Analysis of Pollutants in Local Freshwater Sources Using High-Performance Liquid Chromatography

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By Breanna Christensen

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This honors thesis was prepared under the direction of the candidate's honors thesis advisor, Dr. McConnell, Department of Chemistry at Western Illinois University, and it has been approved by the members of the candidate's thesis committee.

Dr. Matthew McConnell

Thesis Advisor

Dr. Keith Boeckelman

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May 2nd, 2025

Date

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Abstract

Environmental pollutants require intensive monitoring to ensure that freshwater sources are not contaminated and drinking water is kept safe for human use. However, agricultural use of pesticides often results in off-target movement of the chemical into the aqueous environment by way of direct spraying, spray drift, surface runoff, leaching, or subsurface drainage. Ingestion of such chemicals can pose considerable health risks to both humans and aquatic organisms, especially in terms of fertility and cancer, while harming the local ecosystem. Thus, it is necessary to detect and quantify pesticides so that their harm to non-target species may be reduced.

Research aimed to detect and quantify the levels of the pesticide dicamba® in freshwater sources surrounding Macomb, Illinois. Water samples were taken from monitoring wells and several ambient water sources. Analysis was performed using reverse-phase high-performance liquid chromatography with ultraviolet detection. These instruments separate the components of the sample and facilitate quantification of the targeted analyte. The external calibration method could not quantify the level of dicamba® with reasonable precision; the standard addition method experienced an unacceptable amount of variability between samples. The results indicated that high-performance liquid chromatography with ultraviolet detection is not a sensitive enough technique for suitable analysis of dicamba® in water.

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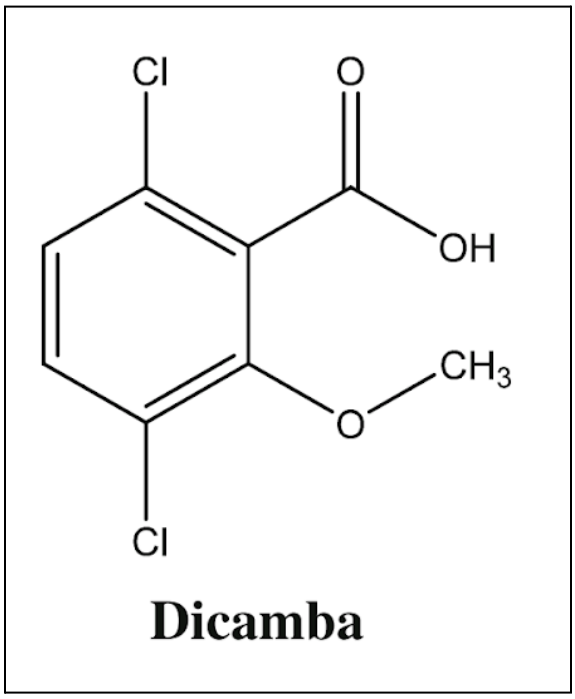
Introduction

Water is often tested for chemical content as certain pollutants pose considerable health and environmental risks. Some persistent, organic contaminants of interest include pesticides like dicamba®, atrazine®, and 2,4-D®. Such contaminants are often found in freshwater and well water, due to the use of these pesticides in agricultural fields. They typically enter the aqueous environment from direct spraying, spray drift, surface runoff, leaching, or subsurface drainage.[1] High concentrations of pesticides in waterways can be deadly for aquatic organisms, and pesticides can cause serious health effects to humans, including cancer.[2] Exposure to endocrine disruptors, like pesticides and estrogenic hormones, may harm reproductive and hormonal processes in humans and fish species alike.[3] As such, it is crucial to monitor chemical content in waterways and well water to prevent them from entering drinking water and harming local ecosystems.

