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Analysis of selected herbicide metabolites in surface and ground water of the United States

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Abstract

One of the primary goals of the US Geological Survey (USGS) Laboratory in Lawrence, Kansas, is to develop analytical methods for the analysis of herbicide metabolites in surface and ground water that are vital to the study of herbicide fate and degradation pathways in the environment. Methods to measure metabolite concentrations from three major classes of herbicides — triazine, chloroacetanilide and phenyl-urea — have been developed. Methods for triazine metabolite detection cover nine compounds: six compounds are detected by gas chromatography/mass spectrometry; one is detected by high-performance liquid chromatography with diode-array detection; and eight are detected by liquid chromatography/mass spectrometry. Two metabolites of the chloroacetanilide herbicides — ethane sulfonic acid and oxanilic acid — are detected by high-performance liquid chromatography with diode-array detection and liquid chromatography/mass spectrometry. Alachlor ethane sulfonic acid also has been detected by solid-phase extraction and enzyme-linked immunosorbent assay. Six phenylurea metabolites are all detected by liquid chromatography/mass spectrometry; four of the six metabolites also are detected by gas chromatography/mass spectrometry. Additionally, surveys of herbicides and their metabolites in surface water, ground water, lakes, reservoirs, and rainfall have been conducted through the USGS laboratory in Lawrence. These surveys have been useful in determining herbicide and metabolite occurrence and temporal distribution and have shown that metabolites may be useful in evaluation of non-point-source contamination. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metabolites; Herbicides; Chemical analysis; Chemical degradation; Surface water; Ground water

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1. Introduction

Herbicides in surface and ground water are a major concern throughout the USA. Numerous studies have been completed by various government agencies, including the US Geological Survey (USGS), and by chemical manufacturers to document occurrences of herbicides in ground water (Kolpin et al., 1996), rainfall (Goolsby et al., 1997; Pomes et al., 1998), and surface water (Thurman et al., 1992). However, there has been little study of the metabolites of these herbicides. Because metabolites are formed in the environment and transported to surface and ground water, it is important to understand herbicide use and the fate of herbicide metabolites.

Modern agricultural practices in the USA often require extensive use of herbicides for production of corn, soybeans, sorghum and other row crops. Data compiled by Gianessi and Puffer (1991) indicate that approximately two-thirds of the 285 000 000 kg of herbicides applied annually in the USA are used in crop production in the Midwest. In 1990 and again in 1992, because of concern about water contamination, manufacturers voluntarily, reduced the maximum recommended application rate by 50% for atrazine, the most used herbicide on corn and sorghum. These application-rate changes have affected the frequency of detection of some of the herbicide metabolites (Scribner et al., 1998).

In 1987, a laboratory for organic geochemistry research was established at the USGS in Lawrence, Kansas. Since that time, analytical methods have been and continue to be developed to measure metabolite concentrations from three major classes of herbicides — triazine, chloroacetanilide and phenylurea. From studies of degradation, fate and transport of herbicides and their metabolites in soil and aquatic environments, numerous journal articles, book chapters and USGS reports have been published.

The principal purpose of this paper is to list the analytical methods that have been developed to measure herbicide metabolites in surface and ground water. Listings of herbicide and metabolite surveys that have been conducted through the

USGS laboratory in Lawrence also are summarized. Brief descriptions and illustrations depicting the degradation pathways for the parent herbicides also are presented.

2. Analytical methods developed

Methods developed include use of gas chromatography/mass spectrometry (GC/MS), high-performance liquid chromatography with diode-array detection (HPLC/DAD), liquid chromatography/mass spectrometry (LC/MS), and solid-phase extraction (SPE) and enzyme-linked immunosorbent assay (ELISA) for analysis of triazine, chloroacetanilide, and phenylurea herbicide metabolites as shown in Table 1. Triazine metabolites include deethylatrazine (DEA), deisopropylatrazine (DIA), hydroxyatrazine (HA), cyanazine acid (CAC), cyanazine amide (CAM), deethylcyanazine (DEC), deethylcyanazine acid (DCAC), deethylcyanazine amide (DCAM), and deiso-pro-pylprometryn. Six triazine metabolites are analyzed by GC/MS according to procedures described by Thurman et al. (1990) and Meyer et al. (1993). Hydroxyatrazine is analyzed by both HPLC/DAD and LC/MS (Lerch et al., 1998). Since 1998, all triazine metabolites are analyzed by LC/MS except for deisopropylprometryn.

