Degradation of Chloroacetanilide Herbicides: The Prevalence of Sulfonic and Oxanilic Acid Metabolites in Iowa Groundwaters and Surface Waters

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Water samples were collected from 88 municipal wells throughout Iowa during the summer and were collected monthly at 12 stream sites in eastern Iowa from March to December 1996 to study the occurrence of the sulfonic and oxanilic metabolites of acetochlor, alachlor, and metolachlor. The sulfonic and oxanilic metabolites were present in almost 75% of the groundwater samples and were generally present from 3 to 45 times more frequently than their parent compounds. In groundwater, the median value of the summed concentrations of acetochlor, alachlor, and metolachlor was less than 0.05 μg/L, and the median value of the summed concentrations of the six metabolites was 1.2 μg/L. All surface water samples contained at least one detectable metabolite compound. Individual metabolites were detected from 2 to over 100 times more frequently than the parent compounds. In surface water, the median value of the summed concentrations of the three parent compounds was 0.13 μg/L, and the median value of the summed concentrations of the six metabolites was 6.4 μg/L. These data demonstrate the importance of analyzing both parent compounds and metabolites to more fully understand the environmental fate and transport of herbicides in the hydrologic system.

Introduction

Chloroacetanilide herbicides such as acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide], alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide], and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxy-1-methylethyl)acetmide] are used extensively for the control of competing vegetation in corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] production in Iowa. In 1995, these herbicides accounted for 38% (6 800 000 kg of active ingredient) of the total mass of herbicides applied in Iowa (*1*). Although the total application of chloroacetanilide herbicides has historically exceeded that of the atrazine in Iowa (*1*), the occurrence of the these compounds in groundwater and surface water has been substantially lower than the occurrence of atrazine (*2, 3*). Chloroacetanilide herbicides have been found to degrade more rapidly than atrazine (*4*), thus reducing their transport to groundwater or streams. Complete mineralization of these compounds, however, has not been established (*4, 5*). Thus, relatively stable and persistent intermediate herbicide degradation products may occur.

Recent research has documented an alachlor degradation product, alachlor ethanesulfonic acid (alachlor ESA: 2-[(2,6-diethylphenyl)(methoxymethy)ammino]-2-oxoethanesulfonic acid), that is commonly found in both groundwater and surface water (*6*−*9*). Previous research has suggested that this sulfonated alachlor metabolite may be the result of a glutathione conjugation process occurring in plants, algae, and terrestrial microorganisms (*10*). Additionally, it has been hypothesized that mobile sulfonated and nonsulfonated metabolites of other chloroacetanilide herbicides may result from this glutathione conjugation pathway (*9*−*13*). With the exception of alachlor ESA, however, little ambient water chemistry data have been available to confirm the presence of these metabolites in the hydrologic system.

The purpose of this paper is to present initial results of a study to determine the occurrence of acetochlor, alachlor, and metolachlor sulfonic (ESA) and oxanilic (OA) acid metabolites in groundwater and surface water in Iowa using a recently developed analytical method. This paper is one of the first to document metolachlor ESA and metolachlor OA in ambient samples from groundwater and surface water. It also substantially adds to the data available for alachlor and acetochlor metabolites. A more detailed discussion of the seasonal, spatial, and hydrogeologic occurrence of these compounds in groundwater and surface water will follow in future publications.

Methods

Field. Groundwater samples were collected from 88 municipal wells in Iowa during the summer of 1996 (Figure 1). Well depth ranged from 6.1 to 130.4 m. (median of 19.2 m.). This groundwater sampling was an extension of the Iowa Ground Water Monitoring Program (*14*). The groundwater sampling protocol for this study was similar to that used for a previous study of groundwater in Iowa (*8*). All wells were pumped a minimum of 30 min prior to measurements of dissolved oxygen, pH, specific conductance, and water temperature. Once the values for the above parameters stabilized, the water samples were collected. Water samples were filtered through a 1.0-μm glass fiber filter into amber baked-glass bottles and immediately chilled.

Surface water samples were collected monthly from March through December 1996 at 12 sites (Figure 1) in eastern Iowa as part of the U.S. Geological Survey's National Water Quality Assessment (NAWQA), Eastern Iowa Basin study unit surface water investigations. To integrate vertical and horizontal water quality variability, samples were collected using a depth-integrated sampler at 5−10 verticals equally spaced across the stream or river (*15*). The samples were then filtered through a 1.0-μm baked glass fiber filter into amber baked-glass bottles. The filtered samples were immediately chilled for shipment to the laboratory.