Dicamba®, also known as 3,6-dichloro-2-methoxybenzoic acid, is the focus of this research project. Figure 1 illustrates the chemical makeup of dicamba®, having a benzoic acid and dichlorobenzene group.[4] It is a crystalline solid that appears colorless in its pure form and buff-colored when technical-grade (~85% purity).[5] It is a derivative of benzoic acid that persists for about 12 months in the environment as an herbicide, posing threats to aquatic species with its toxicity, mobility, and persistence.[4] In the environment, dicamba® is highly prone to volatilization, causing it to linger in the atmosphere as a gas, migrate off-target, and return to the surface as a pollutant.[6] Since the early 1960s, it has been primarily applied in agricultural settings to control broadleaf weed species in pastures and grain/cereal crops, and it is also used residentially, especially for golf courses and lawns.[5,7]

Figure 1. Chemical Structure of Dicamba®.[4]



Dicamba® has fewer exposure risks to humans, as compared to other relevant pesticides, being classified by the U.S. Environmental Protection Agency as unlikely to be carcinogenic to humans.[8] However, dicamba® is a strong irritant and corrosive agent, being severely harmful to the eyes, mildly toxic if ingested–causing symptoms including vomiting, loss of appetite, and muscle weakness–and low in toxicity if inhaled.[8,9] Luckily, dicamba® poses only a low level of toxicity to fish as it does not bioaccumulate, yet, it does function as a potential endocrine disruptor to aquatic species.[10,11] At the same time, dicamba® can be lethal to non-resistant plant species and pollinators/insects who feed on treated crops.[9] It also has a much higher toxicity to birds than to most mammals.[9]

Water samples have been taken from local ambient water sources and wells in and surrounding Macomb, Illinois, as they are potential agricultural runoff sites. Research

involved testing standard concentrations of dicamba® to create a calibration curve from which to calculate the dicamba® content in local water samples. These results have been compared to a standard addition method, as well. High-performance liquid chromatography (HPLC) with ultraviolet (UV) detection was used for separation and analysis. HPLC-UV exhibits peaks at wavelengths of light specific to an analyte, which can then be used to quantify the amount of analyte in the water samples. UV detection is an affordable analysis method, whereas other, more sensitive methods like mass spectrometry are less accessible due to their cost.[4] The research sought to determine to what degree dicamba® is polluting local waterways, which can be applied in determining their dispersion patterns and finding methods to remove the contaminants from the water.

Although the United States does not have a regulatory value for dicamba® in drinking water, Australia has established a guideline of 0.1 ppm, and Canada has set a maximum acceptable concentration of 0.11 ppm.[12,13] Furthermore, Canadian studies from 2011-2020 discovered an average dicamba® concentration of 0.5 ppb, with a maximum of 5 ppb, in municipal drinking water and ambient water sources; for farm dugouts that could be used for drinking water, an average dicamba® concentration of 5 ppb was found, with a maximum quantification of 15 ppb.[13] Because of the known uses of dicamba®, and the trends outlined by the Canadian studies, it was suspected that dicamba® levels in the Macomb, Illinois area would be highest nearby agricultural fields.

Reverse-phase liquid chromatography was the chosen method of analysis for dicamba®. This method utilizes a nonpolar stationary phase and a polar mobile phase. A phenyl column was selected as the stationary phase over the typical C18 column, as a phenyl column can offer heightened sensitivity for aromatic compounds. In the mobile