Two metabolites of the chloroacetanilide herbicides — ethane sulfonic acid (ESA) and oxanilic acid (OXA) — are detected by HPLC/DAD and LC/MS for acetochlor, alachlor and metolachlor (Ferrer et al., 1997; Kalkhoff et al., 1998; Kolpin et al., 1998; Hostetler and Thurman, 1999). Alachlor ESA is also analyzed by SPE and ELISA (Aga et al., 1994).

Phenylurea metabolites of diuron — 3,4-dichloroaniline (DCA), *N'*-(3,4-dichlorophenyl)-*N*-methylurea (DCPU) and 3,4-dichloromethylphenylurea (DCPMU) — are analyzed by LC/MS. DCA is also analyzed by GC/MS (Field et al., 1997). Phenylurea herbicide analysis also includes the metabolites of fluometuron — trifluoromethylaniline (TFMA), trifluoromethylphenylurea (TFMPU) and demethylfluometuron (DMFM) — which are detected by both GC/MS and LC/MS (Coupe et al., 1998).

Table 1

Methods of analysis for triazine, chloroacetanilide and phenylurea herbicide metabolites at the US Geological Survey laboratory, Lawrence, Kansas^a

Metabolite	Method			
	GC/MS	HPLC/ DAD	LC/MS	SPE/ ELISA
<i>Triazine metabolites</i>				
Deethylatrazine (DEA)	X		X	
Deisopropylatrazine (DIA)	X		X	
Hydroxyatrazine (HA)		X	X	
Cyanazine acid (CAC)			X	
Cyanazine amide (CAM)	X		X	
Deethylcyanazine (DEC)	X		X	
Deethylcyanazine acid (DCAC)			X	
Deethylcyanazine amide (DCAM)	X		X	
Deisopropylprometryn	X			
<i>Chloroacetanilide metabolites</i>				
Acetochlor ethane sulfonic acid (ESA)		X	X	
Acetochlor oxanilic acid (OXA)		X	X	
Alachlor ethane sulfonic acid (ESA)		X	X	X
Alachlor oxanilic acid (OXA)		X	X	
Metolachlor ethane sulfonic acid (ESA)		X	X	
Metolachlor oxanilic acid (OXA)		X	X	
<i>Phenylurea metabolites</i>				
3,4-dichloroaniline (DCA)	X		X	
3,4-dichlorophenylurea (DCPU)			X	
3,4-dichloromethylphenylurea (DCPMU)			X	
Trifluoromethylaniline (TFMA)	X		X	
Trifluoromethylphenylurea (TFMPU)	X		X	
Demethylfluometuron (DMFM)	X		X	

^aAbbreviations: GC/MS, gas chromatography/mass spectrometry; HPLC/DAD, high-performance liquid chromatography with diode-array detection; LC/MS, liquid chromatography/mass spectrometry; SPE, solid-phase extraction; and ELISA, enzyme-linked immunosorbent assay.

3. Surveys of herbicides and metabolites

Surveys conducted in the Midwestern USA through the USGS laboratory in Lawrence are: 1989–1990 — surface water runoff at 147 reconnaissance sites in a 10-state area (Scribner et al., 1993); 1990–1991 — rainfall samples from 81 collection sites (Goolsby et al., 1995); 1990–1992 — storm-runoff samples from nine stream basins (Scribner et al., 1994); 1991–1998 — samples from 303 well sites (Kolpin et al., 1993); 1992–1993 — samples collected from 76 reservoirs (Scribner et al., 1996); 1993 — samples from the Mississippi River during flood stage (Goolsby et al.,

1993); and 1994–1995 and 1998 — samples from 53 streams to help determine if changes in herbicide use resulted in a change in herbicide concentrations since the 1989–1990 reconnaissance study (Scribner et al., 1998).

Further surveys of herbicides and their metabolites in the cotton-growing areas of the USA have been made to relate herbicide use to occurrence in streams during 1995–1997 (Coupe et al., 1998). In 1996, surface water samples were collected at 64 sites in the Mississippi Embayment and analyzed in conjunction with the USGS National Water-Quality Assessment (NAWQA) Program. Special emphasis in the 1996 survey was

placed on streams in the Mississippi Delta as described by Thurman et al. (1998).