Analytical. All water samples were sent to the U.S. Geological Survey's Organic Research Laboratory in Lawrence,

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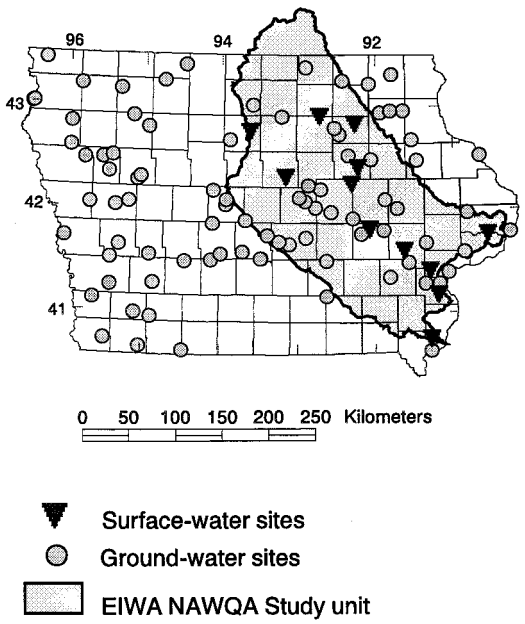

FIGURE 1. Location of the groundwater and surface water sampling sites in relation to Iowa and the Eastern Iowa Basins (EIWA) NAWQA study unit.

KS, to determine concentrations of three chloroacetanilide herbicides and six chloroacetanilide metabolites. The three parent compounds (acetochlor, alachlor, and metolachlor) were analyzed by gas chromatography/mass spectrometry following solid-phase extraction on C_{18} cartridges (*16, 17*). The analytical reporting limit for this method was 0.05 μg/L for all parent compounds. The six chloroacetanilide herbicide metabolites: acetochlor ethanesulfonic acid (acetochlor ESA: 2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)amino-2-oxoethanesulfonic acid), acetochlor oxanilic acid (acetochlor OA: 2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)-amino]-2-oxoacetic acid), alachlor ESA, alachlor oxanilic acid (alachlor OA: 2-[2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid), metolachlor ethanesulfonic acid (metolachlor ESA: 2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid), and metolachlor oxanilic acid (metolachlor OA: 2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid) were analyzed by high-performance liquid chromatography (HPLC) with diode-array detection following solid-phase extraction on C_{18} cartridges (*16*). Quantification of the analytes was achieved by dividing the peak height of the analyte by the peak height of the internal standard (2,4-D) and substituting the peak height into the respective linear regression equation. Complete separation of all analytes was achieved with this method. The analytical reporting limit for all metabolite compounds was 0.2 μg/L, and the relative standard deviation was ±10% for this method. Standards were run with each sample set at concentrations of 0.25, 0.5, 1.0, and 2.0 μg/L. Confirmation by negative ion electrospray (*18*) was achieved for metolachlor ESA and acetochlor, alachlor, and metolachlor OA. Complete separation of alachlor ESA and acetochlor ESA was not possible by HPLC−MS negative ion electrospray. Metabolite standards for this study were obtained from various sources: acetochlor ESA and acetochlor OA was from Zeneca Agrochemicals (London, England), alachlor ESA and alachlor OA were from Monsanto (St. Louis, MO), metolachlor OA was from Novartis (Greensboro, NC), and metolachlor ESA was synthesized according to the method of Aga and others (*16*).

Detection Frequencies. Because the analytical reporting limits for the parent compounds were four times lower (0.05 μg/L) than their degradation products (0.20 μg/L) under investigation, the raw data are inappropriate when comparing the frequencies of detection among compounds. To compensate for differing detection frequencies caused by different analytical reporting limits, a common detection threshold of 0.2 μg/L was used to discuss the frequency of detection for all chloroacetanilide compounds.

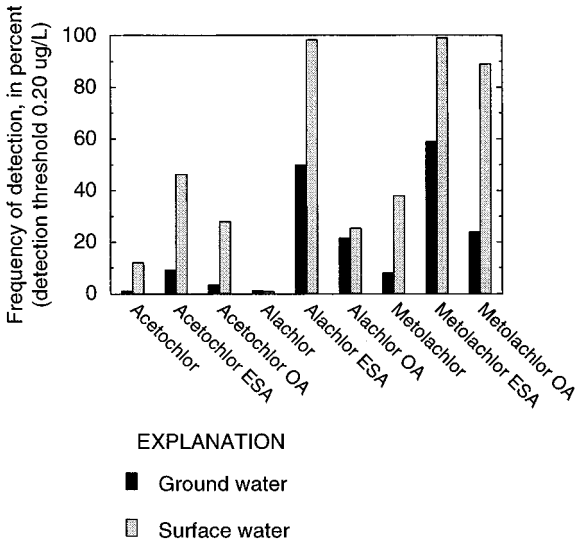

FIGURE 2. Detection rates of chloroacetanilide herbicides and their sulfonic and oxanilic metabolites.

Results

Groundwater. The chloroacetanilide metabolites examined for this study were present in almost 75% of the wells sampled. These metabolites were found more often (Figure 2), and at generally higher concentrations (Figure 3) than their corresponding parent compounds. In general, these metabolites were detected between 3 and 45 times more frequently than their parent compound with over 90% of the total measured concentrations (parent + metabolites) in a given groundwater sample being derived from the metabolites. The median value of the summed concentrations of the three parent compounds was <0.05 μg/L, with the median value of the summed concentrations of the six metabolites being 1.2 μg/L. This study confirms that these chloroacetanilide herbicides degrade to mobile metabolites that are being transported to groundwater before complete mineralization of the parent compounds takes place.

