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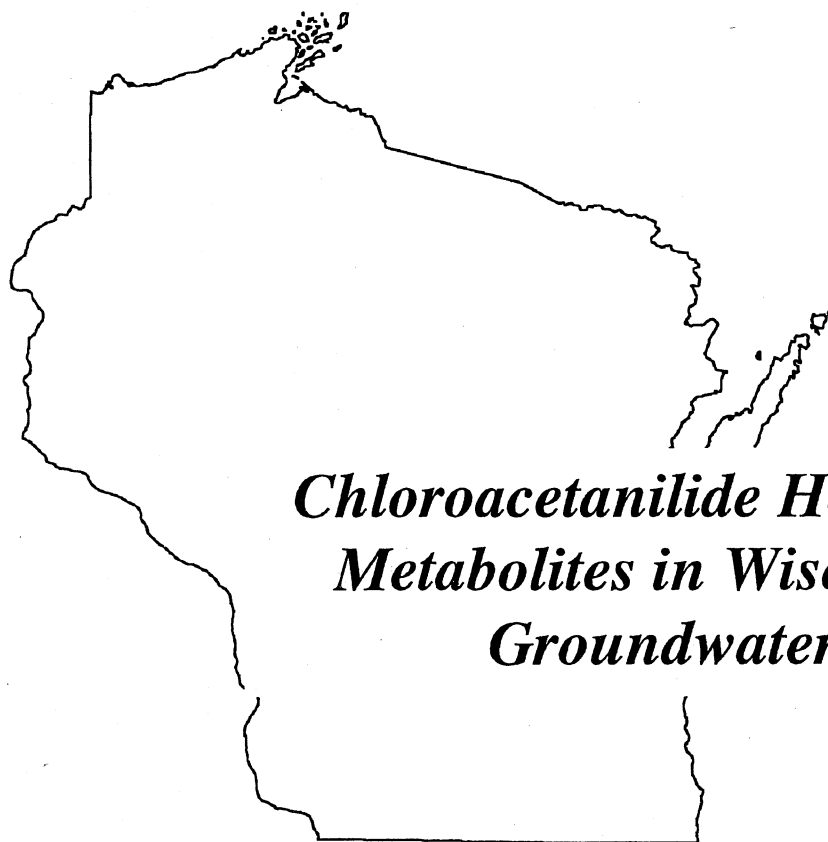
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***Chloroacetanilide Herbicide
Metabolites in Wisconsin
Groundwater***

**Wisconsin Department of Agriculture,
Trade and Consumer Protection**

June 2000



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Chloroacetanilide Herbicide Metabolites in Wisconsin Groundwater

**Final
Report**

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Chloroacetanilide Herbicide Metabolites in Wisconsin Groundwater

ABSTRACT

In this study, 27 monitoring wells, 22 private drinking water wells, and 23 municipal wells in Wisconsin were sampled for alachlor, metolachlor, acetochlor, and their ethane sulfonic acid (ESA) and oxanillic acid (OA) metabolites. The wells sampled for the study were not randomly chosen. Wells were selected based on previous detections of pesticides or proximity to agricultural fields to increase the likelihood of exposure to the compounds of interest. Alachlor, metolachlor, and acetochlor are chloroacetanilide herbicides that are commonly used on corn and other crops in Wisconsin. With the exception of alachlor ESA, no groundwater occurrence data exists for these metabolites in Wisconsin groundwater because laboratory methods have not been available. Sample results showed over 80 percent of the monitoring wells and drinking water wells contained the ESA and OA metabolites of alachlor and metolachlor. The metabolites of acetochlor, which has only been used since 1994, showed a lower frequency of detection. Concentrations of the metabolites in groundwater ranged from near the level of detection to 42 ug/l. The monitoring wells and private drinking water wells showed higher detection frequencies and concentrations than the deeper municipal wells, but the municipal wells did show significant impacts. Fifty-two percent of the municipal wells had a detection of at least one of the compounds of interest. However, no municipal well studied contained pesticide levels that exceeded an enforcement standard.

BACKGROUND

Use of Chloroacetanilide Herbicides in Wisconsin

Alachlor, metolachlor and acetochlor belong to the chloroacetanilide class of herbicides. Their main use in Wisconsin is for pre-emergence control of annual grasses in corn. Alachlor and metolachlor are also used for weed control in soybeans and certain other crops. Products containing metolachlor (Dual) and alachlor (Lasso) have been used in Wisconsin for over 25 years. Acetochlor products (Harness, Surpass) have only been in use since 1994.