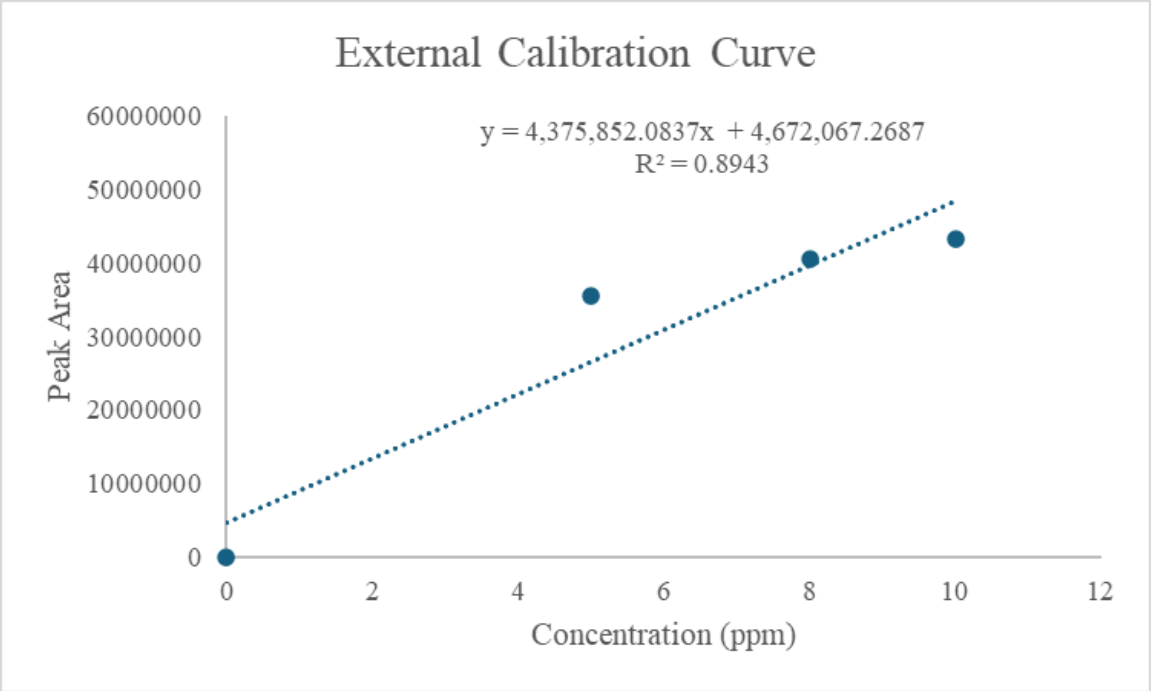
phase, the aqueous phase acts as a weak solvent, while the organic phase, Solvent B, is the strong solvent. Literature suggested that acetonitrile (ACN) was an appropriate choice of organic solvent for analyzing dicamba®.[4] The mobile phase solvents were acidified to improve chromatographic peak shape and control pH, as dicamba® is a weakly acidic analyte, with a pK_a of 1.87 or 1.94.[14] Dicamba® has the slight potential to cause complications from its volatility, 3.4×10^{-5} mm Hg at 25°C, and ability to degrade under UV light.[13,14] By guidance of previous research studies, the UV detector analyzed dicamba® at 225 nm.[14]

Both an external calibration and a standard addition method were investigated, as they offer different benefits for quantifying analytes. Although external calibration offers simplicity, it cannot account for matrix effects in the analysis of the water samples. Matrix effects could have arisen from freeze-thaw cycles of the samples and evaporation, leading to potential adverse impacts on extraction efficiency, recovery, apparent retention time, peak shape, apparent quantitation, and more.[15] A standard addition approach spikes portions of the sample with increasing, known amounts of the target analyte, leaving one portion unspiked.[15] No matter the degree of matrix effects to a sample, the calibration lines of each sample will intersect at the same x-intercept, allowing for quantification regardless of matrix effects.[15] Because of these capabilities, a standard addition method was utilized in expectation of improved accuracy for the complex matrices of pesticides and freshwater samples, as compared to the external calibration method. However, the method's excessive requirement of time and resources limited its use in this research.

Results and Discussion

The retention time for dicamba® in the standards was about 3.64 minutes. An external calibration curve was generated in Figure 2 from the peak areas exhibited by the blank, 5, 8, and 10 ppm dicamba® solutions in ACN. Its linear regression analysis equation is $y = (4.376 \times 10^6)x + (4.672 \times 10^6)$, with an $R^2 = 0.8943$. This R^2 value is lower than ideal, as a more acceptable value would have fallen from 0.95 to 1.00.

Figure 2. Dicamba® External Calibration Curve.



From testing the water samples, the average retention time of dicamba® was 3.484 minutes, with a standard deviation of 0.209 minutes. These calculations exclude the inconsistent retention times obtained from the Well #1 samples, taken at a time when the instrument was having technical difficulties. Figures 3-5 from Site #7 exhibit examples of

desirable chromatograms obtained from the water samples. The chromatograms from each water collection site and sample were mostly similar to one another; however, some displayed small, premature peaks seconds before the large, dicamba® peak.

Figure 3. Chromatogram of Site #7 I Sample.

