# The Acetochlor Registration Partnership Surface Water Monitoring Program for Four Corn Herbicides

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## ABSTRACT

**A surface drinking water monitoring program for four corn (*Zea mays* L.) herbicides was conducted during 1995–2001. Stratified random sampling was used to select 175 community water systems (CWSs) within a 12-state area, with an emphasis on the most vulnerable sites, based on corn intensity and watershed size. Finished drinking water was monitored at all sites, and raw water was monitored at many sites using activated carbon, which was shown capable of removing herbicides and their degradates from drinking water. Samples were collected biweekly from mid-March through the end of August, and twice during the off-season. The analytical method had a detection limit of 0.05 μg $L^{-1}$ for alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)-acetamide] and 0.03 μg $L^{-1}$ for acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)-acetamide], atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine], and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)-acetamide]. Of the 16 528 drinking water samples analyzed, acetochlor, alachlor, atrazine, and metolachlor were detected in 19, 7, 87, and 53% of the samples, respectively. During 1999–2001, samples were also analyzed for the presence of six major degradates of the chloroacetanilide herbicides, which were detected more frequently than their parent compounds, despite having higher detection limits of 0.1 to 0.2 μg $L^{-1}$. Overall detection frequencies were correlated with product use and environmental fate characteristics. Reservoirs were particularly vulnerable to atrazine, which exceeded its 3 μg $L^{-1}$ maximum contaminant level at 25 such sites during 1995–1999. Acetochlor annualized mean concentrations (AMCs) did not exceed its mitigation trigger (2 μg $L^{-1}$) at any site, and comparisons of observed levels with standard measures of human and ecological hazards indicate that it poses no significant risk to human health or the environment.**

ACETOCHLOR is a selective herbicide used for pre- and early post-emergent control of annual grasses and certain broadleaf weeds in corn, often in combination with other herbicides, most typically atrazine. The USEPA granted a conditional registration on 11 Mar. 1994 to the Acetochlor Registration Partnership (ARP), consisting originally of Monsanto and Zeneca, and as of fall 2000, consisting of Monsanto and Dow AgroSciences.

Several unique factors were involved in the registration of acetochlor (USEPA, 1994). The ARP expected, and USEPA required, that market forces following the registration of acetochlor would reduce the mass of corn herbicides applied in the United States by substituting reduced-rate acetochlor formulations for previously registered corn herbicides such as alachlor, metolachlor, atrazine, 2,4-D, butylate, and EPTC. This was borne out by USDA figures (National Agricultural Statistics Service, 2004), which show that the total amount of these six herbicides applied to corn during the first four years of the acetochlor registration (1994–1997) fell by 83.5 million kg from the amount applied the previous four years (Fig. 1). The amount of acetochlor applied during this same period was 40.3 million kg, thereby exceeding the reduction required by USEPA.

In addition to the use reduction target, the USEPA imposed conditions on acetochlor intended to limit potential risks to human health and the environment, including an extensive surface water monitoring program involving 175 CWSs. The ARP agreed to suspend sales and use of acetochlor in any watershed where the time-weighted AMC of acetochlor in drinking water exceeded 2 μg $L^{-1}$ (USEPA, 1994) and to voluntarily cancel the USEPA registration of acetochlor if the AMC exceeded 2 μg $L^{-1}$ in either two large (>100 000 people) CWSs or 10 of any size. The USEPA set this value of 2 μg $L^{-1}$ for acetochlor as a conservative limit based on the 2 μg $L^{-1}$ maximum contaminant level (MCL) it had already established for alachlor (USEPA, 1998) and an unpublished assessment indicating that acetochlor was less toxic than alachlor. When the study began, only active ingredients were measured. In 1999, the ARP agreed to continue the monitoring program for two additional years and expand it to include two soil degradates of acetochlor, acetochlor ethanesulfonic acid (ESA) and acetochlor oxanilic acid (OXA), as well as the corresponding degradates of alachlor and metolachlor (Fig. 2, Table 1). Degradates of atrazine have been monitored by others (e.g., USGS, 1999) and were not included in this program.

Large-scale surveys detail the presence of agricultural chemicals, particularly corn herbicides, in surface water and drinking water derived from surface water in the U.S. Midwest (Richards et al., 1996, 2002; Clark et al., 1999). Following the introduction of acetochlor, several ongoing surface water monitoring programs were expanded to include acetochlor (Clark and Goolsby, 1999; Capel et al., 1995; Kolpin et al., 1996). Programs were expanded to include common soil degradates of acetani-

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**Abbreviations:** AMC, annualized mean concentration; ARP, Acetochlor Registration Partnership; CWS, community water system; ESA, ethanesulfonic acid; GAC, granular activated carbon; LOD, limit of detection; LOQ, limit of quantitation; MOE, margin of exposure; NOEL, no observable effect level; OXA, oxanilic acid; PAC, powdered activated carbon; RfD, reference dose for a toxicity effect.

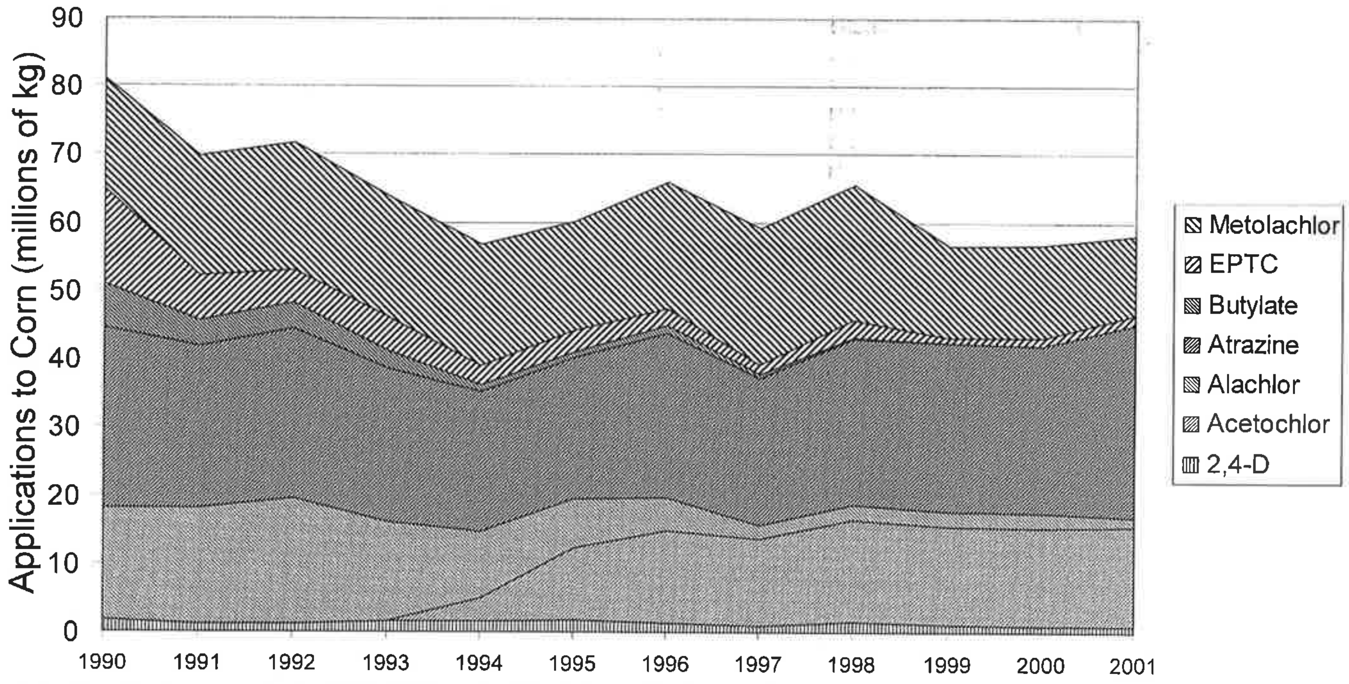

**Fig. 1. Corn herbicide use trends (1990–2001) in the United States (National Agricultural Statistics Service, 2004).**

lide corn herbicides beginning in the mid-1990s (Thurman et al., 1996; Kalkhoff et al., 1998). The results of these numerous, multisite and multiyear studies generally show soil-applied corn herbicides and their degradates to be the most prevalent agricultural pesticides found, both in terms of frequency of detections and the levels observed. The peak concentrations occur in the spring, driven by runoff. This previous work also showed that the soil degradates of the chloroacetanilide class of herbicides occur more frequently than the parent compounds and persist longer throughout the season (Thurman et al., 1996).

This paper presents the methods, results, and interpretation of the acetochlor surface water monitoring program. Two distinct acetochlor ground water monitoring programs are described in companion publications (de Guzman et al., 2005; Newcombe et al., 2005). We begin with the methods used, focusing on site selection and sampling logistics. We then present analytical results and explore the factors that contributed to their variation. We conclude with the application of these findings to risk assessment for both human health and ecological end-points.

