

Environmental Fate and Toxicology of Dicamba

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Abstract

The paper outlines the environmental fate and toxicology of dicamba, a systemic herbicide used in agricultural, industrial, and residential settings to control broadleaf weeds and woody plants. In soil, dicamba is highly mobile and has a relatively short half-life (3–136 days), which is affected by soil conditions. Dicamba enters the atmosphere through spray drift and volatilization and leaves the atmosphere through degradation and deposition. Atmospheric concentrations of dicamba are seasonal and coincide with local applications of the herbicide. Dicamba enters surface water through foliar washoff from precipitation and irrigation and has been frequently detected in California surface waters receiving urban runoff. Dicamba does not pose a significant threat to groundwater due to its short half-life.

Dicamba is not expected to bioaccumulate in organisms and at recommended application rates nor is it expected to exceed threshold levels of concern for aquatic plants or fish. Dicamba is relatively non-toxic for most birds and mammals; however, there is an increased potential of hepatic tumors at higher levels of dietary intake.

1. Introduction

This document reviews the environmental fate and persistence of dicamba—a synthetic systemic herbicide that is used in agricultural, industrial, and residential settings (Bunch & Gervais, 2012; Durkin & Bosch, 2004; EPA, 2006). Dicamba was first registered for use in 1967 and is used for post-emergent control of broadleaf weeds and woody plants (EPA, 2006). Dicamba is commonly applied to right-of-ways, asparagus, barley, corn grasses, oats, proso millet, sorghum, soybeans, sugarcane, wheat, golf courses, and residential lawns (EPA, 2006). Numerous formulations of dicamba exist including dimethylamine (DMA) salt, diglycolamine (DGA) salt, and dicamba sodium (NA) salt (EPA, 2006).

1.1 Use in the United States

As of 2006, there were over 400 registered products within the U.S. which contained dicamba as an active ingredient (EPA, 2006). 258 of those products are registered for sale and use within California (CDPR, 2014a). Common brand name products containing dicamba as the active ingredient include Banvel and Trimec (EPA, 2006).

According to Grube et al. (2011), 1–3 million pounds of dicamba were applied in the home and garden sector in 2005 and 2007. Dicamba was the eighth most commonly used active ingredient in the home and garden sector in 2005 and also in 2007 (Grube et al., 2011). The National Water-Quality Assessment conservatively estimated that 3.1 million pounds of dicamba were applied nationally for agricultural use in 2009 in the U.S (Stone, 2013) (Figure 1, Figure 2). This low estimate assumed that non-reporting Crop Reporting districts had no pesticide applications (Thelin & Stone, 2013).

1.2 Use in California

Dicamba has been registered as a restricted use pesticide in California since 1969 (Rutz, 1997). In 2011, 75,773 pounds of dicamba were applied in California. Of this amount, 26,612 pounds were for corn (forage-fodder), 12,287 pounds were for wheat, and 6,348 pounds were for wheat (forage-fodder) (CDPR, 2014b) (Figure 3, Figure 4).

1.3 Mode of Action

Dicamba is registered for post-emergent control of broadleaf weeds and woody plants (Bunch & Gervais, 2012; EPA, 2006). Dicamba mimics plant auxin hormones that stimulate cell elongation and cellular differentiation leading to rapid growth of stems, petioles, and leaves (Bunch & Gervais, 2012). This abnormal plant growth disrupts cellular transport systems and eventually leads to the death of the plant (EPA, 2006). Non-target plants exposed to even a small quantity of dicamba can experience phytotoxic effects like cupping, malformation, and necrosis of terminal leaves (Egan & Mortensen, 2012). Epinasty, which is the downward bending of leaves and

other plant parts resulting from excessive growth of the upper side, is another commonly observed effect in plants inadvertently exposed to dicamba (Strachan et al., 2010).

2. Physicochemical Properties

The chemical name for dicamba is 3,6-dichloro-2-methoxybenzoic acid or 2-methoxy-3,6-dichlorobenzoic acid (EPA, 2006) (Figure 5). Dicamba is classified as a benzoic acid and can form salts when in an aqueous solution (EPA, 2006). Under standard conditions, dicamba usually exists as crystalline solids; however, it may also exist as a vapor or as particulates (Bunch & Gervais, 2012). Dicamba has a low organic carbon partition coefficient (K_{OC}) and therefore, a low affinity for soil particles and suspended sediment (Comfort et al., 1992) (Table 1). Dicamba has a low octanol/water partition coefficient (K_{OW}) and is resistant to oxidation and hydrolysis under most conditions (Durkin & Bosch, 2004; Krueger et al., 1991).

3. Environmental Fate

3.1 Air

Dicamba has a vapor pressure of 4.5 mPa at 25°C and is characterized as a moderately volatile compound (Bunch & Gervais, 2012). The degree that dicamba volatilizes is dependent on several factors including the amount applied, atmospheric temperature, atmospheric humidity, chemical formulation, and surface upon which it was applied. The herbicide leaves the atmosphere through degradation from photolysis or deposition (Waite et al., 2005).

Behrens and Lueschen (1979) indirectly studied post-application volatility of DMA salt of dicamba using bioassay techniques. Behrens and Lueschen (1979) placed untreated soybean plants in close proximity to dicamba-treated corn, soybean, velvetleaf, glass, blotter paper, and soil at various times after application. After 14 days, the soybeans were removed and assessed for foliar damage. It was assumed that any observed foliar damage was caused by volatilization. Behrens and Lueschen (1979) observed a significant increase in foliar damage when ambient temperatures were increased from 15–30°C; however, no increase in foliar damage was observed when temperatures exceeded 40°C. Increasing relative humidity from 70–95 percent resulted in a significant decrease in foliar damage. One mm of simulated rainfall under laboratory conditions also greatly reduced the amount of volatilization. Behrens and Lueschen (1979) hypothesized that the degree of volatilization was partially dependent upon the surface which the herbicide was applied. A higher degree of foliar damage was observed in plants placed in close proximity to dicamba-treated soil, soybeans, and glass. Conversely, no foliar damage was observed on plants placed near dicamba-treated blotter paper or velvetleaf. Behrens and Lueschen (1979) theorized that since

the leaf area and orientation of velvetleaf and soybean foliage were comparable, volatilization may have been affected by the textural or chemical properties of foliage.

