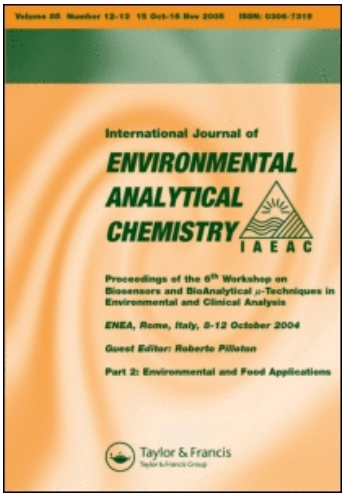


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E. M. Thurman[a]; Lisa R. Zimmerman[a]; Diana S. Aga[b]; Robert J. Gilliom[c]
[a] U.S. Geological Survey, Lawrence, Kansas, USA [b] Dept. Chemistry, University of Nebraska, Kearney, NE, USA [c] U.S. Geological Survey, Sacramento, CA, USA

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# REGIONAL WATER-QUALITY ANALYSIS OF 2,4-D AND DICAMBA IN RIVER WATER USING GAS CHROMATOGRAPHY-ISOTOPE DILUTION MASS SPECTROMETRY

E.M. THURMAN[a*], LISA R. ZIMMERMAN[a], DIANA S. AGA[b] and ROBERT J. GILLIOM[c]

[a]*U.S Geological Survey, 4821 Quail Crest Place, Lawrence, Kansas 66049, USA,*
[b]*Dept. Chemistry, University of Nebraska, Kearney, NE 68849, USA and*
[c]*U.S. Geological Survey, 2800 Cottage Way, Sacramento, CA 95825, USA*

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Gas chromatography with isotope dilution mass spectrometry (GC-MS) and enzyme-linked immunosorbent assay (ELISA) were used in regional National Water Quality Assessment studies of the herbicides, 2,4-D and dicamba, in river water across the United States. The GC-MS method involved solid-phase extraction, derivatized with deuterated 2,4-D, and analysis by selected ion monitoring. The ELISA method was applied after preconcentration with solid-phase extraction. The ELISA method was unreliable because of interference from humic substances that were also isolated by solid-phase extraction. Therefore, GC-MS was used to analyzed 80 samples from river water from 14 basins. The frequency of detection of dicamba (28%) was higher than that for 2,4-D (16%). Concentrations were higher for dicamba than for 2,4-D, ranging from less than the detection limit (<0.05 μg/L) to 3.77 μg/L, in spite of 5 times more annual use of 2,4-D as compared to dicamba. These results suggest that 2,4-D degrades more rapidly in the environment than dicamba.

*Keywords:* GC-MS analysis; ELISA analysis; 2,4-D; Dicamba; Herbicide

## INTRODUCTION

2,4-D (2,4-dichlorophenoxyacetic acid) is the fourth most extensively used herbicide in the United States[1]. Approximately 20 million kilograms of 2,4-D active ingredient are used annually for crop production. Dicamba (2,6-dichloro-2-methoxybenzoic acid) is ranked eleventh and approximately 4 million kilograms are used annually. These herbicides are used for broadleaf

* Corresponding author; Fax: +1-785-832-3559, Email: ethurman@usgs.gov

weeds and are commonly applied to cropland as a mixture. Studies have linked 2,4-D with the development of Non-Hodgkin's lymphoma (NHL), a cancer of the lymphatic system, among farmers that have been exposed to 2,4-D[2]. Although 2,4-D is a moderately toxic compound compared to other pesticides (e.g., organophosphates and organochlorine insecticides), its sublethal toxicity and effect on the environment is of major concern. Hence, it has become increasingly important to analyze for 2,4-D and dicamba both qualitatively and quantitatively. As an important pollutant, 2,4-D is monitored regularly in municipal water supplies and in ground water. The legally established U.S. Environmental Protection Agency maximum contaminant level (MCL) for this herbicide in potable water is 70 μg/L[3].