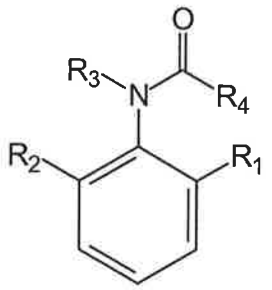

**Fig. 2. Herbicide structure.**

## MATERIALS AND METHODS

### Site Selection and Characterization

A total of 175 CWSs with watersheds in corn-producing areas of Delaware, Illinois, Indiana, Iowa, Kansas, Maryland, Minnesota, Missouri, Nebraska, Ohio, Pennsylvania, and Wisconsin, were selected for the program (Fig. 3), based on anticipated acetochlor use and regulatory requirements. Except for two sites, all CWSs used only surface water or could exclusively sample surface water. The two sites that occasionally blended small amounts of ground water were included at the specific request of the CWS or the relevant state, with the prior approval of USEPA.

Stratified random sampling was used to select CWSs for monitoring (Table 2). Disjoint (non-overlapping) strata were created by placing each CWS from the 12 states into one of five categories based on watershed size and corn intensity, defined as the percent of total watershed area planted in corn based on area-weighted county level USDA data for 1992 (National Agricultural Statistics Service, 2004), as shown in Table 2 and Fig. 3. The selection process was designed to be representative of all CWSs within these 12 states and yet focus on those most likely to be vulnerable to contamination by corn herbicides: smaller watersheds in areas of high corn production. Community water systems using small watersheds with corn intensity less than 5% were not included, as these were judged less likely to contain the corn herbicides of interest.

We employed a stepwise process to define the total target population of qualifying CWSs and select actual monitoring sites. Lists of candidate CWSs for all 12 states came from the USEPA, the American Water Works Association, and the states themselves. Phone interviews confirmed whether the CWS was willing to cooperate, and that it either used only surface water or was able to exclusively sample surface water. The precise locations of the primary and back-up drinking water intakes were confirmed during these calls, which permitted subsequent analysis using geographic information systems (GIS) software to draw watershed boundaries. Each CWS was then placed in a sampling stratum based on its watershed size and corn intensity. A total of 306 CWSs made up the target population.

All CWSs using smaller watersheds with corn intensity greater than 20% were selected for monitoring. In most states, the less vulnerable strata had successively fewer CWSs selected. Whenever fewer than all of the CWSs within a stratum were selected, the selections were made randomly. The final distribution of selected CWSs by state, watershed size, and corn intensity is presented in Table 2. Most of the selected CWSs are located on watersheds with higher corn intensity, but the program also included CWSs from other areas. Characteristics of the CWSs and their primary watershed are listed in Table 3. The categories of water sources include two types of reservoirs. Those formed by dams would be expected to have greater vulnerability than those pumped from rivers, as operators of the latter kind may be able to avoid pumping during times of high pesticide runoff.

Detailed watershed maps were produced for each watershed by hand digitization from a USGS topographic map of the appropriate scale and further spatial processing using GIS. Both historical and contemporaneous average monthly rainfall totals (EarthInfo, 2002) were determined for all of the smaller watersheds using weather stations within or closest to the watershed centroids, as determined by GIS. For watersheds with multiple stations, a simple average was computed. If data were missing, data from the next closest station were used.

All CWSs were inspected to verify site and watershed data and to train CWS personnel on water-sampling procedures. The CWSs served populations ranging from 167 to 5 100 000 people, and their watershed areas ranged from 0.34 to 1 800 000 km$^2$. The method of water treatment at each CWS was recorded. All used disinfection (typically chlorination) and some additional form of conventional treatment (coagulation, flocculation, sedimentation, and filtration). Several CWSs used either granular (GAC) or powdered activated carbon (PAC) as shown in Table 3.

The total number of CWSs was kept at 175 for the first five years, with fewer than three sites requiring replacement in any year (for instance when the site switched to a ground water source). Sites were replaced by CWSs from the same or a higher vulnerability stratum. Several CWSs chose not to continue when the monitoring was extended for a final two years, dropping the number of sites to 156 in 2000, and to 152 in 2001, when the USEPA no longer required a total of 175 sites to be monitored. A total of 189 distinct CWSs were monitored for at least one year.

## Sampling

All sampling and analysis of samples followed USEPA Good Laboratory Practices (USEPA, 1989). Finished drinking water was sampled at the compliance point. Although not the primary focus of the study, raw water was also collected at 44 sites that used activated carbon treatment. These additional raw water samples were collected at the specific request of the CWS or the state.

Systematic sampling (every two weeks) was employed during the herbicide application and corn-growing season, from mid-March through late-August: 12 such samples were collected each year at each site. One sample was collected in November to represent the autumn months, and another in January to represent the winter months. In 2001, the final sample was collected in December rather than November. All samples were collected at prescheduled dates regardless of hydrologic conditions. Only a few (<1%) of all possible sam-

**Table 1. Acetanilide herbicides and their degradates included in the monitoring study.**

| $R_1$ | $R_2$ | $R_3$ | $R_4$ | Common name | Chemical name (CAS) | LOD/LOQ† | CAS number | $K_{oc}$‡ | $DT_{50}$‡ | SWMI‡ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $\mu g\ L^{-1}$ | | $L\ kg^{-1}$ | d | |
| $CH_3$ | $CH_3CH_2$ | $CH_2OCH_2CH_3$ | $CH_2Cl$ | acetochlor | 2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide | 0.03/0.05 | 34256-82-1 | 130 | 13 | 0.5432 |
| $CH_3CH_2$ | $CH_3CH_2$ | $CH_2OCH_3$ | $CH_2Cl$ | alachlor | 2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide | 0.05/0.05 | 15972-60-8 | 170 | 15 | 0.5207 |
| $CH_3$ | $CH_3CH_2$ | $CH(CH_3)CH_2OCH_3$ | $CH_2Cl$ | metolachlor | 2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide | 0.03/0.05 | 51218-45-2 | 200 | 90 | 0.5969 |
| $CH_3$ | $CH_3CH_2$ | $CH_2OCH_2CH_3$ | $CH_2SO_3H$ | acetochlor sulfonic acid | 2-[(ethoxymethyl)(2-ethyl-6-methylphenyl)amino]-2-oxoethanesulfonic acid | 0.20/0.50 | 187022-11-3 | NA§ | NA | NA |
| $CH_3$ | $CH_3CH_2$ | $CH_2OCH_2CH_3$ | $CO_2H$ | acetochlor oxanilic acid | [(ethoxymethyl)(2-ethyl-6-methylphenyl)amino]oxoacetic acid | 0.10/0.50 | 194992-44-4 | NA | NA | NA |
| $CH_3CH_2$ | $CH_3CH_2$ | $CH_2OCH_3$ | $CH_2SO_3H$ | alachlor sulfonic acid | 2-[(2,6-diethylphenyl)(methoxymethyl) amino]-2-oxoethanesulfonic acid | 0.20/0.50 | 142363-53-9 | NA | NA | NA |
| $CH_3CH_2$ | $CH_3CH_2$ | $CH_2OCH_3$ | $CO_2H$ | alachlor oxanilic acid | [(2,6-diethylphenyl)(methoxymethyl) amino]oxoacetic acid | 0.10/0.50 | 171262-17-2 | NA | NA | NA |
| $CH_3$ | $CH_3CH_2$ | $CH(CH_3)CH_2OCH_3$ | $CH_2SO_3H$ | metolachlor sulfonic acid | 2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid | 0.20/0.50 | 171118-09-5 | NA | NA | NA |
| $CH_3$ | $CH_3CH_2$ | $CH(CH_3)CH_2OCH_3$ | $CO_2H$ | metolachlor oxanilic acid | [(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino] oxoacetic acid | 0.10/0.50 | 152019-73-3 | NA | NA | NA |
| | | | | atrazine¶ | 6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine | 0.03/0.05 | 1912-24-9 | 100 | 60 | 0.7184 |

† Limit of detection (LOD) and limit of quantitation (LOQ) of analytical methods used in this study.

‡ $K_{oc}$ is the soil–water partition coefficient normalized by soil organic carbon content. $DT_{50}$ is the time required for first 50% of applied compound to dissipate from soil. SWMI is the Surface Water Mobility Index (Chen et al., 2002). Data for these three columns are from Chen et al. (2002), except for acetochlor data, which is from Gustafson et al. (2004).

§ Not available.

¶ Atrazine, which is not a chloroacetanilide herbicide, was also monitored in this study.