In 1996, alachlor, metolachlor and acetochlor were used on 692,100; 972,500; and 351,000 acres of cropland in Wisconsin, respectively (WASS, 1997). The total amount of active ingredient applied of these three compounds was 1.15, 1.67, and 0.647 million pounds, respectively. In 1996, metolachlor was second only to atrazine in the amount of active ingredient applied to corn in Wisconsin.

Recent trends in the use of these three herbicides show that acetochlor use is increasing, alachlor use is decreasing, and metolachlor use is remaining fairly constant. These trends are expected to continue as new acetochlor products replace older alachlor products.

Previous Groundwater Sampling for Chloroacetanilide Metabolites

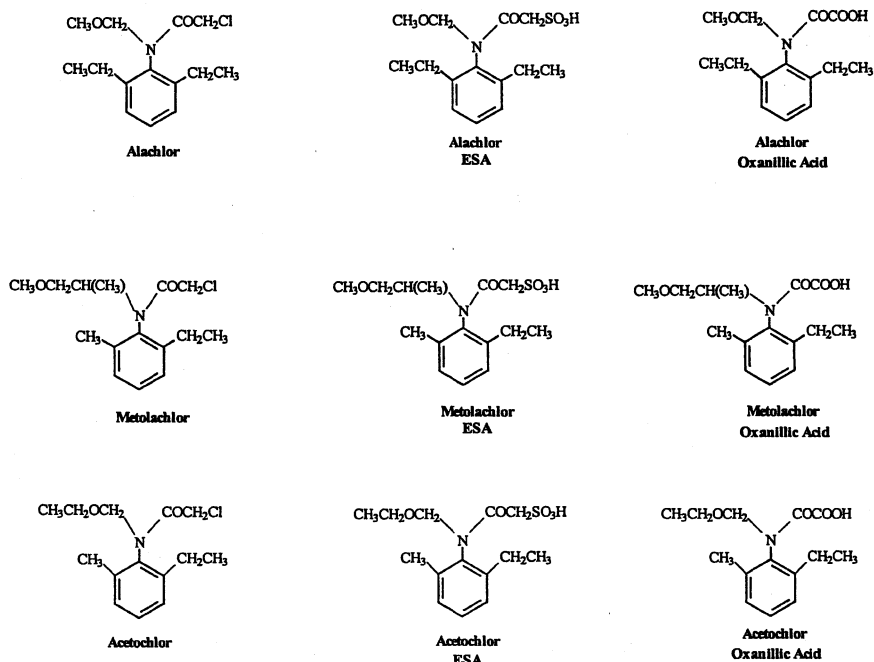
In 1998 the United States Geological Survey (USGS) reported the occurrence of ethane sulfonic acid (ESA) and oxanillic acid (OA) metabolites of chloroacetanilide herbicides in Iowa groundwater and surface water (Kalkhoff, S.J. et. al., 1998). These metabolites were present in almost 75 percent of groundwater samples obtained from municipal wells. The metabolites were detected much more frequently and at higher concentrations than their parent compounds. The authors emphasized the importance of analyzing for both parent compounds and metabolites to fully understand the fate of herbicides in hydrologic systems.

In 1994, the Wisconsin Departments of Agriculture, Trade and Consumer Protection (DATCP) and Natural Resources (DNR) sampled 293 private wells for alachlor ESA. The wells were considered "at-risk" since they had had previous detections of atrazine. In this study, alachlor ESA was found in 70 percent of the private wells at concentrations between 1.1 and 27 ug/l. (Wisconsin Department of Agriculture, Trade and Consumer Protection, 1994). Further studies in Wisconsin have shown that about 7 percent of private wells contain alachlor ESA (LeMasters and Baldock, 1997).

Chemistry and Degradation of Chloroacetanilide Herbicides

Alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide]; metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(methoxy-1-methylethyl) acetamide]; and acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide] are three similar chloroacetanilide herbicides. Each of these three parent compounds break down into unique ethane sulfonic acid (ESA) and oxanillic acid (OA) metabolites. Figure 1 shows the chemical structures of these compounds.