Compared to other herbicides that are used in the United States, the occurrence and distribution of 2,4-D, dicamba, and other alkanoic acid herbicides are not well known. The limited information on the large-scale distribution of these herbicides may be attributed to the difficulty of analysis. Because of the non-volatility and polarity of 2,4-D and dicamba, they cannot be analyzed directly with gas chromatography (GC). Although GC with electron-capture detection (ECD) with derivatization is the conventional method for 2,4-D and dicamba analysis, the use of high performance liquid chromatography (HPLC) with ultraviolet detection has been reported[4–6], as well as liquid chromatography/mass spectrometry[7–8]. Recently, there have been a number of examples where reversed-phase solid-phase extraction was used to isolate chlorophenoxyacetic acids[4–9], and in practice, liquid-liquid extraction is less frequently used now as a method for phenoxy-acid analysis. Thus, conventional methods for quantification of 2,4-D and dicamba now involve solid-phase extraction and analysis by chromatographic methods.

To conduct a large-scale reconnaissance of the distribution of 2,4-D and dicamba at a reasonable cost and time, a simple and sensitive analytical method also is needed. There are a number of new technologies that can be explored to alleviate the problems encountered in the analysis of these compounds. First is the use of automated solid-phase extraction (SPE) for sample preparation. Second is the use of a rapid, cost-effective analytical technique, such as enzyme-linked immunosorbent assay (ELISA) for the detection of herbicides. ELISA has been used to screen for 2,4-D in surface water[10], but most of the samples were less than the detection limit of the assay (0.7 μg/L). A commercial dicamba ELISA is not currently available. A previous study reported the combination of SPE and ELISA (SPE-ELISA) to improve the detection limit of an atrazine immunoassay[11]. A similar SPE-ELISA method may be applied for the analysis of low concentrations of 2,4-D. Third is the use of a simple derivatization method for GC-MS analysis that will allow detection of trace concentrations

of 2,4-D and dicamba in surface water samples. The GC-MS method will allow the confirmation of positive detection by ELISA for an increased confidence in the results.

With these considerations in mind, this paper addresses the following objectives: (1) to isolate trace levels of 2,4-D and dicamba from surface-water samples using SPE for both ELISA and GC-MS, (2) to attempt to develop both an ELISA and an isotope dilution GC-MS method using a simple derivatization procedure for 2,4-D and dicamba, and (3) to apply the ELISA and GC-MS methods in a reconnaissance study of the distribution of 2,4-D and dicamba in selected rivers of the United States.

## EXPERIMENTAL



### Solid-Phase Extraction

Solid-phase extraction of 2,4-D and dicamba (ChemService, Inc; West Chester, PA) was automated on a Waters Millilab workstation (Milford, MA). The trifunctional-$C_{18}$ Sep-Pak cartridges (Waters, Milford, MA) were conditioned sequentially with 2 mL of pesticide-grade methanol (Fisher, Springfield, NJ), 6 mL of pesticide-grade ethyl acetate (Fisher, Springfield, NJ), 2 mL of methanol, and 2 mL of pH 2.2 water (charcoal filtered and glass distilled prior to use). Each sample for GC-MS analysis was spiked with 100 μL of the internal standard 2,4-D-$d_3$ (2.4 ng/μL in methanol) (Cambridge Isotope Laboratories, Woburn, MA) and was adjusted to pH 2.2 with HCl/KCl buffer. One hundred milliliters (100 mL) of sample then were passed through the pre-washed cartridge at a flow rate of 20 mL/min. The cartridge was purged with air for 10 min to remove residual sample water and then eluted with 3 mL of ethyl acetate into a test tube.

### SPE-ELISA procedure

When SPE was linked with ELISA, the SPE procedure described above was followed except that the samples were not spiked with the deuterated 2,4-D- $d_3$. The ethyl acetate eluate was evaporated to dryness under a stream of nitrogen at 45°C using a Turbovap (Zymark, Palo Alto, CA) and reconstituted with 1 mL of 10/90 (v/v) methanol/water mixture. The reconstituted samples were analyzed using the magnetic particle-based RaPID 2,4-D ELISA (Ohmicron, Newtown, PA) following the procedure described in the insert of the ELISA kit.