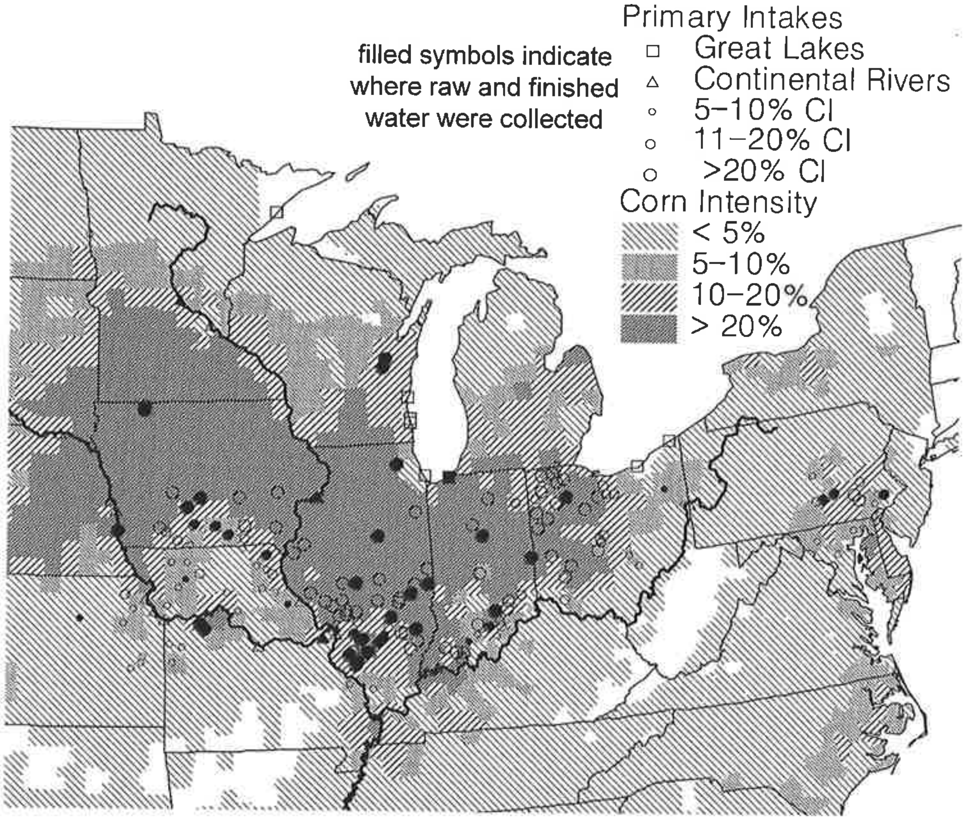

**Fig. 3. Map showing the location of all monitored community water systems (CWSs). CI, corn intensity.**

pling events were missed, and a few sites occasionally collected samples blended from ground water sources due to seasonal or logistical factors. Such blended samples represent less than 1% of the total number collected. A total of 16 528 finished drinking water samples and 3325 raw water samples were collected and analyzed during the program.

Community water system personnel collected and shipped all water samples. Participants followed Standard Operating Procedures (SOPs) for sampling, packaging, and shipping. New operators were trained before their first sample collection. Precleaned 250-mL polyethylene (Nalgene; Nalge Nunc, Rochester, NY) or amber glass bottles were used to collect each sample. All samples were collected in duplicate. Glass bottles were used in the first two to three years, but were replaced by the more rugged fluorinated polyethylene. If the sampling tap did not run continuously, it was allowed to run for 2 min before sample collection. Sample bottles were rinsed twice with sample water before filling the sample bottle with a water sample. Each sample bottle was filled to the shoulder and capped immediately, and the cap was secured with electrical tape. Each bottle was placed in two plastic zipper-lock bags for protection and packed into an insulated shipping container with frozen artificial ice packs. A chain-of-custody form was signed and dated, with a copy of the form placed into a plastic zipper-lock bag and then into the same shipping container, which was then shipped by overnight courier to the analytical facility at Monsanto in St. Louis, MO. A detailed system for tracking sample bottles from each sample event was maintained.

### Sample Analysis

We employed two analytical methods, one for parent compounds and the other for degradates. Both relied on mass spectrometry for detection. Samples were generally not filtered before analysis, although raw water samples occasionally required the use of a sea sand filtration step. Parent herbicides were analyzed using stable isotope dilution gas chromatography–mass spectrometry (GC–MS), preceded by solid phase extraction for cleanup and concentration (Hackett et al., 2003). The method involved addition of deuterated analogs of each analyte, as internal standards, to a 200-mL water sample before extraction, concentration, and analysis.

We analyzed for the oxanilic and sulfonic acid degradates of acetochlor, alachlor, and metolachlor by direct aqueous injection reversed-phase liquid chromatography tandem mass spectrometry (LC–MS–MS). The samples were injected directly into an LC–MS–MS (HP1100/Sciex API-3000; Sciex, Concord, ON, Canada) without prior concentration, cleanup, or filtration (Hackett et al., 2003).

All surface water samples were refrigerated at 2 to 10°C on receipt at Monsanto, before extraction or preparation for analysis. Replicate samples were transferred to a freezer at −20 ± 5°C. Sample extracts were either analyzed immediately or refrigerated at 2 to 10°C until analysis. All reported analytes demonstrated acceptable storage stability under these conditions, which was confirmed both through separate storage stability studies and by analysis of field-fortified samples. The median times from collection to extraction and collection to analysis were 7 and 9 d, respectively.

## RESULTS AND DISCUSSION

### Rainfall Conditions

The amount of rainfall in April, May, and June affects corn herbicide runoff because the herbicides are typically applied during these months. Rainfall during these three months was averaged across all monitored watersheds and compared with historical means (Table 4). These rainfall totals were above average in all years except for 1997. The year with the highest surplus precipitation (132.1 mm) was 1996, when 94% of the watersheds had above-normal rainfall for the April–June period.

## Analytical Results in Finished Drinking Water

To confirm compliance with the acetochlor mitigation trigger, time-weighted AMCs were calculated for all sites as follows:

$$\text{AMC} = \frac{(c_1 + c_0)(t_1 - t_0)/2 + (c_2 + c_1)(t_2 - t_1)/2 + \ldots + (c_n + c_{n-1})(t_n - t_{n-1})/2 + (c_n)(t_f - t_n)}{\text{number of days in the year}} \qquad [1]$$

where $c$ is the concentration, $t$ is the sample occasion, the subscripts refer to the sampling occasions, and $n$ is the number of sampling events in the year. The initial and final concentrations for each year ($c_0$ and $c_n$, respectively) were determined by linear interpolation to the dates 1 January and 31 December, respectively. For the very first (March 1995) and very last (December 2001) samples, the concentration measured was assumed to remain constant before and after that time, respectively. The concentration values used for this determination are the raw numeric response values without censoring or rounding, regardless of whether the value was below the limit of quantitation (LOQ; i.e., concentration below which the measured concentration has a coefficient of variation greater than a specified amount, generally 10%) or limit of detection (LOD; i.e., concentration below which it cannot be concluded with certainty that the analyte was detected). Many of the resulting values are therefore below the LOQ, but these are considered to be the best available estimates of the true AMCs. Unless stated otherwise, all statements presented below as being statistically significant have been evaluated using the standard $t$ test with probability less than 0.05.

Shown in Fig. 4 is a box-plot of the AMCs measured during the seven years of monitoring for the parent herbicides. Alachlor exhibits a steady downward trend, which is consistent with its declining use during this period (National Agricultural Statistics Service, 2004). The significance of this trend was confirmed by showing that more than 5% of individual sites (122/188) exhibited a significant downward trend with time. Atrazine (55/188) and metolachlor (67/188) display weaker downward trends, but are still significant using this same test. Acetochlor concentrations remained relatively stable over the period. Concentrations of all parent herbicides were highest during 1996, probably as a result of the higher April–June rainfall in that year.

The relative order of the concentrations is atrazine > metolachlor > acetochlor > alachlor, generally consistent with relative use (Fig. 1). This is more easily seen in Fig. 5, which shows the detection frequency of each

**Table 2. Sampling frame showing distribution of the 175 initial sampling locations.**

| Sampling stratum | CWS† distribution | State |  |  |  |  |  |  |  |  |  |  |  | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Delaware | Illinois | Indiana | Iowa | Kansas | Maryland | Minnesota | Missouri | Nebraska | Ohio | Pennsylvania | Wisconsin |  |
| Great Lakes | total available |  | 13 | 4 |  |  |  | 4 |  |  | 21 | 2 | 12 | 56 |
|  | number selected |  | 1 | 1 |  |  |  | 1 |  |  | 2 | 0 | 3 | 8 |
| Continental rivers | total available |  | 9 | 2 | 1 | 3 |  | 2 | 12 | 3 | 5 | 3 |  | 40 |
|  | number selected |  | 2 | 2 | 1 | 3 |  | 2 | 3 | 3 | 1 | 0 |  | 17 |
| Small watersheds 5 to 10% Corn intensity | total available | 2 | 3 | 4 | 1 | 5 | 5 | 1 | 25 |  | 16 | 25 |  | 87 |
|  | number selected | 2 | 1 | 4 | 1 | 5 | 5 | 1 | 17 |  | 4 | 3 |  | 43 |
| Small watersheds 11 to 20% Corn intensity | total available |  | 7 | 5 | 6 | 1 |  |  | 3 |  | 13 | 12 |  | 47 |
|  | number selected |  | 5 | 5 | 6 | 1 |  |  | 3 |  | 6 | 5 |  | 31 |
| Small watersheds >20% Corn intensity | total available |  | 33 | 10 | 8 |  |  |  | 2 | 1 | 17 | 2 | 3 | 76 |
|  | number selected |  | 33 | 10 | 8 |  |  |  | 2 | 1 | 17 | 2 | 3 | 76 |
| Total | total available | 2 | 65 | 25 | 16 | 9 | 5 | 7 | 42 | 4 | 72 | 44 | 15 | 306 |
|  | number selected | 2 | 42 | 22 | 16 | 9 | 5 | 4 | 25 | 4 | 30 | 10 | 6 | 175 |

† Community water system.