Figure 1. Chemical Structures for Alachlor, Metolachlor, Acetochlor, and their Ethane Sulfonic Acid and Oxanillic Acid Metabolites



The chloroacetanilide herbicides appear to be degraded primarily by microbial activity in the soil (Zimdahl and Clark, 1982; Potter and Carpenter, 1995). The degradation of the parent compounds to the ESA metabolites results in the removal of a chlorine atom and the addition of a sulfonic acid functional group to the molecule. This greatly increases the water solubility relative to the parent compound and contributes to the increased potential for leaching to groundwater (Thurman et. al, 1996). The metabolites generally have lower molecular weights than the parent compounds or are oxidized which also gives them higher water solubility and increased leaching potential (Potter and Carpenter, 1995).

The potential for degradation of these compounds by microorganisms in groundwater appears to be limited. Once these compounds enter groundwater, they are likely to persist for a long period of time (Potter and Carpenter, 1995).

INTRODUCTION

From October 1999 to May 2000, the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) conducted a groundwater sampling program for the ethane sulfonic acid (ESA) and oxanillic acid (OA) metabolites of the chloroacetanilide herbicides metolachlor, alachlor and acetochlor. Of these metabolite compounds, only alachlor ESA had previously been studied in Wisconsin groundwater. Laboratory methods for the other five metabolites are relatively new and not widely available. Given the documented occurrence of chloroacetanilide metabolites in Iowa groundwater and alachlor ESA in Wisconsin groundwater, DATCP wanted to determine if the metabolites of these three herbicides are present in Wisconsin groundwater.

The budget for the project allowed for the analysis of 72 groundwater samples. The total number of samples was allocated approximately equally among monitoring wells, private drinking water wells, and municipal wells. The design of this sampling program was aimed at detecting chloroacetanilide metabolites in groundwater if they were present. Specifically, the two main goals of the study were to: 1) characterize the presence of chloroacetanilide metabolites in Wisconsin groundwater, and 2) compare the metabolite occurrence data between shallow monitoring wells, private drinking water wells, and municipal wells.

METHODS

Well Selection

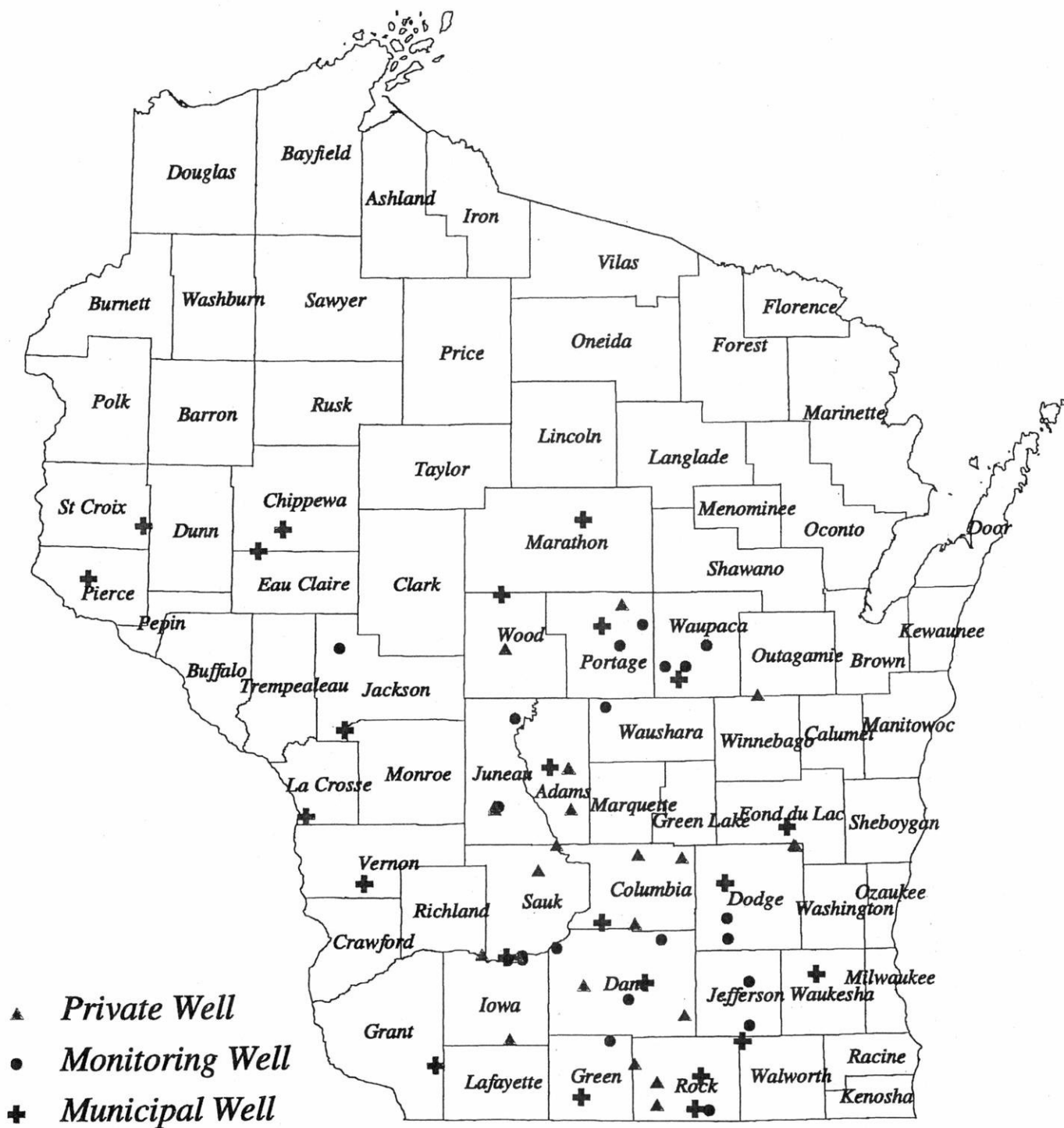
The 27 monitoring wells in the study were chosen from three existing DATCP monitoring well programs: the DATCP Monitoring Program in Susceptible Areas, the Acetochlor Monitoring Well program, and the DATCP Atrazine Reuse Study. These programs all utilize shallow (well screen near the water table) monitoring wells located next to or within agricultural fields. Within these programs, wells were selected based on past detections of chloroacetanilide herbicides and use of these compounds on adjacent agricultural fields.