4. Degradation pathways

Concentrations of metabolites in water commonly may be equal to or even exceed concentrations of parent compounds. It has been found that metabolite concentrations in ground water often exceed parent compound concentrations for both triazine and chloroacetanilide herbicides, whereas in surface water the parent compound is most abundant after the application of herbicides in the spring and is replaced gradually with metabolites throughout the growing season. Metabolites are generally more water soluble than parent compounds and are leached more rapidly through the soil profile into ground water. This leaching process causes metabolite concentrations to be higher in ground water. In the fall, the metabolite concentrations may exceed concentrations of the parent compound (Kolpin et al., 1996, 1998; Kalkhoff et al., 1998). Pathways summarize major degradation products from field-dissipation studies.

Degradation of the phenylurea herbicides of diuron and fluometuron is similar. Both herbicides degrade by N-demethylation under aerobic conditions to metabolites (Ahrens, 1994; Field et al., 1997).

4.1. Triazine metabolites

The triazine herbicides — atrazine, cyanazine, simazine and propazine — are four compounds that have been used on corn and sorghum in the Midwestern USA. Application amounts of these herbicides in 1995 were 20 000 000 kg of atrazine, 11 000 000 kg of cyanazine, and 0.3 000 000 kg of simazine. Propazine use has been discontinued (Gianessi and Puffer, 1991). Triazine herbicides degrade by various pathways to a series of metabolites. Atrazine degrades in soil through both biotic and abiotic reactions to the dealkylated metabolites, DEA and DIA, and the hydroxylated metabolite, HA (Fig. 1). DEA may further degrade to the dealkylated hydroxymetabolites of

didealkyltriazine (DDA), hydroxydeethyltriazine (HDEA) and hydroxydeisopropyltriazine (HDIA). DIA may further degrade to the hydroxy-metabolites of DDA and HDIA. HA may degrade to dealkylated HDIA and HDEA (Lerch et al., 1998). The atrazine degradation pathway includes further dealkylation of DEA, DIA and HA to the opening of the triazine ring and eventual mineralization to carbon dioxide and ammonia (Gunther and Gunther, 1970; Erickson and Lee, 1989). The degradation pathway of atrazine generally is well known and studied extensively during the soil dissipation but is generally poorly understood at the biochemical and genetic level of biodegradation.

Field-dissipation studies of the four chlorinated parent triazine herbicides atrazine, cyanazine, simazine and propazine have found that they all degrade in soil in similar fashion and form at least one of two common dealkylated metabolites, DIA and (or) DEA. Fig. 2 summarizes triazine degradation pathways described by Thurman et al. (1994), which documents work on all four triazine compounds using field-dissipation studies.

Cyanazine is used primarily on corn in the upper Midwest. The work done by the USGS laboratory in Lawrence is the first major integrated research conducted on the geochemistry of cyanazine in surface water of the Midwest. Methods development, field-dissipation, and regional studies by laboratory personnel indicate that cyanazine is more labile than atrazine and that they both have a common metabolite, DIA (Meyer, 1994). Cyanazine degrades by deethylation to DEC, which degrades rapidly to DCAM. DCAM, in turn, degrades to DCAC, which further degrades to DDA. CAM is an important metabolite of cyanazine that is readily detected. CAM degrades to DCAM and CAC. CAC then degrades to DCAC and DIA, which further degrades to DDA. CAC and DCAC may be rapidly transported through the unsaturated zone (Meyer, 1994). Structures and degradation pathways for cyanazine and its metabolites are shown in Fig. 3.

Various studies in the Midwestern USA have demonstrated the importance of the two triazine metabolites, DEA and DIA, which were found to occur in water that has received parent triazine