**Table 3. Characteristics of monitored community water systems (CWSs) and their primary watersheds.**

| | | | Number using activated carbon | | | Median value for primary source of the CWS | |
|---|---|---|---|---|---|---|---|
| Stratum | Source type | Sites | GAC† only | PAC‡ only | GAC + PAC | Watershed area | Corn intensity |
| | | | | | | km² | % |
| >20% Corn intensity | reservoir (D§) | 35 | 5 | 18 | 4 | 12 | 27.4 |
| | reservoir (P¶) | 22 | 1 | 16 | 0 | 4 754 | 26.7 |
| | river | 16 | 0 | 9 | 4 | 687 | 28.3 |
| | lake | 10 | 1 | 4 | 3 | 150 | 29.9 |
| 11 to 20% Corn intensity | reservoir (D) | 18 | 5 | 6 | 1 | 11 | 13.7 |
| | reservoir (P) | 8 | 0 | 4 | 0 | 945 | 17.2 |
| | river | 8 | 1 | 4 | 2 | 289 | 12.6 |
| 5 to 10% Corn intensity | reservoir (D) | 29 | 1 | 20 | 2 | 7 | 8.4 |
| | reservoir (P) | 6 | 0 | 4 | 0 | 1 126 | 9.5 |
| | river | 10 | 0 | 7 | 0 | 275 | 8.9 |
| Continental rivers | river | 19 | 1 | 15 | 1 | 466 632 | 5.6 |
| Great Lakes | lake | 8 | 1 | 6 | 0 | 116 782 | 8.9 |

† Granular activated carbon.
‡ Powdered activated carbon.
§ Reservoir formed by dam.
¶ Reservoir filled by occasional pumping from a river.

herbicide as a function of product use on corn in that year (National Agricultural Statistics Service, 2004). The other main sources of variation in this figure are spring rainfall and environmental fate characteristics. This was shown by fitting a three-parameter linear regression model to the detection frequencies (Table 5). The fitted regression equation ($r^2 = 0.98$) is:

$$\text{detection frequency (\%)} = -3.06 + (5.81 \times \text{SWMI}) + (0.00063 \times \text{PRCP}_s) + (0.20 \times \text{USE}) \quad [2]$$

where the effect of fate properties of the herbicides is represented by the unitless surface water mobility index (SWMI) (Chen et al., 2002). The surplus April–June precipitation (mm) is $\text{PRCP}_s$, as defined in Table 4. The nationwide use on corn (kg ha$^{-1}$) is USE, as plotted on the abscissa of Fig. 5. This regression model should not be extrapolated to other products without suitable testing. Its sole purpose here is to demonstrate that annual detection frequencies for these four corn herbicides are well described (98% of the variability) by three factors alone: fate characteristics, spring rainfall, and use.

Shown in Fig. 6 is a box-plot of the AMCs measured during the three years of monitoring for the chloroacetanilide degradates. There is a high degree of year-to-year consistency, and each degradate occurs at higher levels and more frequently than its corresponding parent. There are differences in the relative abundance of the ESA and OXA degradates for all three herbicides.

**Table 4. Comparison of actual vs. normal April–June precipitation for the monitored watersheds.**

| Year | Surplus April–June precipitation† | Watersheds with above-normal precipitation for April–June period |
|---|---|---|
| | mm | % |
| 1995 | 111.8 | 85 |
| 1996 | 132.1 | 94 |
| 1997 | −4.3 | 40 |
| 1998 | 35.6 | 90 |
| 1999 | 14.2 | 66 |
| 2000 | 15.5 | 76 |
| 2001 | 7.1 | 57 |

† Observed three-month precipitation totals (April–June) minus long-term average precipitation for the same three-month period (average of all watersheds by year).

For acetochlor, OXA is present at higher levels than ESA (mean pair-wise difference in AMCs is 0.03 μg L$^{-1}$). This trend is the opposite of what is seen for acetochlor degradates in shallow ground water, where acetochlor ESA is more frequently detected than acetochlor OXA and at higher concentrations (de Guzman et al., 2005). For both alachlor and metolachlor, ESA is more prevalent in surface water than OXA, by an average of 0.04 and 0.14 μg L$^{-1}$, respectively.

## Effect of Carbon Treatment on Residues

The reduction of parent and degradate concentrations when carbon treatment was present was evaluated for the 44 sites where both raw and finished water were collected. Although raw and finished water samples were collected at the same time, they did not represent true "before and after" samples due to finite residence times within the treatment facilities. This contributes to variability of the calculated reductions, but should not introduce any systematic bias. By comparing AMCs rather than individual sample pairs, any errors due to residence time should cancel out. The averaging effect is particularly strong here because multiple CWSs are considered in each carbon treatment group (see Table 6). It must be emphasized that this represents average reductions across multiple CWSs operating under normal operating conditions, rather than a controlled experiment on the effectiveness of carbon treatment.

On average, activated carbon treatment reduced parent herbicide concentrations by about half. The two carbon treatment types (GAC or PAC) had similar efficacy. Activated carbon treatment also reduced degradate concentrations, but less than for parent. This is likely due to the more polar nature of these degradates, as detailed in a recent laboratory study (Gustafson et al., 2003), which showed that 90 to 95% of the parent herbicides and 40 to 80% of the acetanilide degradates were removed from a variety of water sources using PAC at 20 mg L$^{-1}$ and a contact time of 60 min.

## Detailed Examination of Results

Acetochlor was detected in 18.8% of the finished drinking water samples. Only 0.3% of the 16 528 individ-

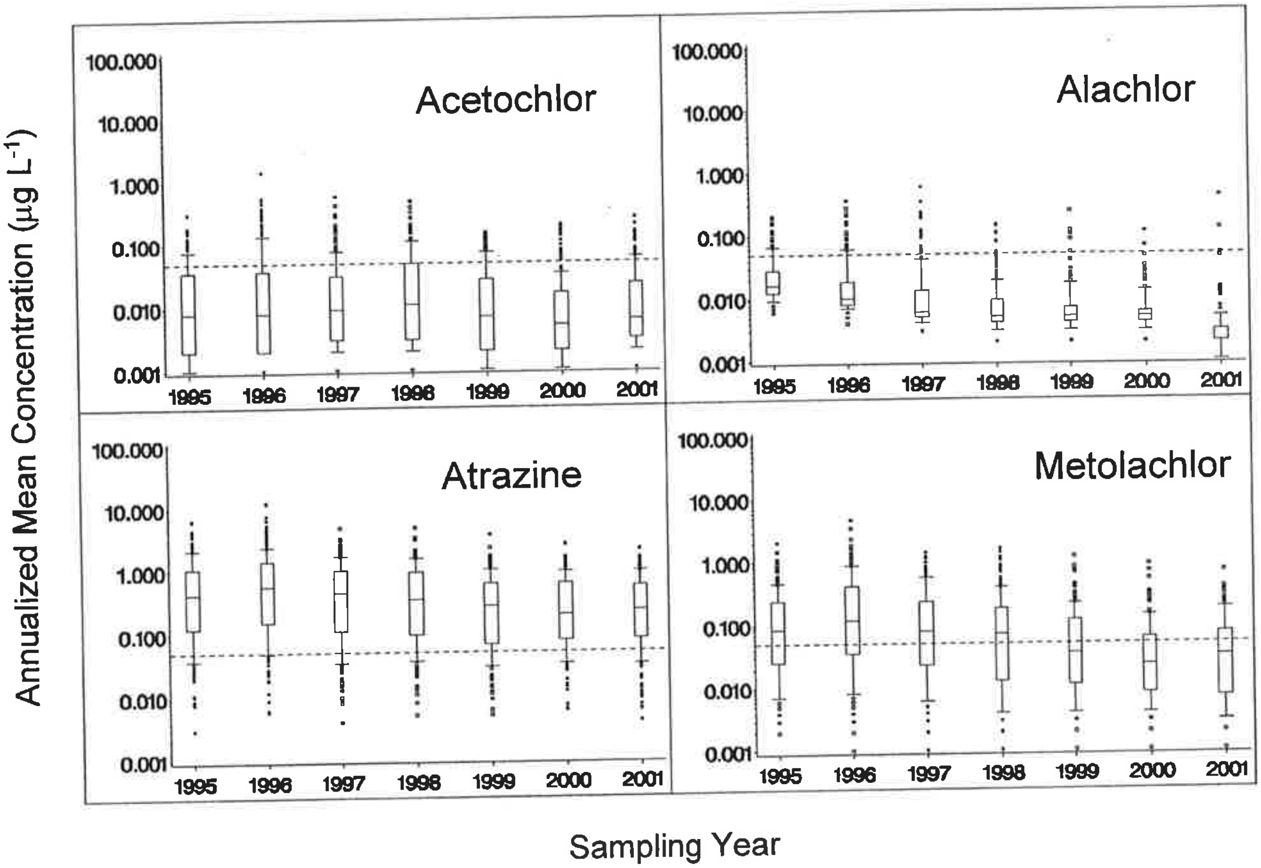

**Fig. 4. Box plot of annualized mean concentrations (AMCs) of parent herbicides in finished drinking water. The dashed line is the limit of quantitation (LOQ) for individual samples.**

ual drinking water samples had acetochlor concentrations greater than 2 µg $L^{-1}$. Such acetochlor residues (>2 µg $L^{-1}$) occurred only in the months of May and June. The highest measured value (18.2 µg $L^{-1}$) was found at Gillespie, Illinois, in a sample collected on 15 May 1996. As at all other sites with higher detections, this acetochlor residue declined quite rapidly, falling to 7.55 µg $L^{-1}$ two weeks later. Gillespie uses as its drinking water source a reservoir on a small watershed (1200 ha) in a region of high corn intensity (30.3%). Like much