Egan and Mortensen (2012) used bioassay techniques to study post-application volatilization of DMA and DGA salt of dicamba. Formulations of dicamba were applied to plots of soybeans. Following the application, potted soybean plants grown in greenhouses were transported to the field plots and placed at varying distances from the application areas for 8–24 hours. The potted soybean plants were then removed from the field and observed for foliar damage. Egan and Mortensen (2012) inferred that foliar damage resulted from the volatilization of dicamba and observed that foliar damage increased with temperatures greater than 25°C. Foliar damage was observed on plants as far away as 21 m from the application plot. Dicamba was detected at a concentration of 0.56 g acid equivalent/hectare, or 0.1% of the application rate, at 21 m from the application plot. In contrast to the laboratory results in Behrens and Lueschen (1979), Egan and Mortensen (2012) found a significant positive correlation between relative humidity and the distance at which foliar damage was observed and the amount of dicamba resettled through vapor drift. The amount of herbicide resettled through vapor drift and the farthest foliage damage observed were both positively correlated with ambient temperature.

Behrens and Lueschen (1979) applied DMA salt of dicamba, at a concentration of 0.28 kg/ha, to corn fields to assess volatilization under field conditions. One hour after application, potted soybean plants were placed at seven locations—0, 3, and 30 m from the application area. In a few of the replicates, potted soybean plants were also placed at 20, 40, and 60 m from the application area. After 24 hours, the soybean plants were removed from the field and placed in greenhouses. The plants were assessed for foliar damage after 14 days in the greenhouse. Behrens and Lueschen (1979) inferred that observed foliar damage resulted from volatilization. Foliar damage was assessed on a relative injury index of 0–100 where 0 = no effect on plant, 40 = malformation and growth suppression of two terminal leaves, 70 = terminal bud death, and 100 = plant death. Maximum foliar damage (injury index = 68) was observed on soybeans placed 0 m from the application area and foliar damage was observed on soybean plants placed as far away as 60 m downwind of the application area. Overall, a decreasing degree of foliar damage was observed on plants placed further away from the application area. An average index rating of 61 was observed on soybeans located 3 m downwind of the application area and an average rating of 32 was observed on soybeans located 30 m downwind of the application area. Behrens and Lueschen (1979) also found that precipitation greatly reduced the amount of volatilization. Three and nine mm of precipitation, which occurred 12 and 14 hours after the application of dicamba respectively, greatly reduced volatilization. These field observations were supported by laboratory experiments where one mm of simulated rainfall reduced volatilization to negligible amounts.

Registrant literature states that the DGA salt of dicamba is eight times less volatile than the DMA salt of dicamba (Egan & Mortensen, 2012). Egan and Mortensen (2012) found that 94 percent less dicamba resettled through vapor drift when using the DGA salt of dicamba versus the DMA salt of dicamba. Behrens and Lueschen

(1979) assessed the relative volatility of different formulations of dicamba. Under laboratory conditions, the DMA salt of dicamba was significantly more volatile than two other formulations of dicamba (diethanolamine and N-tallow-N,N¹,N¹-tri-methyl-1,3-diaminopropane). However, Behrens and Lueschen (1979) found that all three formulations of dicamba caused significant foliar damage in field experiments. This implies that there is a negligible difference in volatility between the three formulations. Behrens and Lueschen (1979) also researched how the pH of the dicamba formulation affects volatilization. In closed growth chamber experiments, Behrens and Lueschen (1979) found that volatilization of DMA salt of dicamba from glass surfaces was reduced from 71–54 percent when the pH of the applied formulation was increased from pH 4.7–8.8. However, these results could not be duplicated in field applications of DMA salt of dicamba to a corn field.

In the particulate phase, dicamba is removed from the atmosphere through wet and dry deposition (Waite et al., 2002). Waite et al. (2002) sampled air for dicamba from two field sites in Saskatchewan, Canada over a two-year period. The highest concentrations of dicamba were observed from early June–July, which coincided with local applications of dicamba. Atmospheric concentrations of dicamba were only detected at one of the two field sites. Detections were rare and atmospheric concentrations ranged 0.027–0.68 ng/m³. A similar study, by Waite et al. (2005), researched seasonal variations in atmospheric dicamba from four field sites in Saskatchewan, Canada. The average atmospheric concentration of dicamba from all four sites was 0.12 ng/m³ with a maximum concentration of 1.12 ng/m³. Dicamba was detected in 68 percent of the samples. Wet and dry deposition revealed that atmospheric dicamba was present from mid-May to mid-July, which coincided with local applications of dicamba. Wet deposition samples were collected from five precipitation events from June–July. Of the five precipitation events, dicamba was detected at trace levels from one sample and at a concentration of 30 ng/L in another sample, but the remaining three samples yielded no detections. Waite et al. (2005) concluded that only a small portion of dicamba leaves the atmosphere through wet deposition. No correlation between precipitation amount and wet deposition concentration was observed in this study.

Waite et al. (2004) researched variations in atmospheric dicamba concentrations at different heights. High-volume air samples were collected from mid-May to mid-July in Saskatchewan, Canada. Air samples were taken at heights of 1, 10, and 30 m and analyzed for dicamba. The highest concentration of dicamba, 0.47 ng/m³, was observed during the first week of July. During this sampling period, concentrations of dicamba were slightly higher in the lower height samples; however, there were no significant differences in concentrations by height. Yao et al. (2006) conducted a similar experiment and assessed atmospheric concentrations of dicamba at 1, 10, and 30 m above the ground. Concentrations of dicamba ranged from 0.01–0.187 ng/m³ and peak concentrations were observed during times of local applications of dicamba. Similar to previous results, Yao et al. (2006) noticed no significant variations in atmospheric concentrations of dicamba at different heights above the surface. These results suggest that there are both local and long distance contributions to atmospheric dicamba.

3.2 Soil

The sorption of pesticides to soil colloids reduces leaching and transport of chemicals through surface runoff. Chemical leaching can occur when chemicals have a low affinity to bind to soils. The soil organic carbon-water partitioning value, or K_{oc} value, for dicamba indicates that this pesticide sorbs weakly to soil colloids and is highly mobile (Comfort et al., 1992). Research suggests that soil properties like texture, incubation time, organic matter content, mineral composition, and temperature only slightly affect the sorption of dicamba.