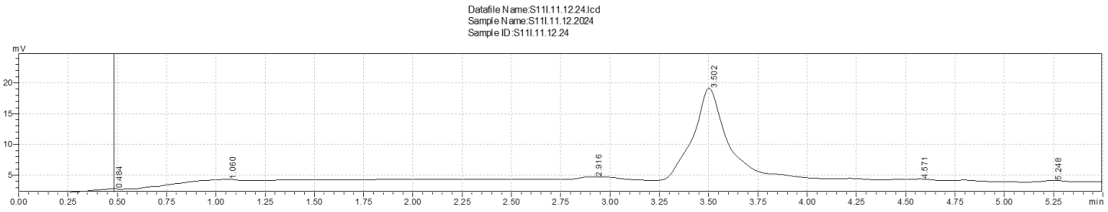


Figure 4. Chromatogram of Site #7 II Sample.

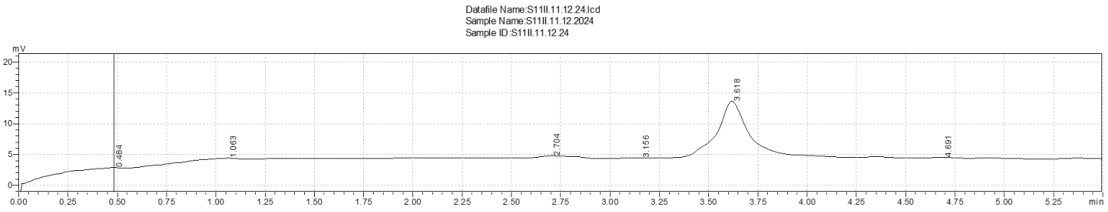
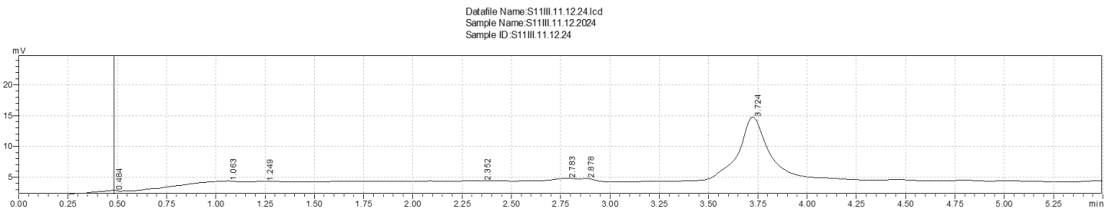


Figure 5. Chromatogram of Site #7 III Sample.



Using Excel, the concentrations of dicamba® associated with the peaks were calculated based on the external calibration curve of the dicamba® standards, where y is the peak area and x is the unknown concentration. These results were recorded in Table 1,

while Table 2 holds the statistical analysis of this data, determining the average concentration, standard deviation, and percent relative standard deviations (%RSD) of each water collection site.

Table 1. Data and Quantitative Analysis of Freshwater Samples.

Water Source	Trial	Ret. Time (min)	Peak Area	Unknown Conc. Dicamba® (ppm)
Site #1	I	3.158	480664	-0.957848
	II	3.444	150052	-1.033402
	III	3.594	100819	-1.044653
	IV	3.477	113460	-1.041764
Site #7	I	3.502	196529	-1.022781
	II	3.618	124053	-1.039344
	III	3.724	141800	-1.035288
Site #8	I	3.297	95581	-1.045850
	II	3.567	218992	-1.017648
	III	3.514	179443	-1.026686
	IV	3.357	93445	-1.046338
Site #9	I	3.188	58810542	12.372099
	II	3.690	48270366	9.963385
	III	3.686	43558475	8.886591
Site #10	I	3.516	36003226	7.160013
	II	3.646	44686779	9.144439
	III	3.653	50277608	10.422094
Well #1	I	2.222	1237824	-0.784817

	II	0.976	27681332	5.258236
	III	1.928	22432553	4.058749
Well #3	I	3.230	36512879	7.276483
	II	3.777	48859298	10.097972
	III	3.038	31317212	6.089133

Table 2. Statistical Analysis of Dicamba® Concentrations in Water Samples.