The relative mobility of the compounds (based on their frequency of detection in groundwater) was identical among the chloroacetanilide herbicides examined, with the ESA compound ≫ OA compound ≫ parent compound (Figure 2). These results imply that the metabolites are more persistent than their parent compounds; however, direct measurements of chemical persistence were beyond the scope of this investigation. There also was a consistent difference in the relative magnitudes of detection frequencies for the ESA, OA, and parent compounds among these chloroacetanilde herbicides, with metolachlor constituents > alachlor constituents > acetochlor constituents. This difference, in part, is due to differences in the amount of active ingredient applied to corn and soybeans in Iowa since 1990 (*1, 19*). Differences in physical properties and rates of degradation (*4, 20)* are also likely contributing factors.

Surface Water. Oxanilic and sulfonic acid metabolites of the chloroacetanilide herbicides investigated were found more often and at greater concentrations in rivers and streams in Iowa than their corresponding parent compounds. One or more of the chloroacetanilide metabolites were present in 100% of the stream samples. Individual ESA and OA

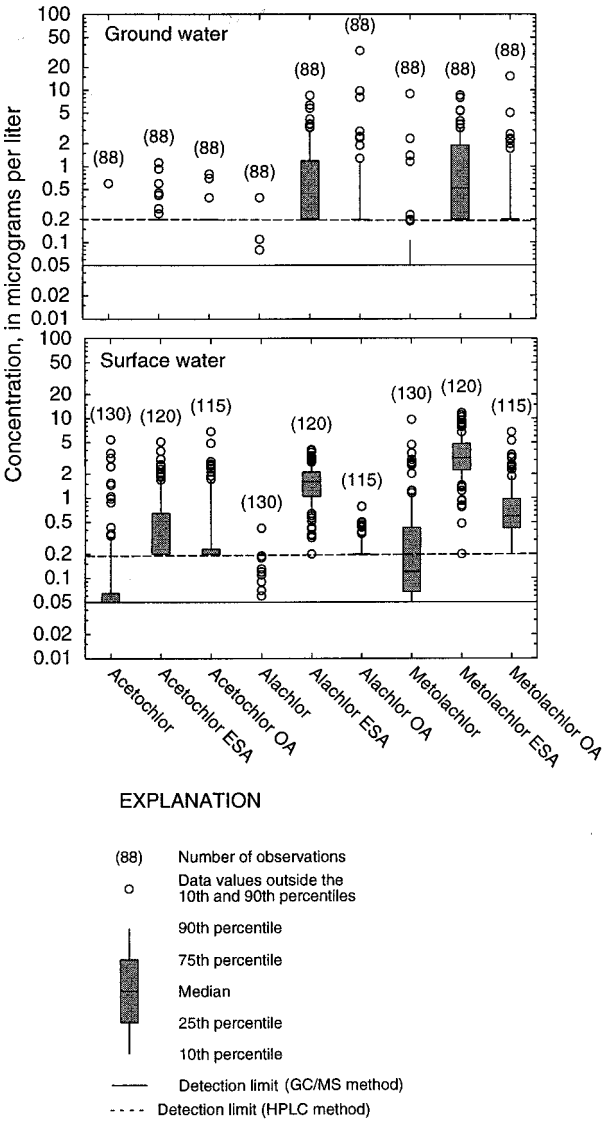

FIGURE 3. Concentrations of chloroacetanilide herbicides and their sulfonic (ESA) and oxanilic acid (OA) metabolites in groundwater and surface water samples in Iowa, 1996.

metabolites were detected from about 2 to more than 100 times more frequently than the parent compounds. Similar to groundwater, the frequency of detection follows the pattern ESA > OA > parent (Figure 2). Alachlor had the greatest difference between parent and ESA metabolite.

Furthermore, more than 80% of the measured mass of chloroacetanilide compounds in surface water was derived from the metabolites. The median value of the summed concentrations of the three parent compounds was 0.13 μg/L, and the median value of the summed concentrations of the six OA and ESA compounds was 6.4 μg/L. The general concentrations of the chloroacetanilide compounds follows the same pattern as that of the rate of detection: ESA > OA > parent compounds.

These results demonstrate that ESA and OA metabolites of three major chloroacetanilide herbicides are commonly present in groundwater and surface water in substantial concentrations. This study also demonstrates the importance of quantifying both parent compounds and metabolites to fully understand the environmental fate and transport of herbicides in the hydrologic system. Because the occurrence of these metabolites has only recently been documented in the hydrologic system, it is unclear what effects there may be from exposure to combinations of herbicides and their metabolites or if chronic exposure to these compounds can cause adverse effects to ecosystems or human health.

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