Some pesticide classes like triazines, acetanilides, and amides exhibit an increase in sorption with increased time in soil (Menasseri et al., 2004). Menasseri et al. (2004) observed that more sorption sites on soil particles may be available when pesticides remain in the soil longer. Menasseri et al. (2004) applied dicamba at a concentration of 0.25 mg/kg to six soils to assess the relationship between residence time and sorption. The soils were analyzed 0, 1, 3, 7, 10, 14, and 28 days after the application. Over 80 percent of the applied dicamba was sorbed to soil particles within seven days, and 99 percent was sorbed by the end of the 28-day trial. Statistical analyses suggest that soil properties like organic carbon content, percent clay, percent sand, and pH had no statistically significant effect on the soil-water adsorption coefficient (K_d). The only significant increase in K_d was observed when less than 15 percent of the applied dicamba remained. This change may have resulted from the mobile dicamba degrading faster than its immobile counterpart.

Menasseri et al. (2004) applied dicamba to unamended and carbon-amended sandy loam and silt loam soils. Dicamba was applied to both soils types of soils and sorption patterns were examined for 28 days. No statistically significant change in sorption patterns between unamended and amended soils was observed after 28 days. At the end of the study, 10 percent of the applied dicamba was bound to soil particles in the carbon-amended sandy loam soils and 26 percent in the unamended sandy loam soils. Six percent of the applied dicamba was bound to soil particles in the carbon-amended silt loam soils and 36 percent to the unamended silt loam soils. Menasseri et al. (2004) observed that the half-life of dicamba was slightly longer, but not statistically significant, in the carbon amended soils.

Johnson and Sims (1998) assessed the mobility of dicamba in six different soils and found dicamba to be highly mobile in all six soils. The researchers also noted that mobility increased in soils with low levels of organic matter, clay, and Fe and Al oxides. R_m values, which is the ratio of the distance traveled by the herbicide to the distance traveled by the solvent front, ranged from 0.80–0.94 for dicamba for all six soils (Johnson & Sims, 1998). Hill et al. (2000) studied the leaching rate of dicamba in four different soils (pH ranging from 5.6–7.6). Soils were spiked with dicamba at a concentration of 120 g dicamba/ha and irrigated. Eluate samples were collected at 0.33, 0.67, 1.3, 3.0, and 4.7 rain-years (one rain-year = 150 mL of irrigation). Similar to the findings of Johnson and Sims (1998), Hill et al. (2000) found that dicamba leached quickly in all soil types. After 0.67 rain years, 84–100% of the applied dicamba was leached.

Soil moisture is hypothesized to increase accessibility to sorption sites on organic carbon (Ochsner et al., 2006). Ochsner et al. (2006) assessed changes in sorption coefficients when dicamba was applied to three unique

soils (loamy sand, silt loam, and silty clay loam) with different water contents. Ochsner et al. (2006) did not observe a significant difference in sorption coefficients for the three soils at low water contents (0.05 kg/kg). Sorption coefficients doubled in silt loam and increased six-fold in silt clay loam at higher water contents (0.19–0.24 kg/kg).

Other studies have suggested that the sorption rate of acidic pesticides may increase with decreasing soil pH (Murray & Hall, 1989). Zhao et al. (1996) assessed the sorption of dicamba at different pH levels in two clay-rich soils over 24 hours. They found that the sorption of dicamba, applied at a concentration of 320 mg/L, increased two-fold when the chemical existed in its molecular rather than ionic form. A study conducted by Murray and Hall (1989) assessed the effects of soil pH on sorption of dicamba in five soil types. Murray and Hall (1989) found that the percent of dicamba sorbed to soil particles increased as soil pH decreased from 6.9–2.0. Less than 5 percent of the applied dicamba was sorbed at pH>6; however, approximately 40 percent was sorbed at pH 2. Azejjel et al. (2008) also observed an increase in dicamba sorption when soil pH was artificially decreased from 5.0 to 2.1 but little change in sorption between soil pH 11.0 and 5.0. Villaverde et al. (2008) assessed sorption of dicamba in five agricultural soils ranging in pH from 6.3–8.4, organic matter content (0.3–1.0 percent), and clay content (3–66 percent). Over an 80-day incubation period, K_d ranged from 0.09–0.22 in the five soils and a negative relationship between sorption and soil pH was observed.

Alternative tillage practices reduce surface soil erosion but also alter the subsurface structure of soil. Preferential flowpaths, which aid in the transport of pesticides in soil, are greatly affected by tillage practices (Watts & Hall, 2000). Conservation tillage, or no-tillage, is a method in which the previous year's crop residues are left on the field to reduce topsoil erosion and runoff. Elliott et al. (2000) assessed the effects of no-tillage and conventional-tillage practices on the transportation of dicamba in soil in tile drained fields over two years. The fields were irrigated with 135–300 mm of water and the effluent from the tile drains was analyzed for dicamba. Over 0.46 percent of the applied dicamba was transported in non-tilled fields while only 0.09 percent was transported in the conventionally tilled fields. In a similar study, Shang and Arshad (1997) noticed changes in soil properties of two fields, one sandy loam and one clay soil field, when subjected to either conventional or conservation tillage. In sandy loam fields, conventionally tilled fields exhibited a higher soil pH (greater than 0.79 pH unit increase) than the conservation tilled fields. In the clay soil fields, a decrease in organic carbon and a 0.3 unit increase in soil pH were observed in conventionally tilled fields when compared to conservation tilled fields. Contrary to Watts and Hall (2000), Shang and Arshad (1997) observed that more dicamba was sorbed in the conservation tillage than the conventional tillage sandy loam soils. Shang and Arshad (1997) hypothesized that lower soil pH in the conservation tilled fields with sandy loam soil resulted in increased sorption of dicamba. The small change in soil pH under the two tillage treatments in the clay soil fields did not affect sorption rates.

Watts and Hall (2000) evaluated the effects of two tillage practices, conventional-tillage and mulch tillage, on the transport of dicamba over three years. Mulch tillage is a practice in which 100 percent of the soil surface is

disturbed. Dicamba was applied at a rate of 0.56 kg dicamba/ha on silty clay loam soil. Root zone leachate and surface runoff from the two field treatments were monitored and analyzed for dicamba. The mulch tilled systems yielded a smaller volume of surface runoff and a larger volume of leachate than the conventionally tilled fields. In the first two years of the study, all leachate samples that contained a significant concentration of dicamba were collected within 21–31 days of the initial application. Watts and Hall (2000) speculated that the quantity of precipitation and the amount of time between application of dicamba and the first leaching event were the two most important factors in determining how much dicamba was leached.