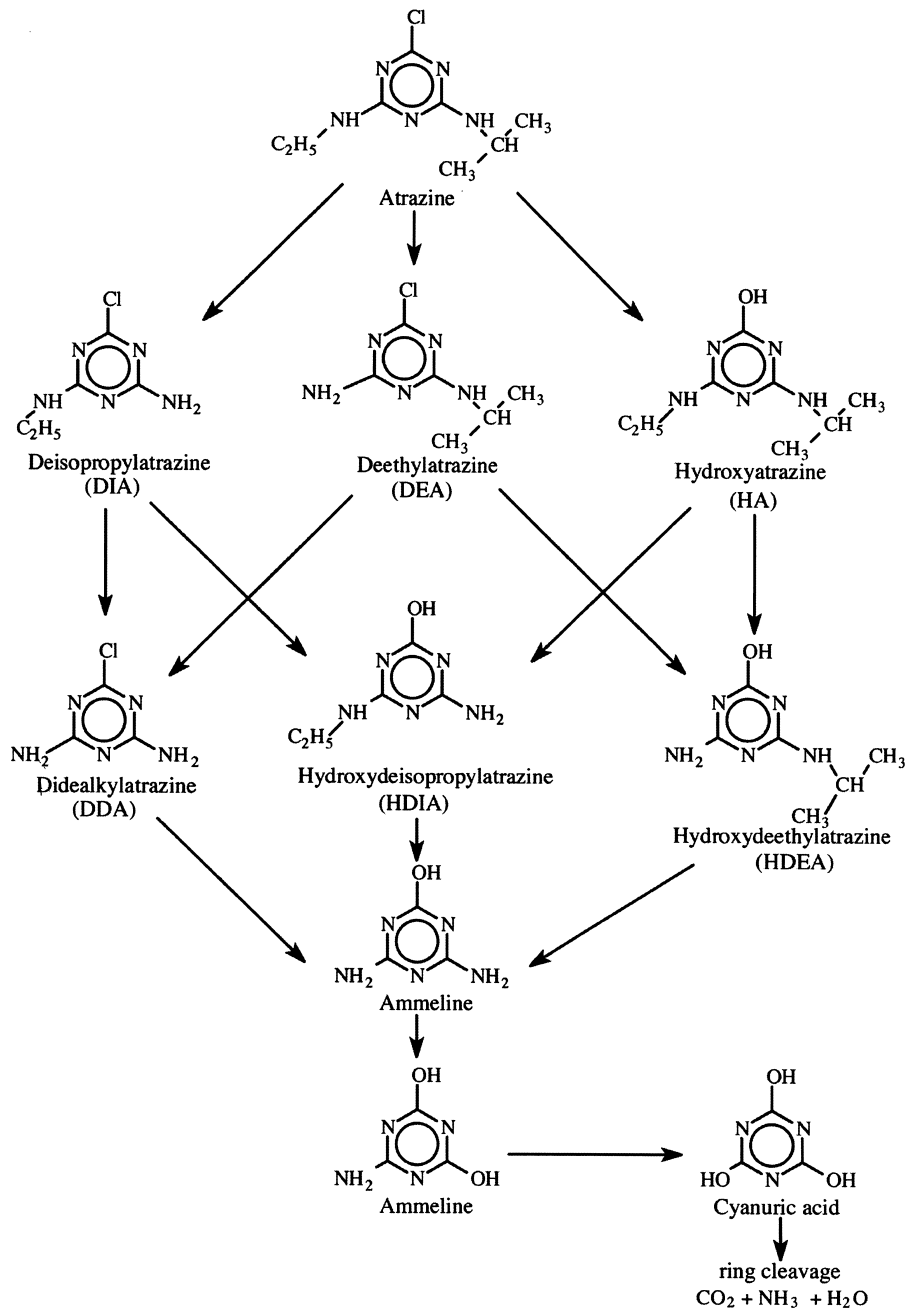


Fig. 1. Pathways for degradation of atrazine.

herbicides. These studies show that DEA has atrazine as its major source (98%) and only trace levels are derived from propazine (Fig. 2). DIA has atrazine as its major source (75%) and cyanazine as a secondary source (25%). Trace amounts

of DIA are contributed by simazine. Propazine and simazine do not contribute substantially to the DIA-to-DEA ratio in surface water (Thurman et al., 1994). When DEA is the major metabolite in the unsaturated zone, the deethylatrazine-to-

