Dicamba, 2,4-D, 2,4,5-T

Acid Herbicides

Background Information

Dicamba, 2,4-D, and 2,4,5-T are selective pre- and post-emergent acid herbicides. Primarily effective for the control of woody plants and broadleaf weeds, these compounds have been widely used throughout the world in areas such as pastures, forests, along railways, fencerows, roadways, and residential lawns. Once applied, they act systemically as synthetic auxin hormones by increasing the plant’s rate of cell division and subsequent growth. This uncontrolled growth continues until the plant can no longer sustain its own nutrient demand.

The chlorophenoxyacetic acid herbicides 2,4-D and 2,4,5-T were developed in the 1940’s and were the two primary ingredients of Agent Orange. These compounds have been made available in a variety of salt and ester forms with the dimethylamine and 2-ethylhexyl ester forms of 2,4-D accounting for over 90% of the total 2,4-D used. While 2,4-D remains one of the most widely used herbicides, 2,4,5-T is on the PIC list (Rotterdam Convention) and therefore banned in the majority of countries.

Agent Orange was a defoliant used in the late 1960’s by the U.S. military during the Vietnam War. Serious illnesses ranging from the skin disease chloracne to a variety of cancers and birth defects have been attributed to the use of Agent Orange. However, it was discovered that the majority of health effects from its use were caused by the existence of the chemical contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and not from the herbicides themselves. TCDD is formed as a side product when the reaction temperature is not properly maintained during synthesis of 2,4,5-T.

As a result of the usage of TCDD laced Agent Orange, large areas of the Vietnam countryside, particularly in Laos and Cambodia and former U.S. military bases, such as Da Nang, are still heavily contaminated with dioxin.

Dicamba, a benzoic acid herbicide, was developed in the early 1960’s and is widely used in the acid and dimethylamine salt forms. Dicamba and 2,4-D are also sold in various premix formulations combined with a wide range of other herbicide products.

The versatility of dicamba and 2,4-D allows for tailored applications by virtue of their various chemical forms. The ester forms have a higher volatility than the salt and acid forms and are therefore better able to penetrate stubbles and protected areas. However, as a result of their volatility they also pose a risk for non-target plants. Development of longer chain ester forms with lower volatility increases their effectiveness in warmer environments.

Because they are absorbed through the plant’s foliage, the esters are considered more potent than the salt forms. This quick absorption makes them useful in pre planting “burn down” applications. Salt forms are more readily absorbed through the root systems and are thus better suited for pre-emergence applications, such as with “no-till” planting.

Degradation of dicamba, 2,4-D, and 2,4,5-T is primarily attributed to microbial action. The half-lives range widely in soil and water, depending on the temperature, pH, and oxygen content, with higher microbial action resulting in a shorter half-life. The average half-life for 2,4-D in soil is reported to be 10 days. Dicamba’s half-life ranges from 30 days in aerobic soils to nearly twice as long in anaerobic soils. Salts and esters are generally converted to the anionic form with degradation occurring more quickly in higher pH environments.

Producers of dicamba include BASF Corporation (Banvel) and Syngenta (Vanquish). 2,4-D manufacturers include AMVAC Chemical Corp. (Citrus Fix) and United Phosphorus, Inc. (Aqua-Kleen).

Dicamba, 2,4-D, and 2,4,5-T are slightly to moderately toxic to birds and bees, but potentially more toxic to fish as the ester form. The tendency of the esters to be more toxic to fish is likely due to higher absorption through the gills. Toxicity to all species increases significantly if the dioxin content is more than a few parts per million.

Although acid herbicides are registered for use around the world, e.g. 2,4-D in France, and dicamba in Argentina, they are not registered for use on tobacco. However, they are of much interest as residues may result from misuse of products or simply accidental ‘drift’ from treated adjacent crops onto off-target tobacco fields.