3.3 Water

Dicamba can enter surface water through foliar washoff caused by precipitation. The amount of dicamba transported through foliar washoff by precipitation depends on the amount of precipitation, precipitation intensity, and foliar mass (Carroll et al., 1993). After an application, the initial amount of dicamba on a leaf is inversely related to its mass (Carroll et al., 1993). Kentucky bluegrass field plots sprayed with dicamba at a concentration of 0.6 kg AI/ha were irrigated with simulated rainfall at two different intensities (20.6 and 39.9 mm/hour) to identify foliar washoff rates. Carroll et al. (1993) determined that precipitation intensity had a small effect on foliar washoff when compared to precipitation amount. After the initial 8 mm of precipitation at both intensities, approximately 50 percent of the applied dicamba was washed off of the foliage. An additional 23 percent was washed off with an added 50 mm of precipitation.

Smith and Bridges (1996) researched the transport of dicamba (applied at a concentration of 0.07 kg/ha) in surface runoff from golf fairways with a 5 percent gradient. Fairways were irrigated with simulated daily irrigation at 24, 48, 96, and 192 hours after treatment with 5.0, 5.0, 2.4, and 2.5 cm of rainfall, respectively. Ten percent of all the dicamba initially applied was recovered in the first sample, which was taken 24 hours after the treatment. The highest concentration of dicamba, 279.2 µg/L, was also recorded from this period. By the last sampling period, 192 hours after the treatment, 24 percent of applied dicamba had been recovered in the runoff. A similar study conducted by Rice et al. (2010) assessed the surface runoff from bentgrass turf after precipitation events. The researchers irrigated the bentgrass with four precipitation events, simulated at a rate of 33±6 mm/hour. The precipitation was stopped 90 minutes after the onset of surface runoff. The average concentration of dicamba in surface runoff over the four precipitation events was 281.2±76.9 µg/liter. On average, approximately 23 percent of the total dicamba applied was recovered in surface water from each precipitation event.

Observed concentrations of dicamba in surface water is often seasonal. Cessna and Elliott (2004) analyzed water samples from prairie farm ponds that receive water input from agricultural runoff and snowmelt. Over three years, Cessna and Elliott (2004) observed that dicamba was consistently detected during the local growing seasons. The maximum detection was 4.5 µg/L with median levels less than 0.05 µg/L. Detections that

occurred during non-growing seasons suggest that under certain environmental conditions, bottom sediments may release sorbed chemicals into the water column.

Ensminger et al. (2013) analyzed water samples collected during storm (within 24 hours after rainfall) and dry season from surface water from 2008-2011 in California. Urban or residential sampling locations in three major California urban centers (San Francisco Bay, Orange County, and Sacramento area) were chosen. Out of 225 samples (119 dry season, 106 storm), dicamba was detected in over 40 percent of the samples. A significant increase in the number of pesticides detected and the concentrations of those detected pesticides was observed in the storm water samples compared to the dry season samples. The median concentration of dicamba was below the reporting limit during the dry season and 0.06 µg/L for storm samples. The maximum concentration of dicamba was higher during the dry season (3.1 µg/L) than during storm events (1.2 µg/L).

The Department of Pesticide Regulation maintains the Surface Water Database, which contains measured concentrations of pesticides detected in surface water samples collected from 19 counties in California (CDPR, 2014c). Out of 1,089 samples, dicamba has been detected in 58 (5.33%) of the samples. The highest concentration of dicamba was 3.07 µg/L from a sample from Placer County. Additionally, the highest frequency of detections occurred in Placer County. Dicamba was detected in 24 of 32 (75%) tested surface water samples from Placer County (CDPR, 2014c).

Pesticides detected in groundwater usually possess high leaching potential, low sorption to soil, and have a half-life greater than 30 days (Smith & Bridges, 1996). While dicamba is characterized by a high leaching potential and low sorption to soil, many studies have reported that due to its short half-life, it is a low risk for groundwater contamination.

Smith and Bridges (1996) studied the potential for dicamba to be transported to surface water and groundwater after being applied to Bermuda grass. Through field experiments, Smith and Bridges (1996) simulated rainfall 24, 48, 96, and 192 hours after applying dicamba to Bermuda grass. The experiment tracked the movement of dicamba through the soil column over 70 days. Only a small portion, 0.4 percent, of the applied dicamba was transported through to the base of the lysimeters, which were located 52.5 cm below the soil surface. The highest concentration of dicamba observed in the leachate was 1.9 µg/L. Research suggests that despite the mobility of dicamba in the soil column, only a small portion of dicamba is transported down to depths where the pesticide may pollute groundwater.

Preferential flowpaths create conduits for the quick transport of pesticides to lower soil horizons and reduce soil sorption and microbial degradation. Tindall and Vencill (1995) researched the transport of dicamba through preferential flowpaths in six field plots with clay pan soils. Lysimeters were installed 1–1.4 m below soil surface and barriers built up around the surface of each field plot to prevent surface runoff. Dicamba was applied at a concentration of 1.46 kg/ha to each field plot and irrigated with 5 cm of water (1.5 cm/h). Following the application, samples were taken approximately every 30 days for the next 6 months. Tindall and Vencill (1995)

observed that preferential flowpaths, resulting from cracking of the claypan, facilitated the transport of dicamba through the soil column. There was a noticeable increase in leaching following major precipitation events 1–2 months after application. By month six, approximately 10 percent of the applied dicamba had been detected in the leachate.

Pang and Letey (1999) determined that vegetation plays a key role in reducing the amount of pesticide leaching. These authors created a series of computer models to identify the effects of salinity, irrigation, and nitrogen input on the leaching of dicamba. The models demonstrate that while dicamba is rapidly transported in the soil column, the chemical quickly degrades due to its short half-life. Pang and Letey (1999) also found that factors that reduce plant growth, like decreased nitrogen input and increased salinity, resulted in increased leaching of dicamba. Jury et al. (1987) created a mathematical model to predict the flow of dicamba in a soil column. The model assumed steady water flow, depth-dependent first-order biodegradation, $K_{oc} = 2.2$ L/kg, and a half-life = 14 days. Under a low-mobility scenario, Jury et al. (1987) determined that it would take 3.5 years and 0.6 years under a high-mobility scenario for dicamba to leach to a depth of 3 m. Most sources cite the half-life of dicamba as 3–150 days, so it is unlikely to be a groundwater pollutant risk in a low-mobility scenario.