The 22 private drinking water wells in the study had all been previously sampled by the DATCP for pesticides and nitrate-nitrogen. They were selected for the current study based on previous detects of metolachlor or alachlor ESA.

The 23 municipal wells were selected based on pesticide detections since 1995. In addition, seven of the largest municipal groundwater systems were chosen regardless of past sampling results. For each municipal system, the specific well that was sampled was chosen based on proximity to agricultural fields, past nitrate levels, and well depth.

Figure 2 shows the location of the 72 wells sampled in this program. The wells are distributed over the southern two-thirds of the state where crop production is prevalent.

Figure 2. Location of 72 wells Sampled for Chloroacetalide
Herbicides and Metabolites



Sampling Methods

Groundwater samples were collected from 27 monitoring wells, 22 private water supply wells and 23 municipal water supply wells. Four well volumes were purged from the monitoring wells using equipment dedicated to each well before sampling. Private well samples were collected from a cold water tap located as close to the wellhead as possible and prior to any treatment devices. The water was allowed to run for at least five minutes and until the pump had been activated. The municipal samples were collected as "raw" water samples directly from a sampling point at the wellhead. All municipal wells were run at least fifteen minutes prior to sampling. Samples were field filtered through a glass fiber pre-filter and 0.45-micron cellulose acetate filter. Samples were collected into amber pre-cleaned glass bottles with Teflon lined caps and immediately chilled.

Laboratory Methods

All samples were analyzed at the USGS lab in Lawrence, Kansas by high-performance liquid chromatography/mass spectrometry for acetochlor ESA, acetochlor OA, alachlor ESA, alachlor OA, metolachlor ESA, and metolachlor OA. The laboratory limit of quantitation (LOQ) for these compounds was 0.05 ug/L.

A split of each sample was also analyzed at the DATCP Bureau of Laboratory Services. The DATCP lab analyzed the samples for parent alachlor, acetochlor, and metolachlor as well as several other pesticide compounds and nitrate-nitrogen. The DATCP lab uses gas chromatography to identify and quantify these compounds and gas chromatography/mass spectrometry to confirm them. The LOQs are 0.10 ug/L for acetochlor, 0.15 ug/L for alachlor, and 0.25 ug/L for metolachlor.