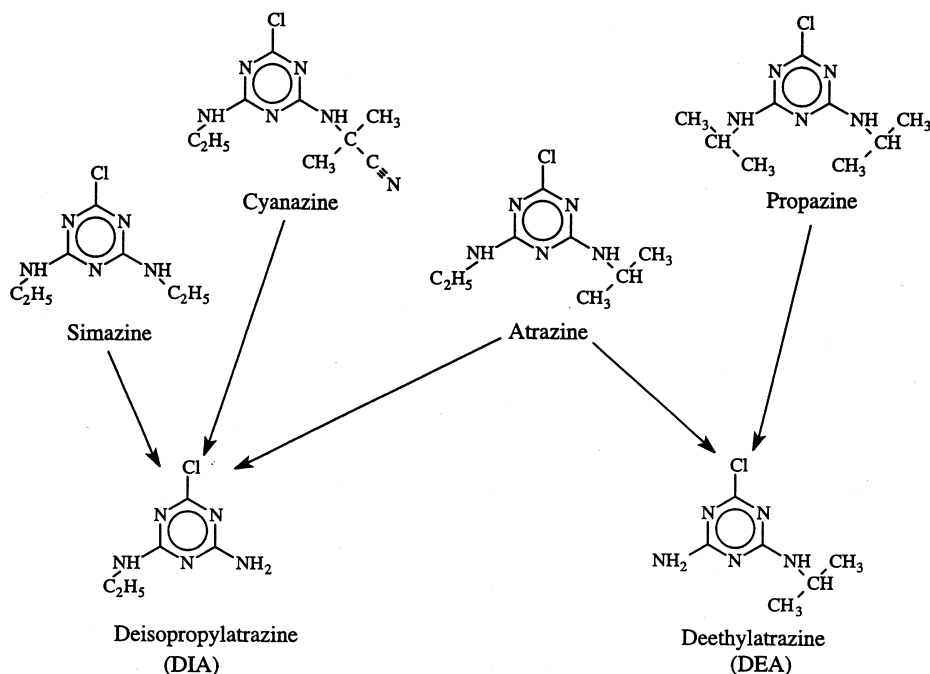


Fig. 2. Pathways for degradation of atrazine, cyanazine, propazine and simazine to DEA and DIA.

atrazine ratio (DAR) may be used to document the first major runoff of herbicides from non-point-source corn fields to surface water (Thurman and Fallon, 1996). The DAR in soil water quickly decreases from approximately 0.5 to less than 0.1 upon application of herbicide and the first major runoff occurrence in a basin. The DAR then gradually increases to values of approximately 0.4–0.6 during the harvest season. Atrazine and DEA have been reported frequently in ground water but less is known about the occurrence of HA in surface water. Lerch et al. (1998) reported that atrazine metabolites accounted for nearly 60% of the atrazine load in northern Missouri streams at preplant, with HA the predominant metabolite present.

Other triazine herbicides analyzed by GC/MS include prometryn. Prometryn is a parent herbicide used in cotton-growing areas of the USA. Its dealkylated metabolite, deisopropylprometryn, also is analyzed by GC/MS. During a recent study in the Mississippi Embayment, prometryn was not detected in water samples at concentrations greater than 1.0 $\mu\text{g}/\text{l}$, and deisopropylprometryn was not detected at concentrations

greater than the reporting level of 0.05 $\mu\text{g}/\text{l}$ (Thurman et al., 1998). The less extensive use of prometryn probably was responsible for the low concentrations in the samples analyzed (Coupe et al., 1998).

4.2. Chloroacetanilide metabolites

The chloroacetanilide herbicides — acetochlor, alachlor and metolachlor — constitute the second major class of herbicides used in the USA. Together with triazine herbicides, chloroacetanilide herbicides account for the majority of herbicides applied to farmland in Midwestern USA (Gianessi and Anderson, 1995). Alachlor and metolachlor have been used for more than 20 years (Thurman et al., 1996). Acetochlor was used for the first time in 1994. In general, chloroacetanilide herbicides are known to degrade more quickly in soil than triazine herbicides, and typical half-lives of the chloroacetanilide herbicides range from 15 to 30 days (Leonard, 1988), compared to 30–60 days for triazine herbicides (Ferrer et al., 1997). Fig. 4 shows the degradation pathway of the chloroacetanilide parent compounds to ESA