Relatively few studies have been conducted on dicamba detections in groundwater. Koterba et al. (1993) conducted a census of shallow wells of the east coast of the United States where the water table was located 0–6 m below the soil surface. Wells located in areas with well-drained soils were more likely to yield a higher number and proportion of pesticide detections. Detections of dicamba were higher in wells located near corn, soybean, and small-grain fields and lower for wells near other crop or non-crop areas. Domagalski and Dubrovsky (1991) tested wells for pesticides in the Central Valley of California. Five wells (2.7 percent of wells tested) tested positive for dicamba residues; however, the maximum concentrations never exceeded 0.01 µg/L. All positive detections for dicamba were from wells located in the Eastern San Joaquin Valley. Domagalski and Dubrovsky (1991) suggests that the fine-grained sediment of the Central Valley reduce permeability and increase the sorption of dicamba to soil particles.

The California Department of Pesticide Regulation maintains the Groundwater Protection List, which identifies pesticides that are potential groundwater pollutants (CDPR, 2014a). Pesticides are added to the Groundwater Protection List based on an analysis of their environmental fate and labelled uses (CDPR, 2014a). DGA, DMA, and the sodium salt formulation of dicamba are currently included on the Groundwater Protection List (CDPR, 2014a). Of over 14,000 groundwater samples analyzed for dicamba from 1984–2011, dicamba was detected five times (CDPR, 2014d). All five detections were at the minimum detection limit of 0.01 ppb (CDPR, 2014d).

4. Biotic Degradation

Table 2 below summarizes degradation rates of dicamba observed under various field conditions in literature. Dicamba is either completely mineralized or biologically degraded in soil (Menasseri et al., 2004). Dimethylation of dicamba produces 3,6-dichlorosalicylic acid (3,6-DCSA), which is hydroxylated to produce 2,5-dihydroxy-3,6-dichlorobenzoic acid (2,5-diOH). Krueger et al. (1991) found the half-life of dicamba to be 31 days under aerobic conditions and 58 days in anaerobic conditions. The EPA (2006) calculated the half-life under aerobic and anaerobic conditions to be 6 and 141 days, respectively.

Soil properties like moisture, temperature, and pH can affect the biological degradation of pesticides (Kah et al., 2007). Rutz (1997) researched degradation rates of dicamba in soil and thatch in two temperature and soil moisture regimes. At a high temperature and high water content (20°C and water content of 0.25–0.28m³/m³), the half-life of dicamba in thatch and soil was 5.5 and 36.2 days, respectively. At a low temperature and low water content regime (4°C and water content of 0.18–0.22m³/m³), the half-life of dicamba in thatch and soil was 23.2 and 136.1 days, respectively. Comfort et al. (1992) researched the degradation rate of dicamba under different temperature regimes and found that dicamba degrades rapidly with temperatures above 20°C. The half-life of dicamba at 12, 20, and 28°C was 151, 38, and 23.5 days, respectively (Comfort et al., 1992).

Voos and Groffman (1997) studied the relationship between soil microbial biomass and the degradation of dicamba in soils from a freshwater aquifer, cornfield, hardwood forest, home lawn, and freshwater wetland. The soils were inoculated with 2.59 mg dicamba/kg soil and the pesticide degradation was measured at 5, 10, 20, 40, and 80 days after application. Voos and Groffman (1997) observed complete or nearly complete dissipation of dicamba by day 80 in the hardwood and wetland soils. However, the aquifer, cornfield, and lawn soils still yielded concentrations ranging from 1.48–2.59 mg/kg of soil. Statistical analyses suggest a significant correlation exists between microbial biomass and soil organic content and the degradation of dicamba. Krueger et al. (1991) isolated eight species of soil bacteria from storm water retention ponds at a dicamba manufacturing plant that are capable of using dicamba as their sole source of carbon. In another study, Kah et al. (2007) applied 2 mg of dicamba/kg of soil to nine temperate, arable soils to evaluate the relationship between microbial activity and the degradation of dicamba within soils. Kah et al. (2007) observed no statistically significant relationship between microbial bioactivity and dicamba degradation but did observe a strong positive correlation between organic carbon content and dicamba degradation.

In water, the degradation of dicamba is microbially mediated. Factors including temperature, vegetation, and turbidity appear to have a small effect on the rate of degradation of dicamba (Scifres et al., 1973). Dicamba was applied at a rate of 4.3 kg/ha of pond surface area to two ponds (one heavily vegetated and the other devoid of vegetation but extremely turbid). The application of dicamba resulted in average initial water concentrations of 11 ppm dicamba in the two ponds. Over the course of 90 days, no significant difference in the rate of degradation of dicamba was observed between the two lakes. The average rate of degradation in the two lakes was 1.6 ppm/day. Dicamba was most rapidly degraded in the initial 7 days following the application and complete

dissipation of dicamba was observed within 40 days. Scifres et al. (1973) conducted additional laboratory experiments to identify factors that affect the degradation of dicamba. Over 133 days, the aquatic degradation of dicamba was assessed under three different laboratory conditions: non-sterile aqueous solution exposed to continuous ultra-violet light, non-sterile aqueous solution exposed to continuous dark, and sterile aqueous solution exposed to continuous dark. Under these conditions, Scifres et al. (1973) observed the most rapid degradation in the non-sterile solutions exposed to continuous ultra-violet light (41 percent loss of dicamba in 133 days) and the least degradation in the sterile solution exposed to continuous dark (5 percent loss in 133 days).

Given the relatively short half-life of dicamba under aerobic conditions, the aerobic degradation pathway is expected under typical agricultural conditions. Taraban et al. (1993) extracted a dicamba degrading consortium consisting of a sulfate reducer, three methanogens, and a fermenter from anaerobic wetland soil. They reported that dimethylation of dicamba by the consortium produced the primary metabolite, 3, 6-DCSA. The production of 3,6-DCSA peaked 20 days after pesticide application and by day 60, production had reduced to negligible levels. 3,6-DCSA was reductively dehalogenated to form a secondary metabolite, 6-CSA, which the consortium was unable to further degrade. Under methanogenic conditions, Gu et al. (2003) hypothesized that the degradation process results in the release of a methyl group that is used by acetogens to form acetate.