## Derivatization and GC-MS

The ethyl acetate eluates were evaporated to dryness under a stream of nitrogen at 45°C using a Turbovap (Zymark, Palo Alto, CA). To each tube, 50 μL of the derivatization agents, pentafluoropropionic anhydride (PFPA) and 25 μL pentafluoropropanol (PFPol) (both from Aldrich Chemical Co. Milwaukee, WI), were added. The test tube was capped, vortexed slightly, and heated at 75°C for 30 minutes. The reaction mixture was evaporated to dryness and then reconstituted with 50 μL of ethyl acetate that contained 120 ng terbuthylazine (Chem Service, Ino. Westchester, PA). Terbuthylazine was used as a qualitative check of the retention time shifts and GC-MS conditions. Samples were transferred to a glass-lined vial for GC-MS analysis.

GC-MS analysis of the eluates was completed using a Hewlett-Packard Model 5890A GC interfaced to a 5970A mass selective detector (MSD) (Palo Alto, CA). Separation of the herbicides was accomplished with a fused-silica capillary column of 5% phenyl methyl silicone (Ultra 2) with a film thickness of 0.33 μm, 12-m × 0.2-mm i.d. (Hewlett Packard, Palo Alto, CA). Helium was the carrier gas at a flow rate of 1 mL/min and a head pressure of 35 kPa. The samples were injected in the splitless mode using an auto injector at an injector temperature of 280°C. The column temperature was held at 60°C for 1 min, ramped at 8°C /min to 190°C, and then ramped at 15°C /min to 250°C where it was held for 4 min.

The source of the mass spectrometer was held at 250°C. The emission current was 70 eV. The electron multiplier was set at 400 V above autotune. The filament and multiplier were not turned on until 14 min into the analysis. A dwell time of 25 ms was used while 11 selected ions were monitored. An autotune using perfluorotributylamine was performed daily prior to analyzing the samples. The calibration curve was prepared based on the area of the base peaks relative to the response of the 355 (amu) ion of 2,4-D- $d_3$ with pentafluoropropanol, the internal standard. Confirmation of the compounds was based on the presence of the molecular ion and two confirming ions and a retention-time match within 0.2% relative to 2,4-D-$d_3$ with pentafluoropropanol and correct area ratios of the confirming ions.

## Reconnaissance study

The surface-water samples used for the reconnaissance study were collected from 14 study units in several States across the U.S. as shown in Figure 1. These basins are part of the U.S. Geological Survey's National Water Quality Assessment (NAWQA) Program[12]. The study units represent different hydrologic systems with different leaching and runoff potentials.

