landscape consisting of susceptible and resistant crops



Lowest Observed Dose Causing Significant Visual Crop Response (Hartzler 2016)

Why Didn't Widespread Complaints Occur About Glyphosate When the First RR Crops Were Introduced??

- The proof is in the potency

Herbicide	Dose Causing Observable Foliar Symptoms g/ha	Dose Causing Yield Loss g/ha
dicamba	5.6	56
glyphosate	112	1121

Conclusions

- Some of the injury problems will not translate to yield losses, but nevertheless might be due to drift

  ✓ However, drift happens, even when BMPs are deployed to the fullest extent

- Some of the injury problems are due to volatilization of dicamba, even though new "sticky" formulations have significantly reduced this mass transfer phenomenon by 10-15 times

  ✓ These cases of injury are not likely to result in yield losses (i.e., economic damage)

- A lot of the airborne (and ultimately deposited) dicamba occurs during spraying itself given the rapid evaporation of carrier from the smallest particles that occur in any spray's particle size distribution

  ✓ The incredibly high potency of dicamba on susceptible soybean cultivars causes notable injury, but injury is not economic damage

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Questions?