Water Source	**Average Concentration Dicamba® (ppm)**	**Standard Deviation (ppm)**	**%RSD**
Site #1	-1.019417	0.041322	-4.05
Site #7	-1.032471	0.008633	-0.84
Site #8	-1.034130	0.014300	-1.38
Site #9	10.407358	1.784664	17.15
Site #10	8.908849	1.643752	18.45
Well #1	2.844056	3.199411	112.49
Well #3	7.821196	2.059182	26.33

Although they had the most desirable %RSD values, within the acceptable range for precision of 5%, the unknown dicamba® concentrations of Sites #1, #7, and #8 were evaluated as less than 0 ppm. These results demonstrate that the concentrations of dicamba® in these water samples were below the instrument's limit of detection. Well #3, Site #9, and Site #10 had much higher concentrations of dicamba® present, ranging from about 8 to 10 ppm. However, their %RSD values, ranging from about 17% to 26%, were much higher than the acceptable limit. Such high %RSD values suggest that there was

too much variability between samples from the same source, meaning the method is not able to produce acceptable levels of precision.

The data from Well #1 is not sufficient for comparison because even though peaks were visualized, extreme inconsistencies occurred with the instrument at the time of analysis, as depicted by the varying retention times and peak areas. Thus, its inflated %RSD value can be partially explained by these technical difficulties, and it is not a true representation of the effectiveness of the method.

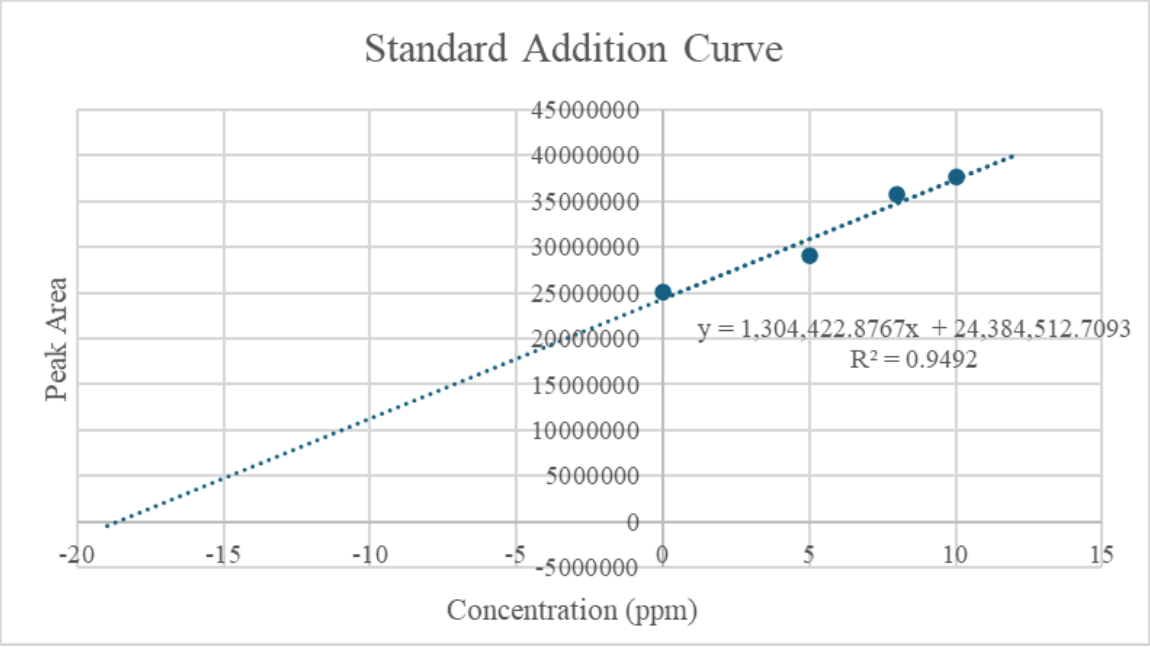
Due to the inability to quantify three of the water samples and the variable levels of precision produced by the external calibration curve and the water samples, a standard addition method was devised to account for matrix mismatch. It was believed that the standard addition method would improve accuracy and sensitivity so that the water samples with lower concentrations of dicamba® may be quantified. This method was tested using a water sample from the site showing the highest levels of dicamba®, Site #9. Its data was recorded in Table 3 below.