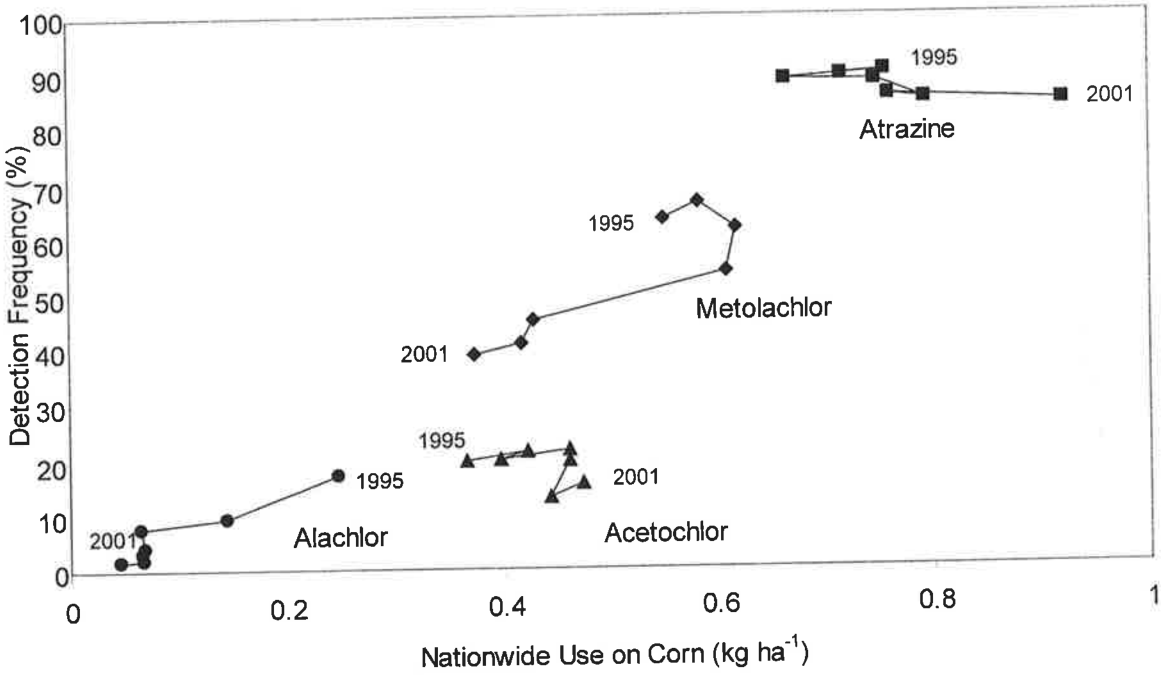

**Fig. 5. Frequency of drinking water detections by year for parent herbicides as a function of use.**

**Table 5. Three-parameter linear regression model for overall frequency of detection in drinking water ($r^2 = 0.98$).**

| Term | Coefficient | Standard error | $p$ |
|---|---|---|---|
| Intercept | −3.06 | 0.22 | <0.0001 |
| SWMI† | 5.81 | 0.43 | <0.0001 |
| Surplus April–June precipitation (mm) | 0.00063 | 0.00019 | 0.0025 |
| Use on corn (kg $ha^{-1}$) | 0.20 | 0.08 | 0.0237 |

† Surface water mobility index.

of the Corn Belt that year, the watershed experienced very heavy rains in the spring, receiving 319 mm of rainfall in the months of April and May alone, an amount expected to fall only once every 20 yr according to historical records (EarthInfo, 2002).

Acetochlor time-weighted AMCs in finished surface water from all sampling sites in all years were below the mitigation trigger level of 2 $\mu g\ L^{-1}$. For all AMCs, 91.9% were less than 0.1 $\mu g\ L^{-1}$ (Table 7), and the maximum AMC was 1.43 $\mu g\ L^{-1}$ at Gillespie in 1996. The second-highest acetochlor AMC was 0.58 $\mu g\ L^{-1}$ at Monroeville, Ohio, in 1997. The Monroeville drinking water intake is on the West Branch of the Huron River, with a drainage area of 56 000 ha. As at Gillespie in 1996, Monroeville received heavy rainfall in 1997, with 302 mm during the months of May and June, a two-month total that has an expected recurrence interval of 11.5 yr. The highest seven-year time-weighted mean concentration measured for acetochlor was at Gillespie (0.28 $\mu g\ L^{-1}$) and the second-highest such mean was at Monroeville (0.18 $\mu g\ L^{-1}$).

The degradates of acetochlor, alachlor, and metolachlor were all detected more frequently than their respective parent herbicides, despite their higher analytical limits of detection. The two acetochlor degradates, acetochlor ESA and acetochlor OXA, were detected in 24 and 42% of the finished drinking water samples, respectively. Where degradates occurred, acetochlor OXA was typically present at higher levels than acetochlor ESA, with 0.5% of the samples containing more than 2 $\mu g\ L^{-1}$ acetochlor OXA, compared with only 0.1% for acetochlor ESA. The highest measured values were 3.32 $\mu g\ L^{-1}$ for acetochlor ESA and 6.34 $\mu g\ L^{-1}$ for acetochlor OXA. The AMCs for acetochlor ESA and acetochlor OXA were also somewhat higher than those for parent acetochlor during the years of simultaneous monitoring (1999–2001). The highest observed AMCs were 1.01 $\mu g\ L^{-1}$ for acetochlor ESA and 1.69 $\mu g\ L^{-1}$ for acetochlor OXA. The percentage of AMCs greater than 0.5 $\mu g\ L^{-1}$ was 4.9% for acetochlor ESA and 8.5% for acetochlor OXA (Table 7).

## Effectiveness of the Sampling Stratification

As shown in Table 7, the monitoring results largely confirm the assumptions made in assigning the CWS to vulnerability strata. An apparent exception is that the continental rivers stratum had a frequency of parent

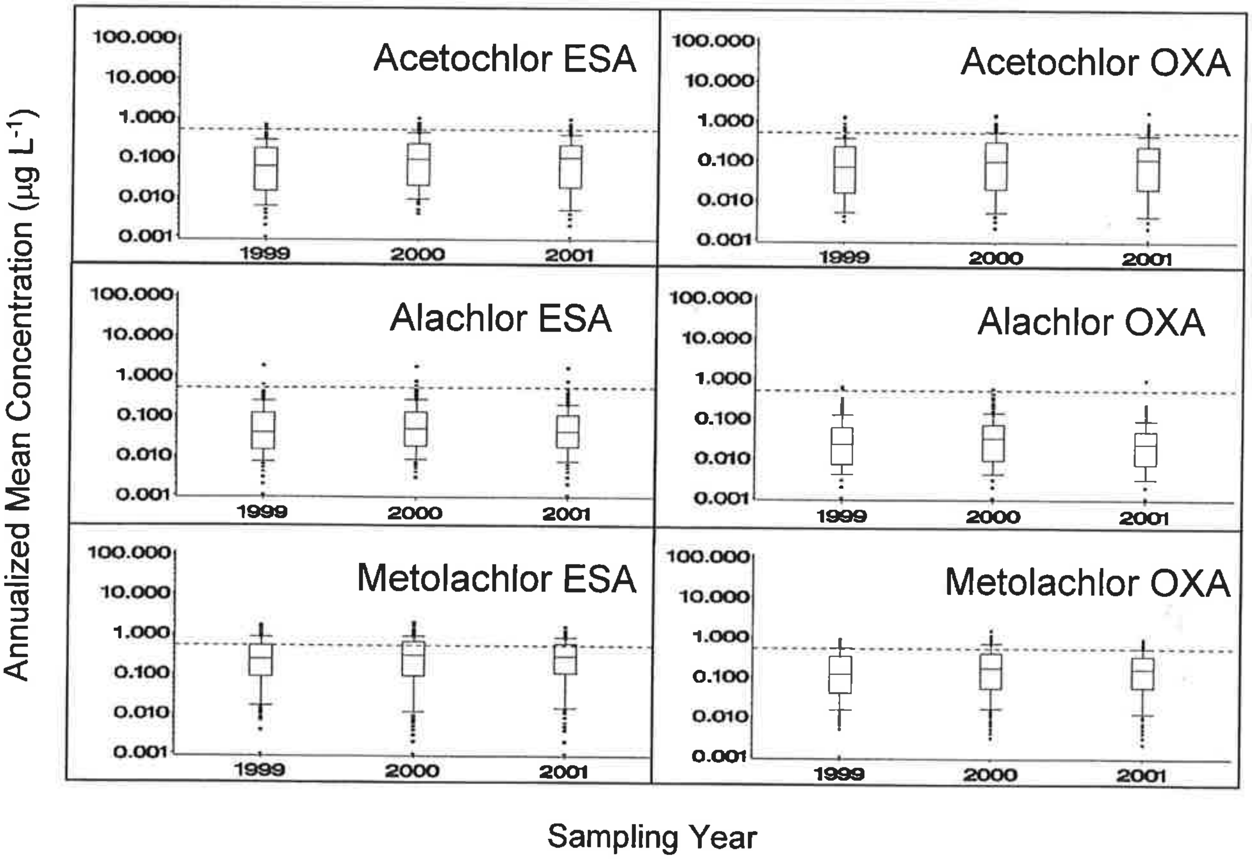

**Fig. 6.** Box plot of annualized mean concentrations (AMCs) of chloroacetanilide degradates in finished drinking water. The dashed line is the limit of quantitation (LOQ) for individual samples. ESA, ethanesulfonic acid; OXA, oxanilic acid.