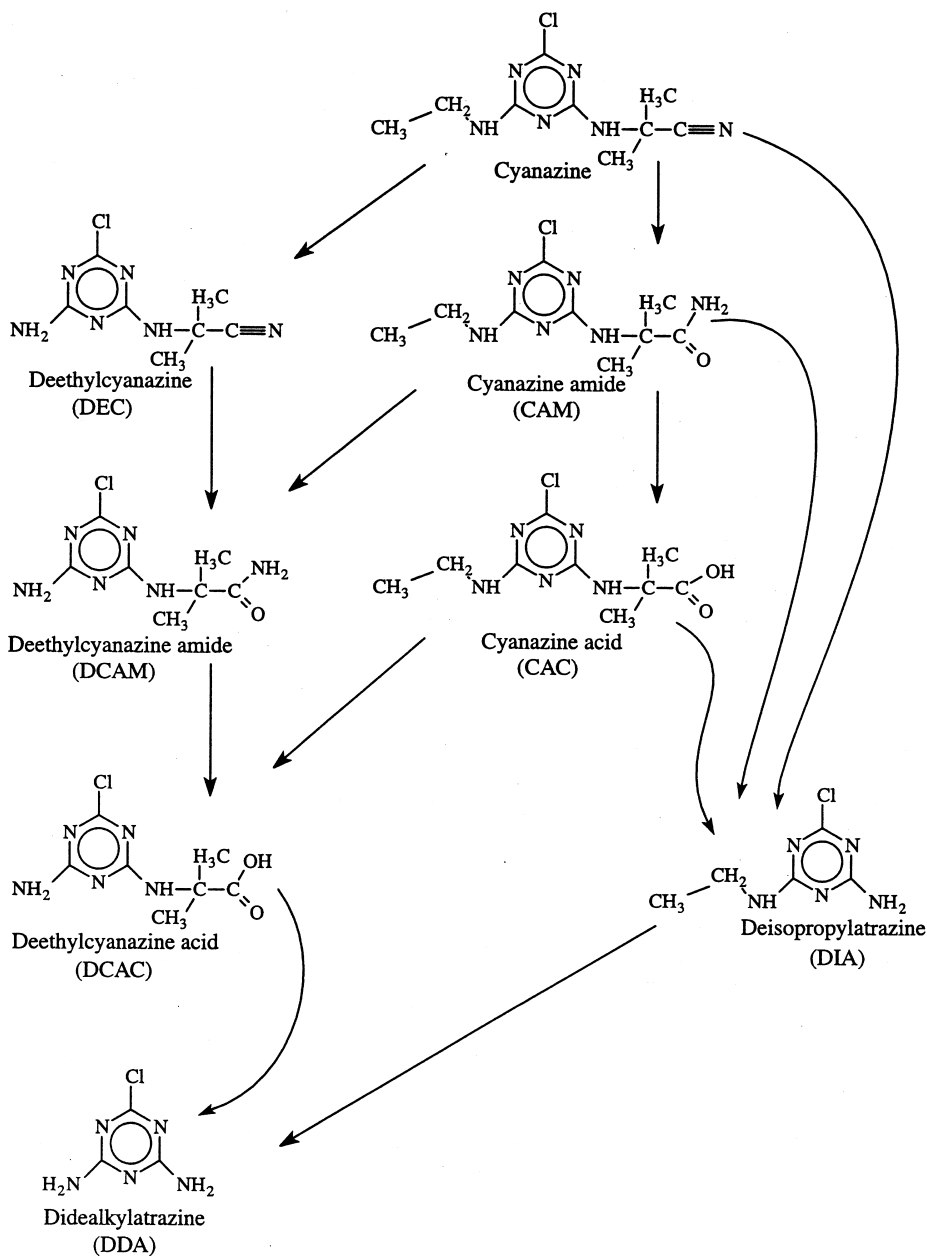


Fig. 3. Pathways for degradation of cyanazine.

and OXA. Chloroacetanilide herbicides have been analyzed by HPLC/DAD (Kolpin et al., 1998), however, since 1998, these metabolites also are analyzed by LC/MS at the USGS laboratory in Lawrence. SPE and ELISA are combined for the trace analysis of the herbicide alachlor and its major soil metabolite, ESA. The method is viable

for the analysis of both surface- and ground water samples and is comparable to GC/MS and HPLC analyses for alachlor and ESA (Aga et al., 1994).