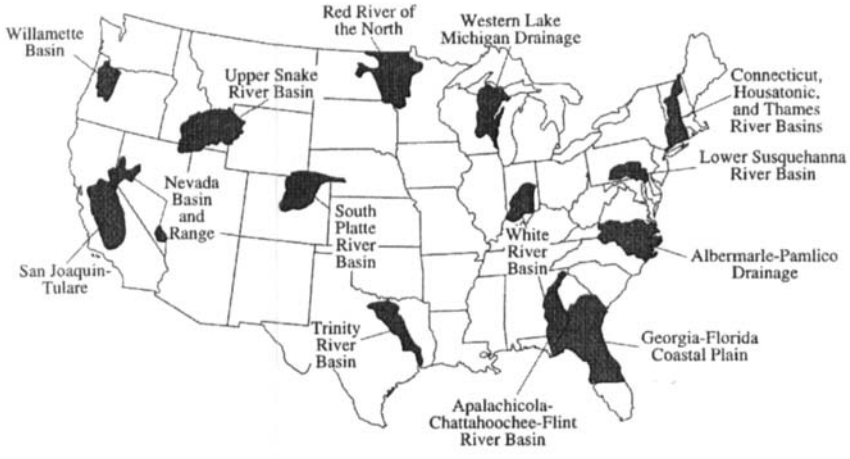


FIGURE 1 NAWQA study units from which surface-water samples were collected



Sample collection was timed with the first major rain following the period of peak 2,4-D application and was determined individually for each study unit. Samples were collected from 80 stream sites according to standard procedure of the U.S. Geological Survey, including depth-integrating techniques at three to five locations at each sampling point. The herbicide samples were collected in glass or Teflon containers, combined in large glass containers, and filtered through 0.7 μm glass-fiber filters (Geotech, Denver, CO) into baked glass bottles, then refrigerated and mailed to the laboratory.

## RESULTS AND DISCUSSION

### Solid-Phase Extraction

Two different types of $C_{18}$-bonded phase silica, trifunctional $C_{18}$ and monofunctional $C_{18}$, were evaluated to determine the most suitable packing material for the efficient recovery of the target analytes. Trifunctional $C_{18}$ is bonded in at least two locations to the silica backbone, whereas monofunctional $C_{18}$ has only one bond to the silica backbone[13]. The result of the extra bonds in the trifunctional silica is that the sorbent is more resilient to acid hydrolysis; thus, the sorbent may be used at much lower pH (from 2 to 8).

Because 2,4-D and dicamba are ionic at a neutral pH, 10% breakthrough was observed using either type of $C_{18}$ material after only 10 mL of sample containing 1 μg/L of each analyte had been passed through the cartridge. At 75 mL, 100% breakthrough was observed. Adjusting the pH of the water sample to ~2.2 with HCl resulted in no breakthrough even after 500 mL of sample had passed the cartridge. Previous studies have shown the successful use of other sorbents for the isolation of these polar ionic herbicides by SPE. For instance, styrene divinylbenzene (SDB) was successfully used to extract various phenoxyacid herbicides at pH less than 2.0 without column "bleed"[5]. Other studies have used a combination of packing materials to isolate several herbicides with a wide range of polarity. Di Corcia and others[4]have used a miniaturized cartridge that contained graphitized carbon black on top and a silica-based strong anion exchanger on the bottom to isolate nine phenoxyacid herbicides. Other work demonstrated the use of a mixture of $C_{18}$ and phenyl packing for the extraction of several acidic herbicides[7–9,14]. All of these sorbents are useful for the extraction of acidic herbicides, the critical factor is that the sorbent is not destroyed by acidification to below the pKa of the acidic herbicides.



## Analysis by SPE-ELISA (Solid-phase-extraction Enzyme-linked-immunoassay)

In previous work it was found that 2,4-D ELISA was insensitive when used directly on water samples. The detection limit of the ELISA was 1 μg/L and only two detections were found from 185 surface-water samples from reservoirs across the United States (unpublished data). This previous result indicated that the detection limit of the assay needs to be improved for this ELISA to be useful in this reconnaissance study of 2,4-D in the environment. With the objective of improving the detection limit of the 2,4-D ELISA, water samples were concentrated by SPE as described, except that the samples were not spiked with 2,4-D-$d_3$. Because 2,4-D has a pKa of 2.6 at 25°C[15], it is anionic at the pH levels typical for surface- and ground-water samples (pH 6 to 9). Therefore, it was necessary to adjust the samples to pH 2.2 to protonate 2,4-D and effect its sorption onto the $C_{18}$ resin used for SPE. A consequence of lowering the pH is enhanced co-extraction of other dissolved organic acids, such as humic substances, that are present in natural waters. The average pKa of dissolved humic substances is 4.2; therefore, at pH 2.2 the majority of the humic material is nonionic and will sorb effectively on the $C_{18}$ resin. During elution with ethyl acetate, some of the sorbed humic substances were eluted with 2,4-D as was evident by the yellow coloration of the eluate.