5. Abiotic Degradation

5.1 Photolysis and Hydrolysis

Photolysis is expected to occur in aqueous environments. Aguer et al. (2000) exposed dicamba to UV light in aqueous solutions and to dicamba sorbed to synthetic clay. Aguer et al. (2000) identified a number of degradates and concluded that the mineralogical composition of the soil and level of soil moisture would have a great impact on the photodegradation pathway. Dicamba is expected to be resistant to hydrolysis under normal conditions (Mullison, 1979).

6. Ecotoxicology

6.1 Microorganisms

Few studies have researched the effects of dicamba on beneficial soil microorganisms. Tu (1994) studied the effects of dicamba on nitrification, ammonia formation, and sulfur oxidation. Tu (1994) observed a temporary decrease in nitrification after two, but not after three, weeks following the application of dicamba. This transient decrease in nitrification is unlikely to affect microbial activity. No effects on ammonia formation or sulfur oxidation were observed. Martens and Bremner (1993) applied dicamba at a concentration of 5 mg/kg soil to four soils of varying pH (pH = 6.0–8.1), texture, and organic carbon content and found that dicamba had no effect on

nitrification. When dicamba was applied at 50 mg/kg soil, a temporary decrease in nitrification was observed in two of the four soils.

6.2 Aquatic Organisms

Fairchild et al. (1996) researched the toxicity of dicamba on two species of aquatic plants (*Selenastrum capricornutum* and *Lemna minor*). The 96-hour EC₅₀ for *S. capricornutum* was 35 mg/L and greater than 100 mg/L for *L. minor*. In a separate study, Durkin and Bosch (2004) identified dicamba as moderately toxic to *L. gibba* with a 14-day NOEC value of 0.25 mg/L. Sensitivity of aquatic plants to dicamba varies by species. The most sensitive aquatic plant species, for which there is available data, is *Anabaena flosaquae*. *A. flosaquae*, a freshwater algae, has an EC₅₀ of 0.061 mg/L and an EC₁₀ of 0.0049 mg/L (Durkin & Bosch, 2004). In general, most species of aquatic plants appear to be less sensitive to dicamba than *A. flosaquae*. Computer simulations indicate that for aquatic non-vascular plants, a threshold level of concern would be exceeded with field application rates of dicamba above 2.0 lbs AE/acre (EPA, 2006).

A limited number of studies have assessed the effects of dicamba on fish and aquatic invertebrates. Durkin and Bosch (2004) provide NOEC values for bluegill sunfish (*Lepomis macrochirus*) (56 mg/L–100 mg/L), rainbow trout (*Onchorhynchus mykiss*) (56 mg/L), and sheepshead minnow (*Cyprinodon variegatus*) (>180 mg/L). The US EPA Office of Pesticide Program acute aquatic life benchmarks for dicamba acid, dimethylamine salt of dicamba (DMA), and sodium salt of dicamba are provided below in Table 3 (EPA, 2014).

6.3 Birds

Based on dietary studies, dicamba is expected to be relatively non-toxic to most birds (EPA, 2006). Edson and Sanderson (1965) orally administered an aqueous sodium salt formulation of dicamba to hens and pheasants for 15 weeks. Body weights of the birds were taken weekly and at the end of the study, the kidney and liver weights were also taken. The LD₅₀ for hens and pheasants was 673 and 800 mg/kg, respectively (Edson & Sanderson, 1965). Durkin and Bosch (2004) report the LD₅₀ values for mallard ducks and bobwhite quail to be about 1300 mg/kg.

The EPA (2006) determined that levels of concern would be exceeded for small birds consuming mean residues of dicamba on short grass, tall grass, broadleaf forage, and small insects. However, chronic development and reproductive problems are not expected in most birds when they are exposed to dicamba that has been applied at the recommended label concentrations (EPA, 2006).

6.4 Mammals

Dicamba is classified as relatively nontoxic to terrestrial mammals (Durkin & Bosch, 2004). LD₅₀ values for male rats ranged from 449–1278 mg/kg for technical preparations of dicamba and 925–1308 mg/kg for formulated

preparations of dicamba. An unpublished study cited in Durkin and Bosch (2004) found significantly decreased offspring growth in rats with daily doses of dicamba (105–135 mg/kg/day). Edson and Sanderson (1965) determined the maximum ineffective intake rate of dicamba in rats to be 19–43 mg /kg/day. In a study conducted by Espandiari et al. (1995), rats ingested feed containing 0, 0.01, 0.1, or 1 percent dicamba for three weeks. Espandiari et al. (1995) found that even at the highest levels, the rats still gained weight at a normal rate and the liver mass was unaffected. Espandiari et al. (1995) did find that when fed dicamba at a 1 percent dietary level, there was a slight to moderate increase in peroxisomal enzymes, which may increase the risk of hepatic tumors.

7. Summary

Dicamba is a synthetic, systemic herbicide used in agricultural, industrial, and residential settings to control broadleaf weeds and woody plants. It is regularly applied to right-of-ways, asparagus, barley, corn grasses, oats, proso millet, sorghum, soybeans, sugarcane, wheat, golf courses, and residential lawns. Dicamba is an acid in its anionic form and is expected to be highly mobile in soils. In soil, dicamba is either mineralized or biologically degraded, with quicker dissipation rates under aerobic compared to anaerobic conditions. The half-life for dicamba in soil ranged from 3–136 days and appears to vary greatly depending on the soil conditions. Increasing soil water content, temperatures, and organic matter generally decrease the half-life of dicamba in soil.

Dicamba is moderately volatile and exists in vapor and particulate phases under standard atmospheric conditions. It enters the atmosphere primarily through spray drift and leaves the atmosphere through degradation by photolysis or deposition. Volatilization of dicamba is affected by factors like the amount applied, temperature, humidity, chemical formulation, and the surface upon which it was applied. Dicamba leaves the atmosphere through degradation, photolysis, or wet or dry deposition. Dicamba can enter waterways from foliar washoff caused by precipitation or irrigation. It has been detected at a fairly high frequency in California surface waters receiving urban runoff. In water, the degradation of dicamba is largely biologically mediated. While dicamba is fairly mobile in the environment, its short half-life in soil means that it does not pose a significant threat to groundwater. Measures should be taken to reduce runoff into surrounding waterways, especially during storm events. Dicamba is not expected to bioaccumulate in organisms. At recommended application rates, dicamba is not expected to exceed threshold levels of concern for aquatic plants or fish. Dicamba is expected to be relatively non-toxic for most birds and mammals. However, there exists an increased potential of hepatic tumors at higher levels of dietary intake.