4.3. Phenylurea metabolites

The phenylurea herbicides, diuron and flu-

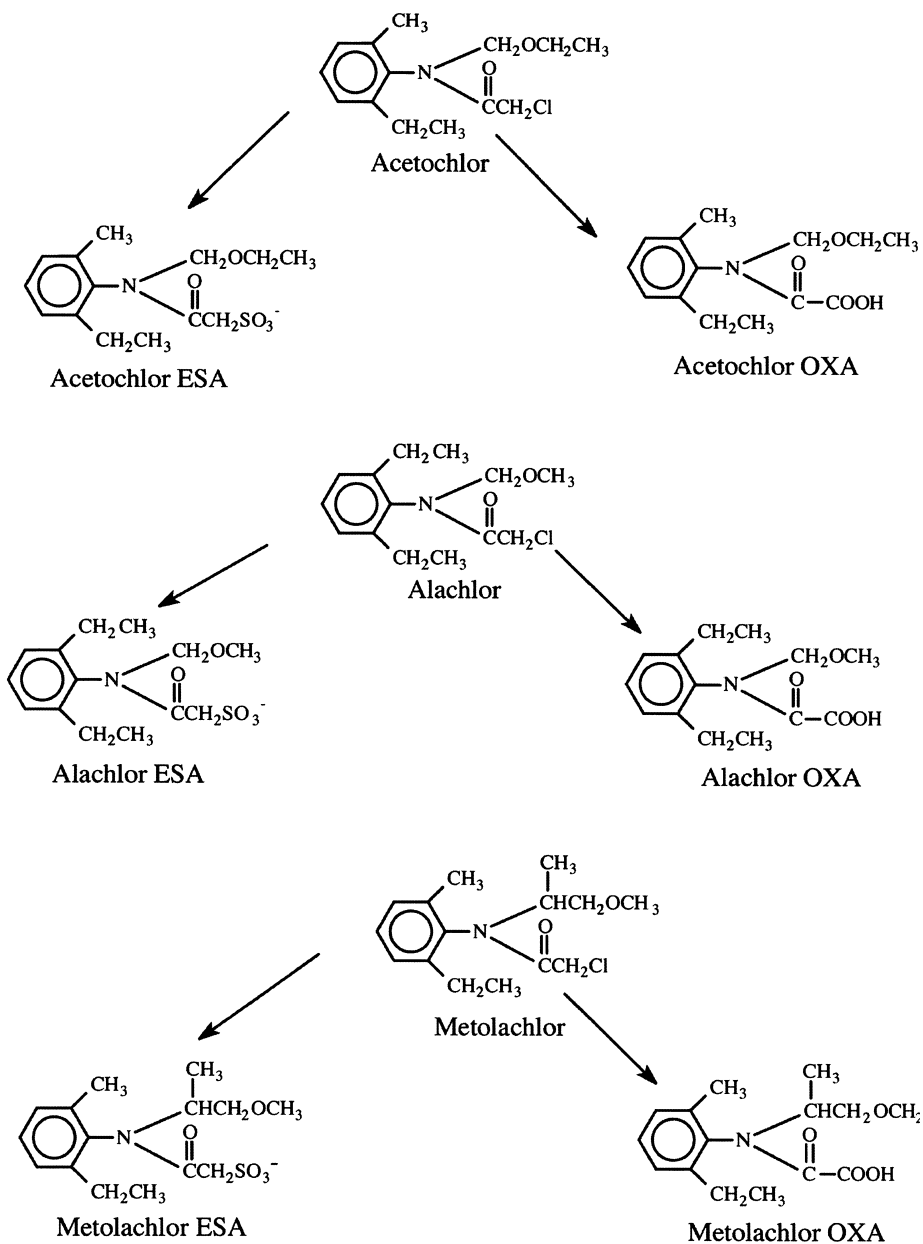


Fig. 4. Pathways for degradation of acetochlor, alachlor and metolachlor to ethane sulfonic acid and oxanilic acid.

ometuron, are used in the cotton-growing areas of the USA. Diuron is also used in many other areas on fruit crops. The annual application of diuron is approximately 1.8000000 kg of active ingredient (Gianessi and Anderson, 1995). It was

ranked as the third most hazardous pesticide to ground water resources (Newman, 1995). Diuron degrades by N-demethylation under aerobic conditions to metabolites including *N'*-(3,4-dichlorophenyl)-*N*-methylurea (DCPMU), 3,4-dichloro-