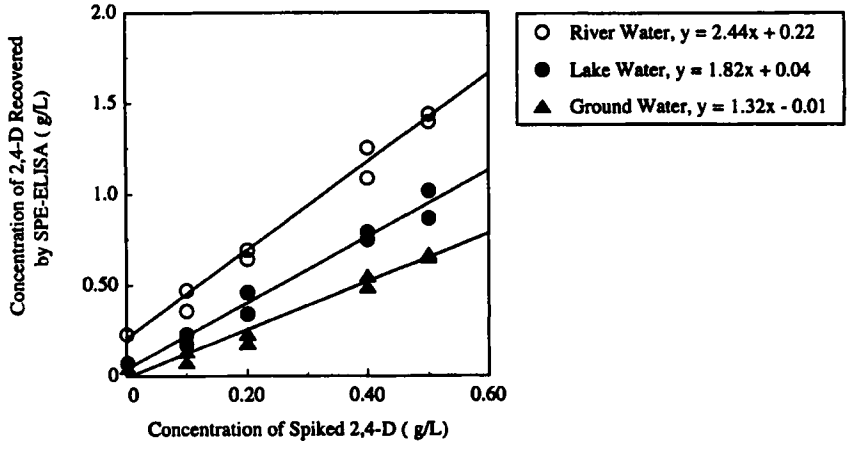


FIGURE 2 Recovery of 2,4-D from spiked river-, lake-, and ground-water samples by SPE-ELISA



Analysis of lake, river, and ground-water samples spiked with low concentrations of 2,4-D (0.1, 0.2, 0.4, and 0.5 μg/L) showed recoveries ranging from 130 to more than 200% by SPE-ELISA. Figure 2 shows that the slopes of the lines of 2,4-D concentration measured by SPE-ELISA versus the spiked concentrations were all greater than 1.0. The highest slope of 2.44 was observed in river-water samples, followed by lake-water samples with a slope of 1.82, and ground-water samples with a slope of 1.32. The differences in ELISA response corresponded to the humic substances content in the samples. Forty unspiked river-water samples that gave detectable concentrations of 2,4-D by SPE-ELISA were verified by the isotope dilution GC-MS method described previously. Only six of these samples contained 2,4-D as confirmed by GC-MS, and the concentrations did not correlate between the two methods because of the interference of humic substances in the immunoassay, indicating that SPE-ELISA was incorrect for 2,4-D.

Although interference of humic substances in immunoassays has not been well characterized, it is speculated that overestimation of analyte concentrations is due to the interaction of the humic substances with the antibody binding site[16], preventing the enzyme conjugate from binding. For the anti-2,4-D antibodies, this postulate may be supported by the fact that humic acids have chemical moieties that are very similar to the phenoxyalkanoic group of 2,4-D. Although the antibodies may have very weak affinity for the humic materials, the binding can be enhanced by the relatively high concentration of humic substances compared to 2,4-D. However, the presence of high amounts of humic substances in the sample matrix does not always result in over estimation of analyte concentration by immunoassay. The effect of humic substances on the assay is governed by the

characteristics of the antibody used. Stearman and Adams[17], for example, did not observe over estimation of atrazine concentrations by ELISA from various soils containing 4.7% organic matter, whereas Stearman and Wells[18] observed interference of as much as 40 ppm of humic acid on atrazine and metolachlor assays only at low concentrations (0.1 and 0.6 μg/L, respectively) of the analyte. Thus, the SPE-ELISA technique, although effective for atrazine[11], it was not an effective technique for 2,4-D because of the co-elution of humic material in the final eluate.

## Analysis by isotope dilution GC-MS

The derivatization reaction for GC-MS analysis is shown in Figure 3. An ester is formed via a nucleophilic reaction between pentafluoropropanol and the carboxylic group of 2,4-D or dicamba. Derivatized samples re-analyzed after 2 weeks gave similar results as the initial analysis, confirming that the derivatization reaction is stable. Storage periods of more than 2 weeks were not tested.