**Table 6. Average percent reduction in annualized mean concentrations (AMCs) between raw and finished water samples at sites using activated carbon.**

| | | Average reduction in AMC | | | |
|---|---|---|---|---|---|
| **Compound†** | ***N*‡** | **Sites using PAC§ only** | **Sites using GAC¶ only** | **Sites using both PAC and GAC** | **Average of all sites** |
| | | % | | | |
| **Acetochlor** | **211** | **52.7** | **59.5** | **61.9** | **59.0** |
| **Alachlor** | **216** | **46.4** | **47.1** | **45.2** | **46.1** |
| **Atrazine** | **237** | **40.1** | **58.6** | **58.9** | **54.3** |
| **Metolachlor** | **228** | **47.6** | **55.4** | **58.4** | **54.9** |
| **Acetochlor ESA** | **85** | **34.5** | **31.7** | **36.5** | **34.5** |
| **Acetochlor OXA** | **95** | **29.7** | **27.1** | **35.6** | **30.8** |
| **Alachlor ESA** | **90** | **48.9** | **44.3** | **50.5** | **48.0** |
| **Alachlor OXA** | **88** | **34.8** | **31.0** | **35.0** | **33.3** |
| **Metolachlor ESA** | **107** | **32.9** | **29.8** | **37.7** | **33.6** |
| **Metolachlor OXA** | **107** | **33.6** | **30.3** | **37.8** | **34.0** |

† ESA, ethanesulfonic acid; OXA, oxanilic acid.

‡ Number of site years in which some reduction was achieved. When raw water AMCs were extremely low, there were some instances where finished water AMCs erroneously appeared higher than raw water AMCs, simply due to analytical noise. Such data were excluded from the averages shown.

§ Powdered activated carbon.

¶ Granular activated carbon.

herbicide AMCs > 0.1 μg $L^{-1}$ similar to that observed in the next two strata. However, the frequency of parent residues > 1.0 μg $L^{-1}$ fit the expected pattern. This suggests that major rivers have broader chemographs with smaller peak concentrations than smaller watersheds, as reported elsewhere (Gustafson et al., 2004).

## Effect of Water Source

The type of water source had no consistent effect on the frequency or magnitude of detections for most analytes, but there was a significant trend for atrazine (Fig. 7). Reservoirs formed by dams were most likely to have an atrazine AMC > 3 μg $L^{-1}$, representing 23 of the 26 total number of sites with such residues. Two of the other three sites also used reservoirs, but of the kind pumped from a river. The fact that the reservoir trend did not hold for the other analytes is probably linked to differences in the fate properties of atrazine, most likely its greater persistence (Table 1).

## Seasonal Variation of Residues

Parent acetochlor and alachlor were more frequently detected during April–June than at other times of the year (Fig. 8). Their frequency of detection fell slightly during the summer period (July–September) and both were rarely detected in the fall and winter periods. By contrast, both atrazine and metolachlor were most frequently detected in the summer period, but the degree of seasonal variation was minimal. This lack of seasonality was similar to the pattern exhibited by the degradates (Fig. 9). The different patterns are in accordance with the relatively short half-lives of both acetochlor and alachlor (Table 1), which apparently cause their concentrations to fall off more rapidly after the application season.

## Comparison with Other Sources

The concentrations found in this monitoring study are largely consistent with the findings of others (Capel et al., 1995; Kolpin et al., 1996; Thurman et al., 1996; Kalkhoff et al., 1998; Clark and Goolsby, 1999; Scribner et al., 2003; David et al., 2003; USEPA, 2004). The principal source of any apparent discrepancies may be assigned to differences in the sampling locations (e.g., CWSs vs. small creeks) and the actual matrix sampled (e.g., finished drinking water vs. raw water). With this

**Table 7. Occurrence of annualized mean concentrations (AMCs) in finished drinking water at various concentrations by sampling stratum.**

| | Occurrence | | | | | |
|---|---|---|---|---|---|---|
| | | | Smaller watersheds | | | |
| **AMC and analyte†** | **Great Lakes** | **Continental rivers** | **5 to 10% Corn intensity** | **11 to 20% Corn intensity** | **>20% Corn intensity** | **Overall** |
| **μg $L^{-1}$** | % | | | | | |
| **>0.1 Acetochlor** | **0.0** | **5.0** | **2.4** | **8.5** | **12.8** | **8.1** |
| **>1.0 Acetochlor** | **0.0** | **0.0** | **0.0** | **0.0** | **0.2** | **0.1** |
| **>0.5 Acetochlor ESA** | **0.0** | **0.0** | **0.9** | **1.0** | **10.6** | **4.9** |
| **>0.5 Acetochlor OXA** | **0.0** | **0.0** | **5.2** | **5.2** | **15.0** | **8.5** |
| **>0.1 Alachlor** | **0.0** | **0.0** | **3.1** | **5.8** | **2.6** | **2.9** |
| **>1.0 Alachlor** | **0.0** | **0.0** | **0.0** | **0.0** | **0.0** | **0.0** |
| **>0.5 Alachlor ESA** | **0.0** | **0.0** | **0.9** | **3.1** | **1.5** | **1.4** |
| **>0.5 Alachlor OXA** | **0.0** | **0.0** | **2.6** | **0.0** | **0.5** | **0.8** |
| **>0.1 Atrazine** | **7.6** | **70.3** | **58.7** | **85.7** | **86.2** | **74.4** |
| **>1.0 Atrazine** | **0.0** | **0.8** | **12.5** | **30.5** | **25.8** | **19.8** |
| **>0.1 Metolachlor** | **0.0** | **36.4** | **25.4** | **44.0** | **44.7** | **37.1** |
| **>1.0 Metolachlor** | **0.0** | **0.0** | **1.7** | **2.7** | **3.0** | **2.2** |
| **>0.5 Metolachlor ESA** | **0.0** | **5.8** | **15.5** | **29.9** | **45.9** | **29.4** |
| **>0.5 Metolachlor OXA** | **0.0** | **0.0** | **6.0** | **20.6** | **16.4** | **12.4** |

† ESA, ethanesulfonic acid; OXA, oxanilic acid.

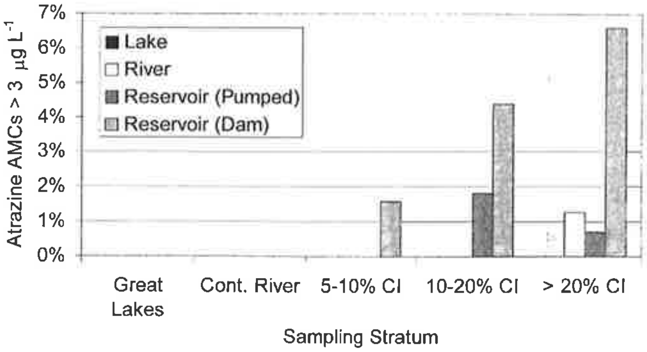

Fig. 7. Frequency of atrazine annualized mean concentrations (AMCs) $> 3$ µg $L^{-1}$ by source type and sampling stratum. CI, corn intensity.

caveat, broad consistency exists, particularly with respect to the relative concentrations of the various corn herbicides and their degradates.

## Use of Monitoring Data for Human Health Risk Assessment

Risk assessments were conducted to assess the potential impact of acetochlor residues in surface water on human health. The toxicology endpoints used for the acute and chronic risk assessments were those previously identified by the USEPA (1999). Potential acute health risks were assessed using an acute reference dose (RfD) of 1.5 mg $kg^{-1}$ $d^{-1}$. However, because this RfD was based on in utero effects observed in a rat teratology study, the USEPA indicated that the only population subgroup of potential concern was females aged 13 and older. Acute risk assessments for other population subgroups were not conducted since no other acute toxicology endpoints were identified. Potential chronic risks were assessed using a chronic RfD of 0.02 mg $kg^{-1}$ $d^{-1}$, based on results from a one-year dog study.