RESULTS

Monitoring Wells

Table 1 shows the parent and metabolite results for the 27 monitoring wells in the study. These results show that the ESA and OA metabolites of metolachlor and alachlor were commonly detected in the shallow groundwater accessible by these wells. Acetochlor metabolites were detected less frequently, probably because acetochlor products have only been in use in Wisconsin since 1994. One monitoring well result exceeded the Wisconsin interim health advisory level of 20 ug/l for alachlor ESA. The parent compounds were detected at a lesser frequency in the monitoring wells: metolachlor was detected in four wells and acetochlor in one.

Table 1. Summary of Sampling Results for Chloroacetanilide Herbicides and Metabolites in 27 Monitoring Wells in Wisconsin

<i>Compound</i>	<i>Wells Sampled</i>	<i>Wells with Detects</i>	<i>Percent Detect</i>	<i>Average Detect (ug/l)</i>	<i>Highest Detect (ug/l)</i>	<i>Groundwater Enforcement Standard (ug/l)</i>
Alachlor	27	0				2
Alachlor ESA*	27	22	81	4.7	33	
Alachlor OA	27	11	41	2.0	15	
Metolachlor	27	4	15	1.7	2.1	15
Metolachlor ESA	27	21	78	14	42	
Metolachlor OA	27	17	63	9.2	32	
Acetochlor	27	1	4	1.2	1.2	
Acetochlor ESA	27	9	33	2.9	6.4	
Acetochlor OA	27	5	19	0.94	1.8	

* Wisconsin Interim Health Advisory Level = 20 ug/l

Private Drinking Water Wells

Table 2 shows the parent and metabolite results for the 22 private drinking water wells in the study. As with the monitoring well results, the private drinking water wells showed a high frequency of detection of metolachlor and alachlor metabolites and a lower frequency of detection of acetochlor metabolites. Over 90 percent of these wells had detections of alachlor and metolachlor ESA. Metolachlor parent was detected in eight private wells and alachlor parent was detected in three private wells.

Table 2. Summary of Sampling Results for Chloroacetanilide Herbicides and Metabolites in 22 Private Drinking Water Wells in Wisconsin

<i>Compound</i>	<i>Wells Sampled</i>	<i>Wells with Detects</i>	<i>Percent Detect</i>	<i>Average Detect (ug/l)</i>	<i>Highest Detect (ug/l)</i>	<i>Groundwater Enforcement Standard (ug/l)</i>
Alachlor	22	3	14	0.23	0.28	2
Alachlor ESA*	22	20	91	3.5	9.0	
Alachlor OA	22	16	73	3.2	34	
Metolachlor	22	8	36	1.4	5.9	15
Metolachlor ESA	22	20	91	4.9	18	
Metolachlor OA	22	19	86	3.7	23	
Acetochlor	22	0				
Acetochlor ESA	22	3	14	1.8	3.4	
Acetochlor OA	22	2	9	1.1	1.9	

* Wisconsin Interim Health Advisory Level = 20 ug/l

Municipal Wells

Table 3 shows the parent and metabolite results for the 23 municipal wells in the study. As with the monitoring well and private well results, the municipal wells showed a higher frequency of detection of metolachlor and alachlor metabolites than the other analytes. There were no detections of acetochlor or acetochlor metabolites, probably due to the relatively short period that acetochlor products have been used in Wisconsin and the longer groundwater flow paths for municipal wells. In general, the frequency of detections was less for the municipal wells than for the monitoring and private wells, but the municipal wells did show significant impacts. Fifty-two percent of the municipalities had a detection of at least one of the metabolites. Of the seven largest municipalities in the study, three contained alachlor and metolachlor metabolites. One municipal well contained parent alachlor at 0.67 ug/l, which is above the Wisconsin preventive action limit (PAL) for this compound.