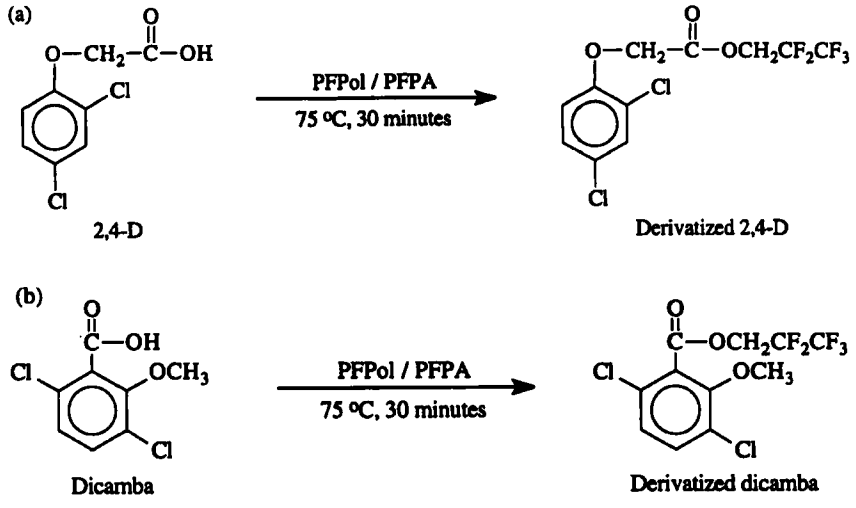


FIGURE 3 Derivatization of (a) 2,4-D and (b) dicamba by pentafluoropropionic anhydride (PFPA) and pentafluoropropanol (PFPol)

The mass spectra of the esterified 2,4-D and dicamba are shown in Figure 4a-b. The ion fragment that was used for 2,4-D quantification under selected ion monitoring (SIM) was the molecular ion (352 amu), whereas for verification, the 354 amu (M+2, chlorine signature) and 175 amu (molecular

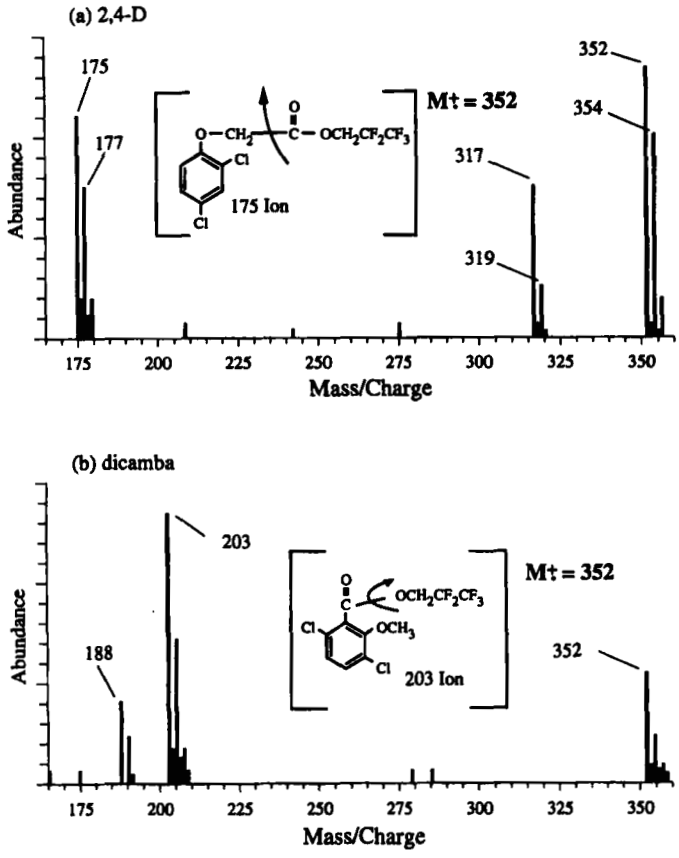


FIGURE 4 Mass spectra and fragmentation patterns of (a) 2,4-D and (b) dicamba. Fragmentation is described in the text

ion-$COOCH_2CF_2CF_2$) fragments were used. For dicamba, the 203 amu (base peak, molecular ion -$COOCH_2CF_2CF_2$) was used for quantification, and the 352 amu (molecular ion) and 188 amu (molecular ion -$COOCH_2CF_2CF_2$ and -$CH_3$) were used for verification. It is important that the ions used in the quantification and verification were higher molecular weight ions that contain the main part of the analyte rather than the derivatizing reagent. The use of the fragment ions that remain after the loss of the pentafluoropropionic group eliminates background interference that result from compounds that have been co-derivatized and increase the specificity of the analysis.