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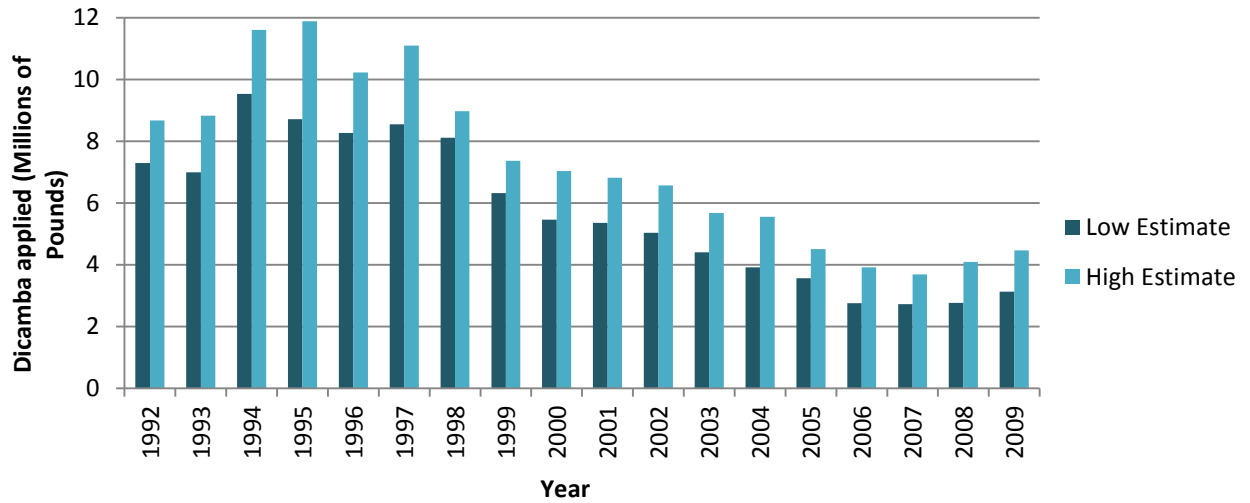


Fig. 1 Estimated total pounds dicamba applied nationally (Stone, 2013)

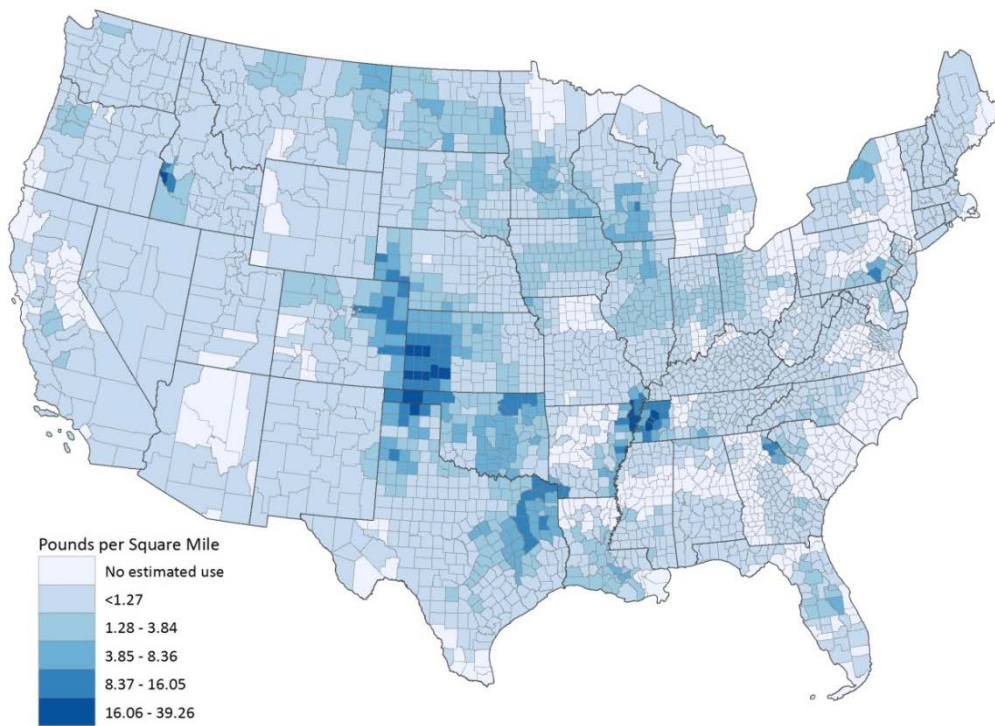


Fig. 2 Low estimate of pounds dicamba applied per square mile, by county, in 2009 (Stone, 2013)

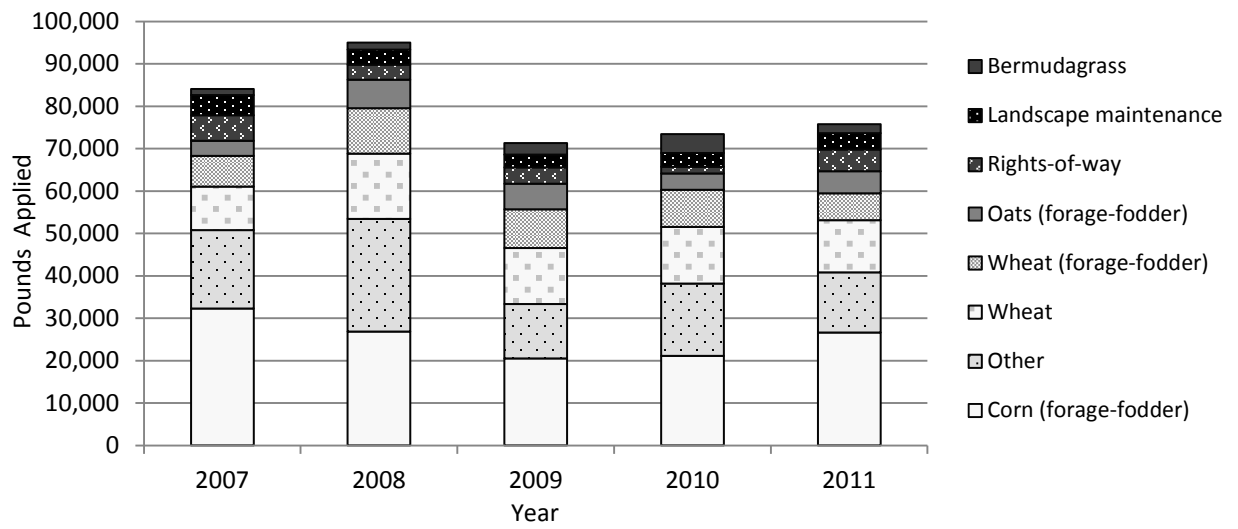


Fig. 3 Total pounds of dicamba and its salts applied by category in California from 2007–2011 (CDPR, 2014c)