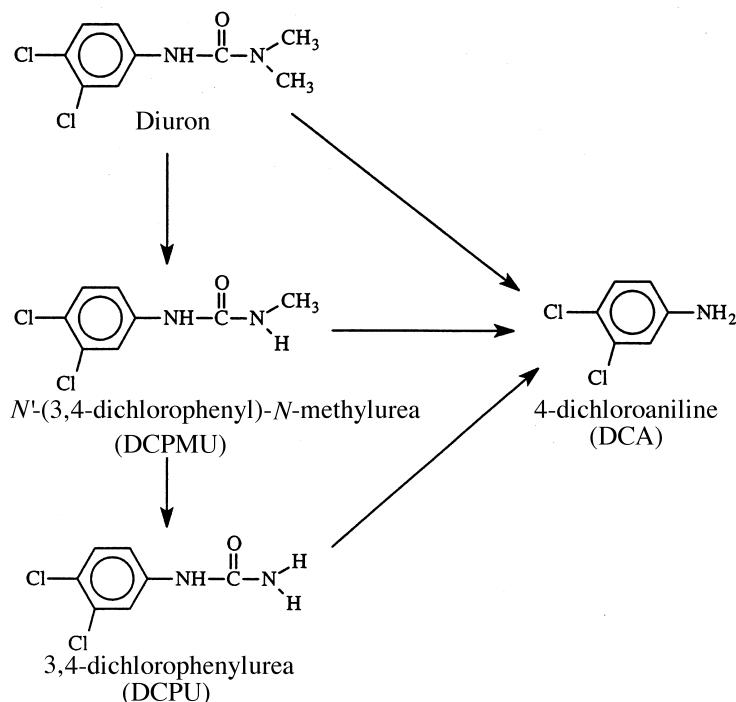


Fig. 5. Pathways for degradation of diuron.

phenylurea (DCPU) and 3,4-dichloroaniline (DCA) (Dalton et al., 1966). The degradation pathway for diuron and its metabolites, DCPMU, DCPU and DCA, is shown in Fig. 5.

Fluometuron is used primarily in Mississippi and in the eastern coastal plain (Gianessi and Anderson, 1995) as a pre-emergent herbicide for broadleaf and grass control in cotton, therefore, the timing of the highest concentrations of fluometuron in surface water is much different than for corn because application times are different (4.7 average annual applications on cotton vs. 1.2 average annual applications on cotton vs. 1.2 average annual applications on corn). Application of fluometuron in the USA totaled approximately 1.5 000 000 kg in 1996 at an average rate of approximately 0.81 kg/ha of active ingredient (National Agricultural Statistics Service, 1997). Three fluometuron metabolites that have been analyzed are TFMA, TFMPU and DMFM. In a study using GC/MS (Coupe et al., 1998), analyses showed that DMFM was the most common and was

present in the highest concentration. TFMPU was not detected in any of the samples and TFMA was detected infrequently and in low concentrations (Coupe et al., 1998). The degradation pathways of fluometuron and its metabolites are shown in Fig. 6.

5. Summary

The US Geological Survey laboratory in Lawrence, Kansas, was established in 1987 to enhance scientific knowledge in the field of organic geochemistry. Special emphasis has been on water-quality analysis as related to problem areas involving contamination of surface and ground water. Analytical methods continue to be developed to assess the nature, amount and movement of herbicides and their metabolites in soil and water. This scientific work is important to define water quality and its relation to non-point-source contamination.

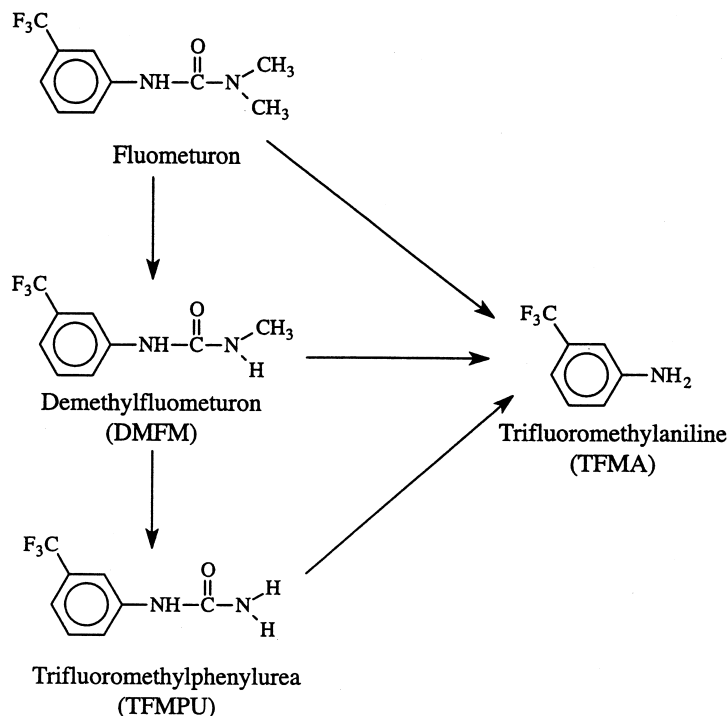


Fig. 6. Pathways for degradation of fluometuron.

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