The standard curve (Figure 5) generated using the area ratio of the quantifying ions to the 355 amu (molecular ion) ion of deuterated 2,4-D results in a linear

working range of 0.05 to 10.0 μg/L. The detection limit for both compounds was 0.05 μg/L in river water samples when using a 100-mL sample. In Figure 5, the open circles represent the area of the quantifying ion of 2,4-D to that of the deuterated 2,4-D. This figure shows that if quantification were based on terbuthylazine as the internal standard, the data would not be reliable because of variation in derivatization efficiency. This fact illustrates the point of the necessity of having a deuterated internal standard and using isotope dilution mass spectrometry for quantitation. Because 2,4-D-$d_3$ mimics the naturally occurring target compounds in all steps, from the solid-phase extraction, to derivatization, to GC-MS analysis, the isotope dilution method is accurate. Therefore, even though some steps may not be 100% efficient, the concentration of the analytes in the samples are automatically corrected.

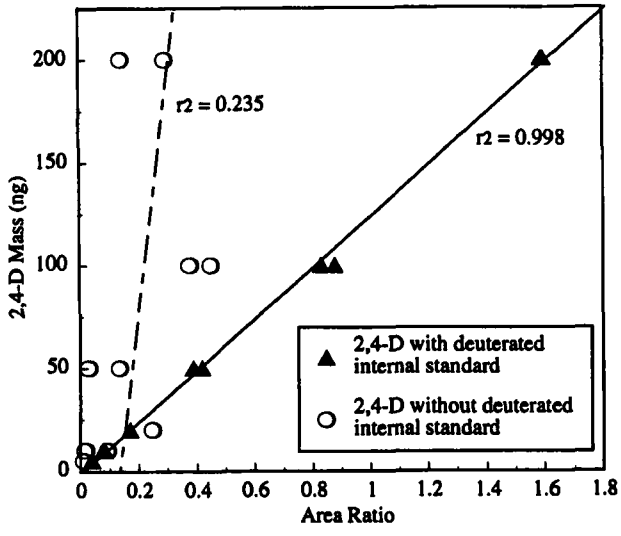


FIGURE 5 GC-MS standard curves with and without a deuterated internal standard

## Distribution of 2,4-D and Dicamba

Because SPE-ELISA did not provide reliable results for the analysis of low concentrations of 2,4-D in surface-water samples, this method was not used further for the reconnaissance study. Instead, the isotope dilution GC-MS method described in this paper was used to quantitatively determine the concentrations of 2,4-D and dicamba in the 80 water samples obtained from the 14 NAWQA river basins within the United States.

TABLE I Concentration and percent detections of 2,4-D and dicamba in NAWQA study units

