

The Chemistry Behind Low-Volatility Dicamba

BY DR. WILLIAM ABRAHAM / Formulations and Delivery Lead at Monsanto

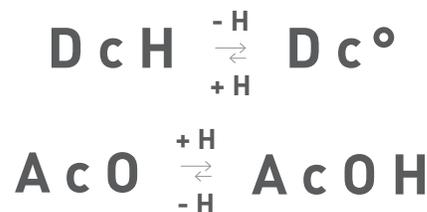
Low-volatility dicamba formulations resist changes to system pH, which prevents the formation of free dicamba acid.

DICAMBA 101 & THE SCIENCE BEHIND LOW-VOLATILITY XTENDIMAX

Dicamba is 3,6-dichloro-2-methoxybenzoic acid with a pKa of 1.87 and is governed by the typical acid-base equilibrium of a weak carboxylic acid. Most dicamba products are formulated as dicamba salts of organic amines. These salts when dissolved in water dissociate into dicamba anion and counterion which is invariably an organic ammonium cation. The dicamba anion can combine with any available proton (H+) in solution to form the volatile dicamba acid. This equilibrium is described by the classic Henderson-Hasselbalch equation that relates the degree of dissociation of a weak acid to the pH of the solution and the pKa of the acid (as shown below). As the pH of the formulation shifts away from the pKa of dicamba and towards higher pH levels, more of dicamba is dissociated and only a very small fraction of dicamba is in the free acid form in this equilibrium. The undissociated free acid is the volatile form of dicamba. For a starting pH of 5.0, only 0.1% of the dicamba is in the free acid form. Thus, the starting pH of a formulation is an important factor, but the ability to maintain the pH close to this initial pH throughout the use of the product is critical in controlling dicamba volatility potential from that formulation and any other additives added to the spray solution to be applied.



Henderson-Hasselbalch equation



VaporGrip® Technology in XtendiMax

The chemistry behind XtendiMax® addresses important questions around the volatility potential of dicamba during its use – as the product is dispersed in the spray tank, sprayed within the label use conditions over the field, and as the spray droplets dry on foliage or soil. The VaporGrip® Technology in XtendiMax® uses an acetic acid-acetate buffering system to scavenge any extraneous protons that could be brought into the system from the tank mixtures, or on the surface of foliage or soil as the spray droplets dry, thus significantly limiting the formation of volatile dicamba acid.

Acetic acid was chosen as the VaporGrip® Technology ingredient for XtendiMax® from a careful consideration of its pKa and vapor pressure. The pKa of acetic acid is 4.75, which is three log units above the pKa of dicamba acid. This makes the acetate ion (also known as the conjugate base) a far more powerful base than the dicamba anion. In other words, when XtendiMax® is discharged in a spray tank, and as the dicamba salt dissociates, acetate also dissociates. All these components remain in the fully dissociated form in spray solution. Any extraneous protons from tank additives in the spray solution would be readily scavenged by the buffering action of acetate, thus maintaining the pH at or very close to the starting pH of the formulation, and therefore preventing the formation of dicamba acid during and after spray application.

As the product is sprayed onto foliage/soil and the spray droplets dry, the residue will be the same composition as that of the spray solution along with silicates, organic matter and residual ions, such as Ca⁺⁺ and Mg⁺⁺, that are commonly found in soil. Any extraneous protons available on leaf or soil surface would be sequestered effectively by the acetate in VaporGrip® during droplet drying process far more effectively than dicamba anion, thus preventing the formation of volatile dicamba acid. Any rehydration of the residue from dew or rain does not change the composition as VaporGrip® would continue to prevent the formation of volatile dicamba acid.

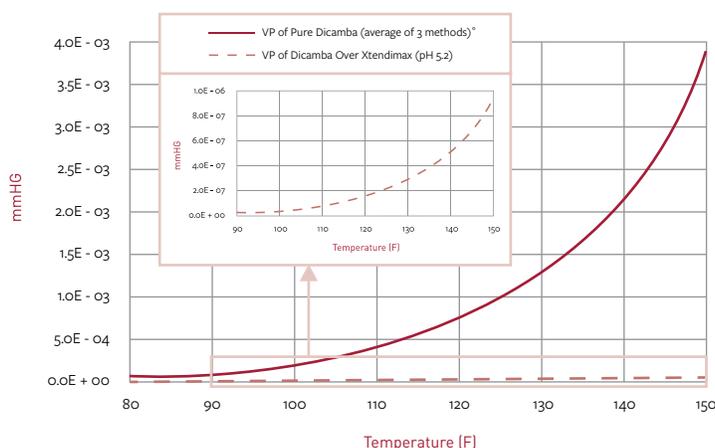
While growers cannot control the composition of foliar surface or soil, the formulation is designed through the buffering capacity of VaporGrip® Technology to control potential changes in pH and prevent the formation of volatile dicamba acid. Considering most agricultural soils conducive to plant growth and development have a resulting pH well above any that would influence increased volatility of this technology, the buffering capacity of VaporGrip® Technology is adequate to resist any changes in the pH of the residue from the spray. In addition, other available cations such as calcium or magnesium present in the soil would form insoluble salt of dicamba and do not affect the volatility of dicamba residue on the soil surface.