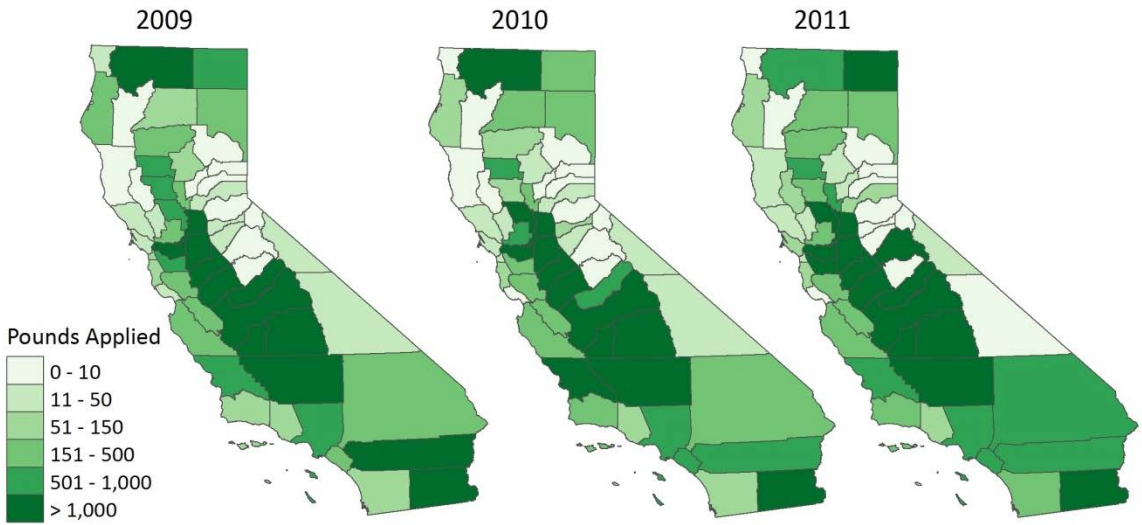


Fig. 4 Dicamba usage in California, 2009–2011(CDPR, 2014c)

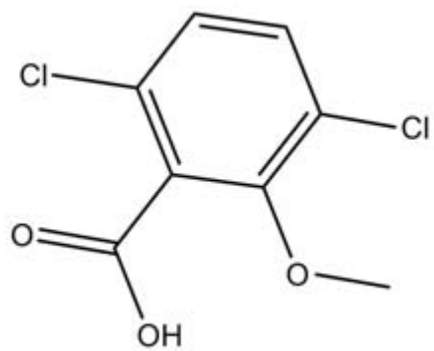


Fig. 5 Structure of dicamba (Bunch & Gervais, 2012)

Pure physical state	White to brown crystals ^b
CAS number	1918-00-9 ^a
DPR chemical code	200 ^c
Molecular weight (g/mol)	221.04 ^b
Molecular formula	C ₈ H ₆ Cl ₂ O ₃ ^b
Density (g/mL)	1.484
Melting point (°C)	114–116 ^b
Water solubility (mg/L)	4,500 ^a
Vapor pressure at 25°C (mPa)	4.5 ^a
Octanol-water partition coefficient (log K _{OW})	-0.55— -1.9 ^a
Henry's law constant at 25°C (Pa m ³ mol ⁻¹)	1.0 X 10 ^{-04 a}
Soil adsorption (K _{oc}) (L/kg)	1.42 ^d

^a Bunch and Gervais (2012)

^b Mullison (1979)

^c CDPR (2014a)

^d Comfort et al. (1992)

Table 1 Physico-chemical properties of dicamba, not including its salts

Reference	Study Condition	$t_{1/2}$ (day)
Gu et al. (1992)	Fine-loamy, siliceous wetland soil at 15°C	37
	Fine-loamy, siliceous wetland soil at 25°C	49
	Fine-loamy, nonacid tidal wetland soil at 25°C	3.2
	Coarse-loamy, nonacid tidal wetland soil at 25°C	2.1
Comfort et al. (1992)	Clay at 28°C	23.5
	Clay at 20°C	38
	Clay at 12°C	151
Krueger et al. (1991)	Loam soil, aerobic conditions	31
	Loam soil, anaerobic conditions	58
Roy et al. (2001)	Thatch at 20°C	5.5—6.3
	Thatch at 4°C	11.2—23.2
	Sandy loam soil at 20°C	36.2—37.9
	Sandy loam soil at 4°C	92.2—136.1
Gu et al. (2003)	Red soil (loam) at 15°C	29
	Brown soil (clay) at 15°C	161.2
	Black soil (sandy clay loam) at 15°C	34.1
	Red soil (loam) at 25°C	21.7
	Brown soil (clay) at 25°C	27.9
Krzyszowska et al. (1994)	Black soil (sandy clay loam) at 25°C	25.0
	Low application rate	10
	High application rate	17
Menasseri et al. (2004)	Intermediate application rate	15-17
	Sandy loam soil	3
	Silt loam soil	<6
	Carbon amended sandy loam soil	5
Villaverde et al. (2008)	Carbon amended silt loam soil	<6 days
	Loam soil	4.8
	Sandy soil	9.5
	Sandy loam soil	8.4
	Sandy clay loam soil	5.4
	Clay soil	4.4

Table 2 Half-life values for dicamba in various media

	Fish	Invertebrates	Non-vascular plants	Vascular plants
Dicamba acid	14	>500	0.061	>32.5
Dimethylamine salt (DMA)	488.5	781.5		
Sodium salt of dicamba	253.6	17.3		

Table 3 Office of Pesticide Program acute aquatic life benchmarks (mg/L) (EPA, 2014)