The USEPA originally classified acetochlor as a B2 carcinogen and recommended a linear (Q*) approach for cancer risk assessment based on the formation of rat nasal tumors (USEPA, 1994). However, the ARP has subsequently generated data indicating that the tumors were a result of a nongenotoxic, species-specific, and threshold-mediated mechanism to which the rat is particularly sensitive (Ashby et al., 1996; Green et al., 2000). Based on very similar data (Heydens et al., 1999), the USEPA concluded that a margin of exposure (MOE; i.e., ratio of the highest no effect dose to the received dose) approach should be used to assess potential carcinogenic risks for alachlor (USEPA, 1998). In addition, the USEPA has recently determined that acetochlor and alachlor share a common mechanism of toxicity for formation of rat nasal tumors (USEPA, 2001). Although the USEPA has not yet determined how to conduct a cumulative cancer risk assessment with these two chemicals nor the carcinogenic no observable effect level for a toxic effect (mg $kg^{-1}$ $d^{-1}$) (NOEL) for acetochlor, we used a MOE approach to assess potential cancer risks associated with residues of acetochlor, both alone and in combination with alachlor. The endpoints we used for this cancer risk assessment were the unequivocal NOELs for nasal tumor formation by alachlor and acetochlor in rats, which are 0.5 mg $kg^{-1}$ $d^{-1}$ (USEPA, 1998) and 10 mg $kg^{-1}$ $d^{-1}$ (unpublished data), respectively.

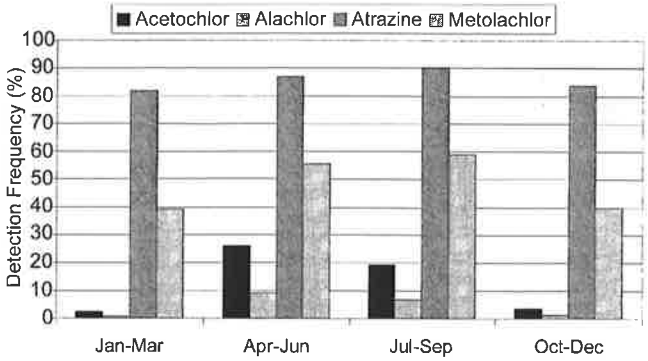

Fig. 8. Frequency of drinking water detections by season for parent herbicides.

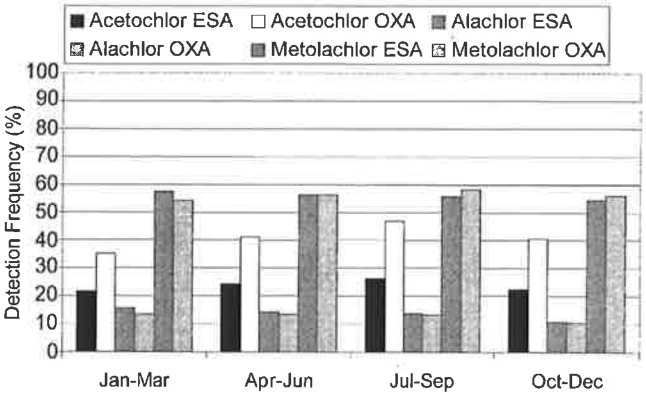

Fig. 9. Frequency of drinking water detections by season for degradates. ESA, ethanesulfonic acid; OXA, oxanilic acid.

The acetochlor degradates (acetochlor ESA and acetochlor OXA) were included in the acute and chronic assessments and were assumed to be toxicologically equivalent to parent. This is a very conservative assumption because both degradates appear to be less toxic than parent in all species tested (Lamb and Clapp, 1999). However, the degradates were not included in the cancer risk assessment, as they exhibit similar toxicological characteristics (unpublished data) to alachlor ESA (Heydens et al., 1996, 2000), which was judged by the USEPA as unlikely to be carcinogenic and was not included in their cancer risk assessment for alachlor (USEPA, 1998).

We performed this deterministic risk assessment by combining a suitably conservative daily drinking water consumption amount (USEPA, 2000) with one of three high-end concentrations from the drinking water monitoring results: 90th, 95th, and 99th percentile values. For the acute and chronic noncancer risk assessments, we estimated exposure to combined residues of acetochlor, acetochlor ESA, and acetochlor OXA. For the first four years of data, we estimated combined residues from parent using regression equations (one for instantaneous concentrations and one for AMC) fit to the last three years of monitoring results. For the acute analysis we estimated the 99th percentile residue at each of the

**Table 8. Risk assessment for acetochlor-related exposure in high-percentile surface drinking water supplies within the acetochlor use area.**

| Toxicology end-point and assumptions | Residues considered† | Percentile site | Residue | Exposure (as a percent of RfD‡) | Margin of exposure§ |
|---|---|---|---|---|---|
| | | | $\mu g\ L^{-1}$ | % | |
| Acute | acetochlor + acetochlor ESA + acetochlor OXA | 99th | 8.12 | 0.02 | NA¶ |
| Based on 99th percentile peak concentration | acetochlor + acetochlor ESA + acetochlor OXA | 95th | 5.57 | 0.02 | NA |
| 60-kg Adult female drinks 2 L $d^{-1}$ | acetochlor + acetochlor ESA + acetochlor OXA | 90th | 2.26 | 0.01 | NA |
| Chronic noncancer | acetochlor + acetochlor ESA + acetochlor OXA | 99th | 2.38 | 1.19 | NA |
| Based on AMCs# | acetochlor + acetochlor ESA + acetochlor OXA | 95th | 1.23 | 0.62 | NA |
| 10-kg Child drinks 1 L $d^{-1}$ | acetochlor + acetochlor ESA + acetochlor OXA | 90th | 0.8 | 0.40 | NA |
| Cancer | acetochlor | 99th | 0.135 | NA | 2 590 000 |
| | alachlor | 99th | 0.096 | NA | 182 000 |
| Based on 7-yr mean concentrations | acetochlor + alachlor | 99th | | NA | 170 000 |
| | acetochlor | 95th | 0.107 | NA | 3 280 000 |
| | alachlor | 95th | 0.052 | NA | 337 000 |
| 70-kg Adult drinks 2 L $d^{-1}$ | acetochlor + alachlor | 95th | | NA | 306 000 |
| | acetochlor | 90th | 0.013 | NA | 27 800 000 |
| | alachlor | 90th | 0.037 | NA | 468 000 |
| | acetochlor + alachlor | 90th | | NA | 460 000 |

† ESA, ethanesulfonic acid; OXA, oxanilic acid.

‡ Reference dose for a toxicity effect.

§ Margin of exposure (MOE) is the ratio of no observable effect level (NOEL) to exposure. Cumulative MOE given by Eq. [3] in the text.

¶ Not applicable.

# Annualized mean concentrations.

189 sites with at least some monitoring data. For the chronic analysis we selected the desired percentile from among the 1193 available AMCs. Each such residue value was multiplied by an appropriate daily water consumption figure and expressed as a percentage of the RfD (Table 8). The resulting exposures to acetochlor residues via drinking water represent 0.02% or less of the acute RfD and 1.22% or less of the chronic RfD.

For the cancer risk assessment, cumulative exposure to both alachlor and acetochlor was considered. As both herbicides were monitored directly during the entire seven years of the study, there was no need for the regression estimation methods employed for the degradates. We had seven continuous years of monitoring data from 144 sites, which we used to estimate potential lifetime exposure concentration to both molecules. For each monitored location, we estimated separate MOEs for both acetochlor and alachlor relative to their carcinogenic NOELs. We then calculated an overall MOE ratio using the following equation:

$$\mathrm{MOE}_{\mathrm{overall}} = [\ (1/\mathrm{MOE}_{\mathrm{acetochlor}}) + (1/\mathrm{MOE}_{\mathrm{alachlor}})\ ]^{-1} \quad [3]$$

This approach is one of the options proposed for cumulative risk assessment and provides the advantage of maintaining separate assessments for each chemical (Wilkinson et al., 2000). As with the acute and chronic noncancer risk assessments, we present the 99th, 95th, and 90th percentile results, which yielded overall cancer MOEs of 170 000, 306 000, and 460 000 (Table 8).

## Use of Monitoring Data for Ecological Risk Assessment

We chose to base this risk assessment on the 90th-percentile instantaneous raw surface water concentration, as this is the established default return frequency for such assessments. As pointed out previously, these sites represent a stratified random sample with greater inclusion of watersheds expected to contain higher residues of acetochlor, including a focus on the smaller watersheds where aquatic organisms may be present. We considered concentrations measured during mid-March through late August. This corresponds to the time when concentrations are at their highest and when aquatic organisms are most likely to be present.

The 90th percentile parent acetochlor concentration from among such raw water samples is 0.18 $\mu g\ L^{-1}$. The lowest aquatic environmental concentration affecting 50% of a species ($EC_{50}$) for acetochlor in the USEPA ECOTOX database (Office of Pesticide Programs, 2000) is 1.43 $\mu g\ L^{-1}$ for an algal species, *Selenastrum capricornutum*. According to current USEPA policy, the acceptable risk quotient ($EEC/EC_{50}$) for non-endangered, non-target plants is 1.0, where EEC represents the estimated environmental concentration. The risk quotient calculated using this formula is 0.13, indicating an acceptable risk to non-endangered, non-target aquatic organisms. Any potential risk to endangered species is beyond the scope of this simple assessment methodology.