The CORESTA Guidance Residue Level (GRL) established for dicamba is currently set at 0.20 mg/kg, while the GRLs for 2,4-D and 2,4,5-T are 0.20 and 0.05 mg/kg, respectively.
Dicamba

![Dicamba structure](image)

**IUPAC name:** 3,6-Dichloro-2-methoxybenzoic acid  
**Formula:** C₈H₆Cl₂O₃  
**Mass:** 221.04  
**CAS RN:** 1918-00-9  
**Form:** White crystalline solid  
**Solubility:** Water (6500 mg/L @ 25 °C)  
Ethanol (922 g/L)  
**Stability:** Reacts with organic and inorganic bases to form salts. May react with strong oxidizing agents.  
**pKa:** 1.97  
**Melting Point:** 114 – 116 °C  
**Production:** Dicamba is produced by methylation of 3,6-dichlorosalicylic acid with dimethyl sulfate.

2,4-D

![2,4-D acid structure](image)

**IUPAC name:** (2,4-Dichlorophenoxy)acetic acid  
**Formula:** C₈H₆Cl₂O₃  
**Mass:** 221.04  
**CAS RN:** 94-75-7  
**Form:** Yellow to white powder  
**Solubility:** Water (900 mg/L @ 25 °C)  
**Stability:** Reacts with organic and inorganic bases to form salts. Reacts with strong oxidizing agents.  
**pKa:** 2.64  
**Melting Point:** 138 °C  
**Production:** 2,4-D is produced through condensation of 2,4-dichlorophenol with monochloroacetic acid under heat in alkaline conditions.

2,4,5-T

![2,4,5-T structure](image)

**IUPAC name:** (2,4,5-Trichlorophenoxy)acetic acid  
**Formula:** C₈H₅Cl₃O₃  
**Mass:** 255.49  
**CAS RN:** 93-76-5  
**Form:** White to yellow crystalline solid  
**Solubility:** Water (238 mg/L @ 30 °C)  
**Stability:** Reacts with organic and inorganic bases to form salts. Reacts with strong oxidizing agents.  
**pKa:** 2.88  
**Melting Point:** 153 °C  
**Production:** 2,4,5-T is produced from 2,4,5-trichlorophenol and monochloroacetic acid.

Salts of dicamba, 2,4-D, and 2,4,5-T are produced through reaction with the appropriate metal or amine base. Esters may be obtained through reaction of the chlorinated phenol starting material with the selected ester of monochloroacetic acid.
Sample Extraction

Following application and incorporation into the plant, dicamba, 2,4-D, and 2,4,5-T are translocated through symplastic and apoplastic movement; however, the plants are not able to significantly metabolize the herbicide compounds and motility varies by plant species. Ester and salt forms will generally convert to the acid form within the plant; although the rates of conversion may be environment and pH dependent.

Modes of Analysis

The analysis of dicamba, 2,4-D, and 2,4,5-T is amenable to the use of a multi-residue method approach. Historical gas chromatographic (GC) methods require methylation of the acids prior to instrumental analysis. Derivatization may be accomplished with the use of reagents such as diazomethane or tetrabutylammonium hydroxide and methyl iodide. Detection and measurement of the analytes are typically made by halogen specific detectors such as an electron capture detector (ECD) or electro-conductivity detector. Alternatively, the use of GC with selected ion monitoring mass spectrometry is suitable.

Extraction of dicamba, 2,4-D, and 2,4,5-T from plant material should take into consideration the potential presence of the various acid, salt, and ester forms of these herbicides. Generally, a hydrolysis step within the method is recommended in order to ensure a comprehensive extraction. Validation of the methodology should include an evaluation of the accuracy of the extraction procedure using representative forms of esters and salts, as well as the acids.

The advent of liquid chromatography coupled with tandem mass spectrometry has allowed for direct analysis of the herbicide acid forms without derivatization.
References


3. **2,4-D Fact Sheet.** Retrieved from: [http://www.pmi-uk.org/pestnews/Actives/24d.htm](http://www.pmi-uk.org/pestnews/Actives/24d.htm) (verified July 2013)


17. *2,4-Dichlorophenoxyacetic acid (2,4-D). International Programme on Chemical Safety (IPCS), Environmental Health Criteria 29.* Retrieved from: [http://www.inchem.org/documents/ehc/ehc/ehc29.htm#SubSectionNumber:1.1.1](http://www.inchem.org/documents/ehc/ehc/ehc29.htm#SubSectionNumber:1.1.1) (verified July 2013)