Using the standard addition curve created to find the absolute value of the x-intercept, the calculated concentration of dicamba® in Site #9 II was 18.69 ppm. While the constructed standard addition curve, in Figure 6, had a higher and more ideal R^2 value than the external calibration curve, it is still not adequate. This is because the retention times exhibited by dicamba® had extreme variance, and many inconsistencies occurred throughout the elution. Thus, the calculated concentration of dicamba® in this water sample was likely inaccurate, and this method still cannot be considered acceptable for dicamba® analysis.

Table 3. Standard Addition Curve Analysis for Site #9 II Sample.

Site #9 II		
Concentration (ppm)	**Ret. Time (min)**	**Peak Area**
(Blank) 0	1.835	25145561
5	0.945	28999950
8	3.457	35781347
10	2.986	37612919
Dicamba® Present in Sample		**18.693717 ppm**

Figure 6. Standard Addition Curve of Dicamba® for Site #9 II Sample.



Methodology

Solvent Preparation

HPLC-grade solvents of ACN, 0.5% acetic acid in ACN, H_2O, and 0.5% acetic acid in H_2O were utilized. To prepare 1 L of the 0.5% acetic acid in H_2O solvent, a 5-mL

transfer pipette was used to transfer 5 mL of acetic acid into a vial. A small amount of HPLC-grade H_2O was added to the vial, and then the contents of the vial were syringe-filtered.

To syringe-filter, a 1.0-mL, plastic disposable syringe was used to withdraw about 0.5 mL of the sample from the vial at a time. A 0.22 µm pore syringe filter tip was attached to the syringe, and then the contents of the syringe were emptied through the filter into a 1-L volumetric flask. This process was repeated until the necessary amount of sample was filtered into the appropriate vial, using a new syringe filter tip for each aliquot. Another small portion of H_2O was added to rinse the vial, which was also syringe-filtered. This solution was diluted to volume with the H_2O and mixed sufficiently. The same process was repeated to make 1-L portions of 0.5% acetic acid in ACN, using HPLC-grade ACN in place of the HPLC-grade H_2O. For storage, the solutions were stored in sealable glass bottles in the refrigerator.

Calibration with Standards

The 1000 ppm stock solution of dicamba® in ACN was obtained using approximately 0.0100 g of the solid standard from Sigma-Aldrich, measured on an analytical balance. Dilutions of the dicamba® in concentrations of 5, 8, and 10 ppm were then created. Dilutions were prepared in 25-mL volumetric flasks, using ACN as the solvent. A micropipette was used to transfer the appropriate amount of dicamba® stock to the volumetric flasks accordingly. The solutions were diluted to volume with ACN and sufficiently mixed. The standards were returned to the freezer for storage after being transferred to small vials with caps.

To filter the dicamba® standards for HPLC, about one mL of each standard was added to a capped vial labeled “Unfiltered.” Using the same syringe-filter process as used in the solvent preparation, the necessary amounts of each standard were filtered into fresh vials labeled “Filtered.” A new syringe was used for each standard, and the filter tips were replaced after expelling each aliquot, as before. Pasteur pipets were then used to withdraw from the filtered solutions to fill autosampler vials for each standard and a blank (100% ACN). The vials were capped and labeled appropriately for each concentration. The filtered vials were stored in the freezer, and the autosampler vials were stored in the refrigerator.

A Shimadzu HPLC with an SPD-20A UV/Visible detector was utilized for all experimentation, as well as a 3.9 x 150 mm Nova-Pak® Phenyl 4 µm reverse-phase column. The HPLC parameters found in Table 4 were followed for analysis. Before running the samples, Pumps A and B were purged at 2 mL/min for five minutes, and the column was equilibrated with Solvent B, then A for 10 minutes each at 1 mL/min. To reduce blending between samples, the column was washed with ~2x its volume after each run. The data was extracted for analysis using LabSolutions software.

Table 4. Instrumental Parameters for Dicamba® Standard Calibration and Water Sample Analysis.