Table 3. Summary of Sampling Results for Chloroacetanilide Herbicides and Metabolites in 23 Municipal Wells in Wisconsin

<i>Compound</i>	<i>Wells Sampled</i>	<i>Wells with Detects</i>	<i>Percent Detect</i>	<i>Average Detect (ug/l)</i>	<i>Highest Detect (ug/l)</i>	<i>Groundwater Enforcement Standard (ug/l)</i>
Alachlor	23	1	4.3	0.67	0.67	2
Alachlor ESA*	23	11	48	1.9	4.4	
Alachlor OA	23	4	17	0.81	1.4	
Metolachlor	23	0				15
Metolachlor ESA	23	9	39	1.3	4.6	
Metolachlor OA	23	8	35	0.57	2.7	
Acetochlor	23	0				
Acetochlor ESA	23	0				
Acetochlor OA	23	0				

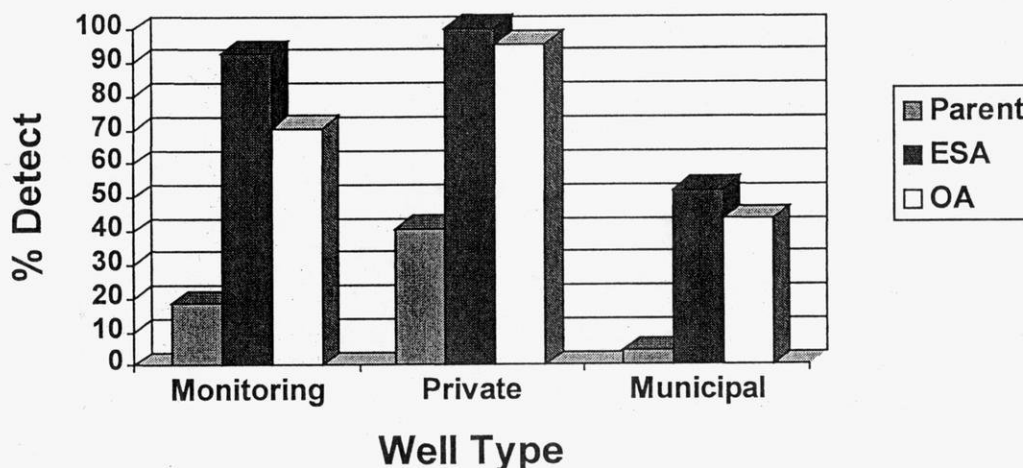
* Wisconsin Interim Health Advisory Level = 20 ug/l

DISCUSSION

In this sampling program, the metabolites of alachlor, metolachlor and acetochlor were detected much more frequently than their respective parent compounds. Investigators in other states (Kalkhoff, S.J. et. al., 1998) have reported similar findings. This is probably because the metabolites have higher water solubility than the parent compounds (Thurman et. al, 1996). In the monitoring well portion of the study, for example, alachlor and metolachlor ESA were detected in approximately 80 percent of the wells that were tested whereas parent metolachlor was detected in only 15 percent of these wells and parent alachlor was not detected at all. This same trend was also observed on the private

and municipal wells. Figure 3 shows the frequency of detection for the parent compounds, ESA metabolites, and OA metabolites.

Figure 3. Percent Detection of Parent Compounds, ESA Degradates, and OA Degradates, by Well Type



The general order of detection frequency in this study was ESA metabolites → OA metabolites → parent compound. Alachlor and metolachlor ESA were detected at approximately the same frequency, but metolachlor OA was detected somewhat more frequently than alachlor OA. Acetochlor metabolites were detected less than alachlor and metolachlor metabolites, probably because acetochlor products have only been in use in Wisconsin since 1994. Future use patterns and groundwater studies will determine if acetochlor metabolites become as common in Wisconsin groundwater as the metabolites of alachlor and metolachlor.

A wide range of concentrations was found for the analytes detected in this study. Metolachlor ESA was detected at the highest concentrations with average detect concentrations of 14 ug/l in monitoring wells, 4.9 ug/l in private wells, and 1.3 ug/l in municipal wells. The highest concentration detected in the study was a metolachlor ESA level of 42 ug/l in a monitoring well. The only metabolite with a water quality guideline in Wisconsin is alachlor ESA which has an interim health advisory level of 20 ug/l. One monitoring well exceeded this level. No water quality standards exist for the other five metabolites in this study.

The municipal wells, which are generally deeper and have well casing to a greater depth, were impacted somewhat less than the monitoring wells and the private drinking water wells. However, alachlor ESA, metolachlor ESA, and metolachlor OA were detected in 48, 39 and 35 percent, respectively, of the municipal wells. Average concentrations of detections were also lower in the municipal wells.

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