Furthermore, dicamba is readily degraded by microorganisms once it is in contact with most agricultural soils. The U.S. EPA reports a single half-life of six days for dicamba acid soil degradation from one laboratory study. In the dicamba registration data packages submitted to the U.S. EPA and the EU regulatory agencies, the half-lives of dicamba soil degradation ranged from two to eight days with a median half-life value of 4.4 days across all soils. The results of the field trials conducted in Europe and the United States also confirm the rather fast dissipation of dicamba with field half-lives in all cases of less than three weeks, and typically less than seven days.

When older dicamba DGA formulations are mixed with co-herbicides such as glyphosate, the pH of the spray solution could drop close to four owing to the buffering capacity of glyphosate. XtendiMax® is designed to enable tank mixing of potassium glyphosate formulations and maintain the pH close to the starting pH of five. However, certain tank additives, such as ammonium sulfate or other ammonium containing products, are not allowed for tank-mixing with XtendiMax®. Ammonium ion dissociates into volatile ammonia and proton and the amount of ammonium sulfate, used as a water conditioning treatment, added in the tank and the resulting protons in solution overwhelm the buffering capacity of VaporGrip® Technology, leading to significant increase in volatility of dicamba. This limitation of the technology limits the use of ammonium sulfate and is prohibited on the use label of this product.

Another property of dicamba that is often raised as an ogre in volatility conversation is the vapor pressure of pure dicamba acid. While the temperature dependence of vapor pressure is governed by fundamental principles of a molecule's increased energy with temperature, the potential increase in volatility of dicamba from soil surfaces that can reach up to 150°F is negated by the very low mole fraction of dicamba present as dicamba acid in XtendiMax®. At a mole fraction of 0.001 for undissociated dicamba acid calculated using Henderson-Hasselbalch equation as noted above, the effective vapor pressure from a formulation at pH 5 is reduced by three orders of magnitude compared to the pure dicamba acid. The effective vapor pressure of dicamba from this product while showing an exponential increase with temperature as estimated using Antoine equation*, even at a soil temperature of 150°F, does not reach levels of vapor pressure of pure dicamba acid at a much lower temperature of 75°F. Thus, by maintaining the fraction of the volatile dicamba acid at very low levels in this formulation high soil temperature concerns are eliminated.

Like all new pesticides, XtendiMax® was [comprehensively tested](#) before it was approved for use to ensure the product could be used safely and effectively. These tests were conducted according to [Good Laboratory Practice \(GLP\) standards](#) and confirmed the significant reduction in volatility compared to previous generations of dicamba products.



Indeed, when used within label requirements, research and field data have shown that XtendiMax® will not move off-target in quantities that will affect non-target plants. The label and buffer requirements enable this effective weed management tool to be used in a safe manner. By coupling two carefully selected acid-base equilibria, a robust formulation has been developed with the capacity to resist changes to the pH of the system and prevent the formation of free dicamba acid beyond the extremely low amount determined by the working pH of this product. VaporGrip® Technology maintains low volatility throughout the use of this product when used within label requirements.

*The Antoine Equation for Vapor-Pressure Data, Chemical Reviews, 38(1), 1-39, (1946)

DR. WILLIAM ABRAHAM

William Abraham is the Program Director of Formulations and Delivery Technology at Monsanto with responsibility in overseeing R&D program charged with formulations and delivery of chemical and biological actives for foliar and soil applications and seed treatment to enable Monsanto's system solutions to crop protection. After graduating from Vanderbilt University with a PhD in physical chemistry, William started as a postdoctoral fellow and continued as research scientist at the University of Iowa Medical School. Then he had a research career in pharmaceutical industry developing drug delivery systems. He served as an adjunct professor at the USC School of Pharmacy for five years. Over the past 21 years he has held several roles within Chemistry and Crop teams at Monsanto before moving into the current role. As a member of ACS for over 30 years, William enjoys visiting local schools and speaking to elementary and middle school children about chemistry. William has authored more than 20 scientific publications in surfactant science and epithelial barrier function, and over 25 patents and publications in herbicide formulations.