Parameter	**Value**
Column	3.9 x 150 mm Nova-Pak® Phenyl 4 µm
Mobile Phase	Eluent A: 0.5% acetic acid in H_2O Eluent B: ACN
Mobile Phase Mode	Isocratic Flow

Mobile Phase Composition	40% A / 60% B
Flow rate	0.5 mL/min
Injection Volume	3 µL
Run Time	6 minutes
Max Pressure	3000 psi
Wash Cycle	Washed at least 2x column volume, with 100% B, then 100% A, 1 mL/min
Detection	Wavelength Ch1: 225 nm Wavelength Ch2: 254 nm

Water Samples

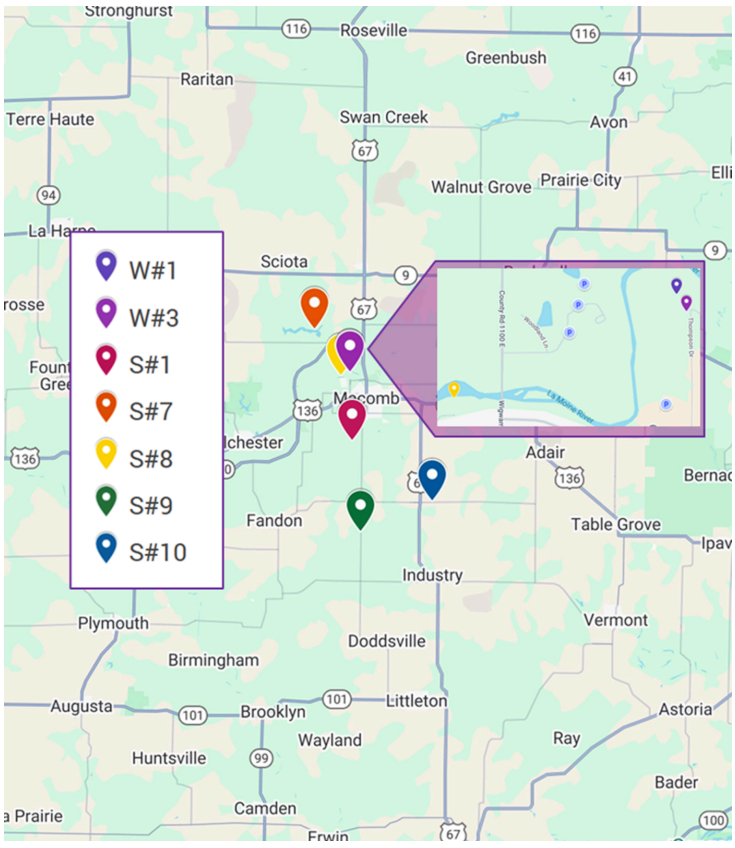
The water samples were obtained from the fall of 2023 to the spring of 2024; their locations are as described in Table 5 and pictured in Figure 7, with the well samples being taken from monitoring wells on the Western Illinois University (WIU) campus. To hold water samples, ~12 fl. oz. plastic bottles, cleaned with DI water, were used. Water samples were collected by either lowering the bottles into the water body or submerging them in the water by hand until the bottles were roughly half full. The monitoring wells required a pump to first expel the muddy water on top until the water ran clear, and then a power drill configuration to fill the sample bottle from a tube. Three-to-four samples were collected at each site at once. Once collected, the samples were vacuum-filtrated using a Büchner funnel and filter paper. Samples were stored in the freezer.

Table 5. Water Sample Locations.

Water Sample	Dates Collected	Coordinates
Well #1 (WIU Campus)	5/1/2024	40.477984, -90.688025

Well #3 (WIU Campus)	5/1/2024	40.477474, -90.687629
Site #1 (Lazy Creek)	4/6/2024	40.426472, -90.685472
Site #7 (Spring Lake)	4/9/2024	40.509343, -90.722333
Site #8 (La Moine River)	4/6/2024	40.474914, -90.696710
Site #9 (Camp Creek)	10/9/2023	40.358944, -90.677348
Site #10 (Camp Creek)	10/9/2023	40.381615, -90.607406

Figure 7. Map of Water Collection Sites in Macomb, IL Area.