| *NAWQA Study Unit* | *N* | *2,4-D* | | | *Dicamba* | | |
|---|---|---|---|---|---|---|---|
| | | *Median Concentration (μg/L)* | *Percent Detections* | *Maximum Concentration (μg/L)* | *Median Concentration (μg/L)* | *Percent Detections* | *Maximum Concentration (μg/L)* |
| Albermarle-Pamlico | 12 | <0.05 | 8 | 0.11 | <0.05 | 8 | 0.33 |
| Apalachicola- Chatta-hoochee-Flint River | 1 | <0.05 | 0 | <0.05 | <0.05 | 0 | <0.05 |
| Connecticut, Housatonic, and Thames Rivers | 2 | <0.05 | 0 | <0.05 | <0.05 | 0 | <0.05 |
| Georgia-Florida Coastal Plain | 10 | <0.05 | 10 | 0.20 | <0.05 | 10 | 0.05 |
| Lower Susquhanna River | 2 | <0.05 | 0 | <0.05 | <0.05 | 0 | <0.05 |
| Nevada Basin and Range | 3 | <0.05 | 0 | <0.05 | <0.05 | 0 | <0.05 |
| Red River of the North | 9 | <0.05 | 44 | 0.14 | <0.05 | 22 | 0.25 |
| San Joaquin-Tulare | 9 | <0.05 | 33 | 0.59 | <0.05 | 0 | <0.05 |
| South Platte River | 6 | <0.05 | 16 | 0.98 | 2.04 | 85 | 3.77 |
| Trinity River | 5 | <0.05 | 20 | 0.07 | <0.05 | 40 | 0.13 |
| Upper Snake River | 3 | <0.05 | 0 | <0.05 | <0.05 | 0 | <0.05 |
| Western Lake Michigan | 4 | <0.05 | 0 | <0.05 | 0.11 | 75 | 1.49 |
| White River | 7 | <0.05 | 29 | 0.64 | 0.12 | 86 | 1.01 |
| Willamette River | 7 | <0.05 | 0 | <0.05 | <0.05 | 29 | 0.35 |

Concentrations of 2,4-D ranged from below detection (<0.05 μg/L) to 0.98 μg/L and dicamba ranged from <0.05 μg/L to 3.77 μg/L (Table I). The 2,4-D was detected in 13 (16%) of the samples and dicamba in 22 (28%) of the 80 samples. The detection of 2,4-D was most common in the NAWQA units where usage of 2,4-D is greatest (Table II). There were 44% detections of 2,4-D in the Red River of the North, 33% detections in the San Joaquin-Tulare, and 29% detections in the White River (see Figure 1 for locations). The three major NAWQA sites for dicamba detection were the White River (86% detections), South Platte River (85% detections), and Western Lake Michigan (75% detections). Approximately half of the NAWQA sites (7 sites) had no detection of 2,4-D and 6 sites had no detection of dicamba (Table I).

TABLE II Percent detections of 2,4-D and dicamba in various NAWQA study areas. Refer to Figure 1 for site locations

| *NAWQA Study area* | *Percent Detections of 2.4-D* |
|---|---|
| Red River of the North | 44 |
| San Joaquin-Tulare | 33 |
| White River | 29 |
| Trinity River | 20 |
| South Platte River | 16 |
| Georgia and Florida | 10 |
| Albermarle-Pamlico | 8 |
| | *Percent Detection of Dicamba* |
| White River | 86 |
| South Platte River | 85 |
| Western Lake Michigan | 75 |
| Trinity River | 40 |
| Willamette River | 29 |
| Red River of the North | 22 |
| Georgia and Florida | 10 |
| Albermarle-Pamlico | 8 |

The median concentration of 2,4-D was <0.05 μg/L for all 80 samples and dicamba was also <0.05 μg/L. Thus, many of the samples were non detects and this result suggests that in spite of the high use of 2,4-D (19 million kg annually),

the median concentration is still low. This result further suggests that the degradation of 2,4-D proceeds rapidly and that the parent compound does not persist in the environment. However, the fact that dicamba was detected in 28% of all the samples versus 16% for 2,4-D suggests that dicamba is more resistant to degradation than 2,4-D. This is in spite of the fact that about five times less dicamba is applied than 2,4-D.

To our knowledge, there have not been any previous large-scale studies to relate persistence and occurrence of 2,4-D and dicamba in river water of the United States. This reconnaissance study indicated that a more intensive sampling is needed to understand the fate of these low concentrations of 2,4-D and dicamba in surface water and to understand where the 2,4-D has dissipated in the environment. Further studies should be directed at those NAWQA sites where the most frequent detection occurred (Table II).

### *Acknowledgements*

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