For the acetochlor degradates, *Selenastrum* is also the most sensitive aquatic species tested. The three-day $EC_{50}$ values for acetochlor ESA and acetochlor OXA for *Selenastrum* are 8 and 44 mg $L^{-1}$, respectively (unpublished data). These values are several orders of magnitude greater than the highest values actually found in raw surface water (all less than 10 $\mu g\ L^{-1}$), leading to a simple risk assessment conclusion that these acetochlor degradates are unlikely to be present in surface water at concentrations that would result in acute effects to non-target aquatic organisms.

## CONCLUSIONS

The results of the ARP seven-year surface drinking water monitoring program for acetochlor and other major corn herbicides show that 81.2% of samples contain no detectable acetochlor, even though the stratified random sampling favored the most vulnerable sites. Detections of acetochlor occurred mainly in spring, but were more seasonally dispersed for the degradates. No acetochlor AMCs reached the 2 $\mu g\ L^{-1}$ mitigation trigger level mandated by USEPA. One acetochlor AMC exceeded 1 $\mu g\ L^{-1}$, and less than 10% of the AMCs exceeded 0.1 $\mu g\ L^{-1}$. Atrazine was detected more frequently than acetochlor and at higher concentrations, with 87% of the drinking water samples containing detectable atrazine. Nearly 20% of the atrazine AMCs exceeded 1 $\mu g\ L^{-1}$, and 74.4% exceeded 0.1 $\mu g\ L^{-1}$.

The stratified design used for site selection was shown to be sound. The stratification assumed that residues in the Great Lakes would be the lowest, followed next by the continental rivers, and then by the smaller watersheds with the three increasing levels of corn intensity: 5 to 10, 11 to 20, and >20%. The frequency of atrazine detections greater than 2 $\mu g\ L^{-1}$ in these five strata were 0, 3.7, 6.5, 11.7, and 12.7%, respectively, in the order expected before study initiation.

The degradates of acetochlor, alachlor, and metolachlor were detected more frequently than their respective parent compounds, despite their higher analytical detection limits. About 24 and 42% of the finished water samples contained detectable residues of acetochlor ESA and acetochlor OXA, respectively (compared with 19% for parent acetochlor). Alachlor and its degradates were detected less frequently than acetochlor, in 7, 14, and 13% of the samples for alachlor, alachlor ESA, and alachlor OXA, respectively. Metolachlor and its degradates were detected more frequently than acetochlor, in 53, 56, and 57% of the samples for metolachlor, metolachlor ESA, and metolachlor OXA, respectively.

The AMCs for all parent herbicides and their degradates generally increased as a function of corn intensity and seasonal rainfall, and atrazine tended to be higher in reservoirs. Spring rainfall during the monitoring study was typically above normal, with total rainfall for the months of April, May, and June higher than the historical average during every year except 1997. The AMCs of alachlor, atrazine, and metolachlor decreased over the seven years of the program. There was no significant change in acetochlor AMCs over the seven years of the program, nor was there any trend in residue levels for the six degradates over the three years they were monitored. Activated carbon use (both PAC and GAC) reduced concentrations of parent herbicides and, to a lesser extent, soil degradates, relative to the corresponding raw water.

Risks to human health based on acute and chronic noncancer end-points were assessed using the measured concentrations of acetochlor and its degradates. For cancer, combined exposure to alachlor and acetochlor was considered. Large margins of exposure exist for all endpoints and demonstrate that the low residues present in surface water from continued use of acetochlor do not appear to represent a significant threat to human health, even in vulnerable systems using relatively small reservoirs in areas of high corn intensity. Ecological risk assessments based on the ARP monitoring data indicate that levels of ecological concern are unlikely to be exceeded. Thus, the acetochlor residues found in surface water are unlikely to pose a significant risk to health or the environment.

## ACKNOWLEDGMENTS

The co-authors of this and companion articles on the acetochlor water monitoring program wish to dedicate this paper to our fondly remembered and respected colleague, Amy Hackett, who passed away in March 2003 after a long illness. She bravely fought a terrible disease and tirelessly committed herself to scientific excellence in the conduct of this surface water monitoring study, serving as its study director from inception to its successful completion. We marvel at her dedication to this work despite her painful adversity, and wish to honor her memory as the fruits of her work are published here in the scientific literature.

This vast study would not have been possible without the tireless commitment and contributions of nearly 1000 people, including hundreds of volunteers at the community water systems. Contributing scientists at Stone Environmental, the field contractor, included Carl and Marian Hanson, Pamela DeAndrea, Joan Kahn, and Lori Barg. Individuals participating in overall program design at the USEPA included R. David Jones and Betsy Behl. Numerous current and former employees at Monsanto Company also contributed. Those playing major roles included several on the analytical team (Sue Horton, Mimi Dahl, Mark Allan, Joanne Warren, Bharti Parikh, Rudi Lauer, John Cowell, Mike Manning, Will Ridley, Monte Marshall); Jack Milligan and his sample handling team; several from the Quality Assurance Unit (Tina Berman, O.P. Tanner, DeAnn Holden, Vic Saeger); those providing administrative support (Phyllis Faintich, Terry Bix); and those providing statistical analyses (Larry Holden, Kirk Remund, Changjian Jiang). Norm Hoffman (Carnac Inc.) provided critical computer database support. Paul Swidersky, Angela Psenicska, and Dean Hill (QAI) provided professional quality assurance support for the entire ARP program.

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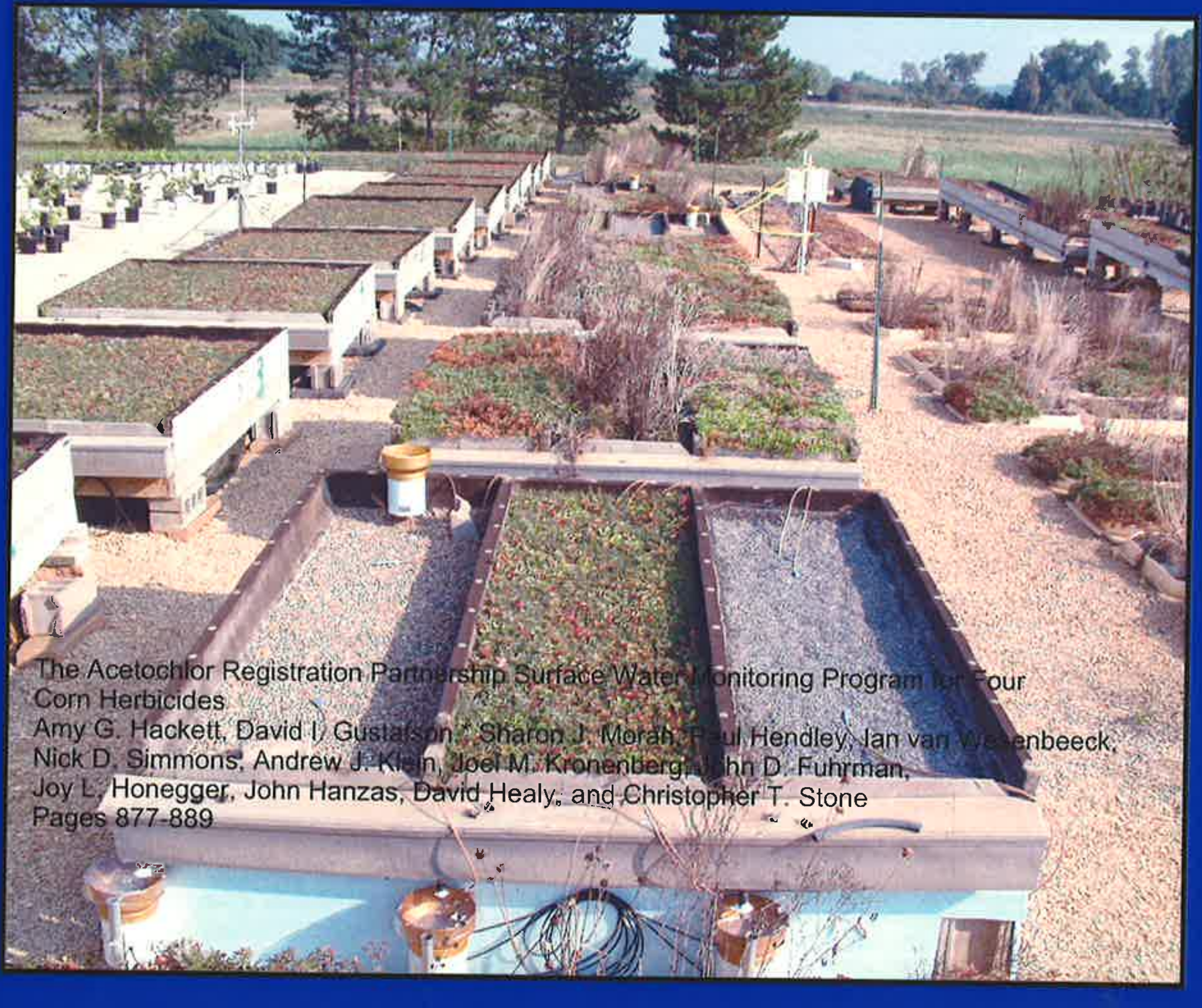

The Acetochlor Registration Partnership Surface Water Monitoring Program for Four Corn Herbicides
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