To prepare these water samples for HPLC-UV analysis, they were allowed to melt completely, and the necessary amounts of sample were transferred to small vials. For water samples from Well #1 and Well #3, about 2.5 mL of each sample was placed in

glass vials and then dried in the oven at ~75°C. The dried samples were then dissolved in about 2.5 mL of ACN before continuing. Samples from Sites #1 and #7-#10 were not dried in the oven. The same syringe-filtering process was repeated for all water samples, using a new syringe for each sample of each site, and replacing the filter tip with each aliquot. Likewise, the necessary amount of each filtered water sample was added to unique autosampler vials, labeling them with the site/well number and trial number I-III, or I-IV. The autosampler vials were then stored in the refrigerator between uses. The same instrumental parameters as described in Table 4 were used for the HPLC-UV analysis of the water samples, including the washing of the column between samples.

Standard Addition Method

A standard addition method was attempted on the sample Site #9 II, as samples from Site #9 contained the highest levels of dicamba®, according to the calibration curve. Five milliliter portions of the water sample were syringe-filtered, as previously described, and then dried in the oven at ~75°C. After cooling, the portions were dissolved separately in one milliliter of either 5 ppm, 8 ppm, 10 ppm, or 0.5% acetic acid in ACN (to create the blank) using a transfer pipette. These four solutions were then syringe-filtered again and added to autosampler vials, using the same processes as previously described. These solutions were stored in the refrigerator between uses.

For HPLC-UV analysis, the parameters described in Table 6 were followed, using the same instruments and software as before. Prior to sample analysis, Pumps A and B were purged at 2 mL/min for five minutes, then the column was equilibrated with 5%

Solvent B for 20 minutes at 1 mL/min. Following each run, the column was washed with ~4x its volume.

Table 6. Instrumental Parameters for Standard Addition Analysis.

Parameter	**Value**
Column	3.9 x 150 mm Nova-Pak® Phenyl 4 µm
Mobile Phase	Eluent A: 0.5% acetic acid in H_2O Eluent B: 0.5% acetic acid in ACN
Mobile Phase Mode	Isocratic Flow
Mobile Phase Composition	40% A / 60% B
Flow rate	0.5 mL/min
Injection Volume	3 µL
Run Time	6 minutes
Max Pressure	3000 psi
Wash Cycle	Washed 4x column volume, 5% B, 1 mL/min
Detection	Wavelength Ch1: 225 nm Wavelength Ch2: 254 nm

Conclusions

The coefficient of determination achieved by the external calibration curve was less than ideal, suggesting excessive variance occurred between the dicamba® standards. Even though the presence of dicamba® was validated in all of the water samples by the visualization of dicamba® peaks in the chromatograms, quantification of dicamba® was not successful. In over half of the cases, the %RSD values were large and unacceptable, indicating extreme variances between samples from the same collection site and a lack of

precision in analysis. Furthermore, research demonstrated that HPLC-UV was not sensitive enough to quantify the lowest concentrations of dicamba® in the water sources, as they were evaluated below the limit of detection.

The standard addition method proved to have similar difficulties, as the analysis faced many inconsistencies and had unacceptable variance in retention times for dicamba®. It is possible that further method optimization could improve the standard addition method and produce results with consistent retention times. However, some dicamba® quantities may still lie below the limit of detection of the instrument, making it impossible to quantify. Moreover, standard addition methods require significantly more time and resources to analyze in comparison to the external calibration method, making it unnecessarily costly and impractical for routine analysis.

Although the quantification of the water samples may not be as accurate or precise as possible, it is worth noting that the water samples from Sites #9 and #10 had significantly higher dicamba® concentration estimates than the other sites. This disproportionality may suggest that the composition of Camp Creek is more heavily influenced by agricultural herbicide use than the other locations sampled; this would be consistent with expectations, as the collection sites directly bordered agricultural fields, unlike the other locations. Nonetheless, such quantification results cannot be reported due to the unacceptable levels of precision in the methods. Both the external standard calibration method and the standard addition methods of analysis lacked precision and replicability for quantification. It is clear from this research that HPLC-UV is not a suitable method for the analysis of dicamba® in water.

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