

Degradates Provide Insight to Spatial and Temporal Trends of Herbicides in Ground Water

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Abstract

Since 1995, a network of municipal wells in Iowa, representing all major aquifer types (alluvial, bedrock/karst region, glacial drift, bedrock/nonkarst region), has been repeatedly sampled for a broad suite of herbicide compounds yielding one of the most comprehensive statewide databases of such compounds currently available in the United States. This dataset is ideal for documenting the insight that herbicide degradates provide to the spatial and temporal distribution of herbicides in ground water.

During 2001, 86 municipal wells in Iowa were sampled and analyzed for 21 herbicide parent compounds and 24 herbicide degradates. The frequency of detection increased from 17% when only herbicide parent compounds were considered to 53% when both herbicide parents and degradates were considered. Thus, the transport of herbicide compounds to ground water is substantially underestimated when herbicide degradates are not considered. A significant difference in the results among the major aquifer types was apparent only when both herbicide parent compounds and their degradates were considered. In addition, including herbicide degradates greatly improved the statistical relation to the age of the water being sampled. When herbicide parent compounds are considered, only 40% of the wells lacking a herbicide detection could be explained by the age of the water predating herbicide use. However, when herbicide degradates were also considered, 80% of the ground water samples lacking a detection could be explained by the age of the water predating herbicide use. Finally, a temporal pattern in alachlor concentrations in ground water could only be identified when alachlor degradates were considered.

Introduction

Complete mineralization of most herbicide parent compounds occurs slowly in the environment (Stamper et al. 1997; Larsen and Aamand 2001), with relatively stable and persistent degradates (also referred to as metabolites in the literature) being formed during transformation of many of these herbicides (Coats 1993; Aga and Thurman 2001). Research has shown that herbicide degradates are prevalent in ground water (Kolpin et al. 1995; Phillips et al. 1999;

Kolpin et al. 2000, 2001), often being more frequently detected than their parent compounds. Thus, simply stating that relatively few detections of herbicide parent compounds were observed in ground water provides a false impression that little chemical transport to ground water is occurring from herbicide applications at the land surface. Herbicide degradates can either be less toxic (Stamper and Tuovinen 1998; Heydens et al. 2000) or have similar or greater toxicity than their parent compounds (Tessier and Clark 1995; Belfroid et al. 1998; Tixier et al. 2001). An extensive review of the available pesticide ecotoxicity data found 30% of the degradates examined to be more toxic than the parent compound (Sinclair and Boxall 2003). Thus, obtaining data on parent compounds and their primary degradates is critical for understanding the fate of herbicides in the hydrologic system.

The purpose of this paper is to provide specific examples of the insight that can be gained when data on both herbicide parent and herbicide degradate compounds are obtained in ground water samples. Results from the sampling of 86 municipal wells across Iowa during the

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summer of 2001 are presented to illustrate the importance of herbicide degradates in a spatial analysis. In addition, the results from municipal wells in Iowa that have been repeatedly sampled from 1995 to 2001 are presented to illustrate the importance of herbicide degradates in a temporal analysis. These spatial and temporal datasets represent one of the most comprehensive datasets on herbicide degradates available in the United States. The research is an extension of the Iowa Ground Water Monitoring (IGWM) program (Detroy 1985; Kolpin et al. 1997b). IGWM is a joint study by the Iowa Department of Natural Resources, Iowa Geological Survey and the U.S. Geological Survey (USGS).

Methods

During 1992, a network of 90 sampling sites were randomly selected from an inventory of more than 2000 Iowa municipal wells representing all major aquifer types—alluvial, bedrock/karst region, glacial drift, and bedrock/nonkarst region. The alluvial aquifers consist of sand and gravel deposits associated with present-day streams. The bedrock aquifers in the karst region are carbonates with solution-enhanced features with generally < 30 m of glacial overburden. Glacial drift aquifers are composed of discontinuous permeable lenses of sand and gravel typically interbedded with less permeable clay and silts. The bedrock aquifers in the nonkarst region can include carbonates and sandstones, and generally have > 30 m of glacial overburden. The number of selected sampling sites from the major aquifer types was designed to represent the distribution of all municipal wells in Iowa. The water samples collected from 86 of the 90 wells (Figure 1) represent the sampling carried out for IGWM during 2001 (32 samples from alluvial aquifers, 20 from bedrock/karst, 12 from glacial drift, and 22 from bedrock/nonkarst).

The sampling protocol for this study has been reported previously (Kolpin et al. 1997a). All samples were collected to be representative of the quality of water in the aquifer itself and not necessarily that in the finished drinking-water supply. Thus, water samples were collected as close to the wellhead as possible and prior to any treatment (e.g., chlorination). All wells were pumped for at least 30 min before dissolved oxygen, pH, specific conductance, and water temperature were measured. Once the values for these parameters stabilized, water samples were collected.

Water samples were filtered through a 0.7 μm glass fiber filter into 125 mL amber baked-glass bottles, immediately chilled, and sent by overnight air express to the USGS Organic Research Laboratory in Lawrence, Kansas. Concentrations of 45 herbicide compounds (Table 1) were analyzed by a combination of gas chromatography/mass spectrometry (Zimmerman and Thurman 1998) and liquid chromatography/mass spectrometry methods (Lee et al. 2001a, 2001b; Zimmerman et al. 2002). The analytical reporting level was 0.05 $\mu\text{g/L}$ for most compounds (Table 1). This sampling represents the first time that deethylhydroxyatrazine, deisopropylhydroxyatrazine, didealkylatrazine, dimethenamid, dimethenamid ethanesulfonic acid, dimethenamid oxanilic acid, flufenacet, flufenacet ethanesulfonic acid, flufenacet oxanilic acid,

glyphosate, amino methyl phosphonic acid (AMPA), and glufosinate have been examined in ground water across Iowa and represents some of the earliest such data in the United States.

All water samples analyzed for tritium had a reporting level of 0.09 tritium units (TU, where 1 TU = 1 tritium atom/ 10^{18} hydrogen atoms) with an analytical precision of 0.1 TU. Guidelines by Clark and Fritz (1997) indicate that ground water with < 0.8 TU represents recharge to the water table prior to 1953. Water with 0.8 to 4 TU may represent a mixture of water that contains recharge from before and after 1953. Water with > 5 TU is most likely recharged after 1953.

Nonparametric statistical techniques were used for this study. These methods are appropriate because the data did not exhibit normal distributions and because of the presence of censored data (concentrations less than analytical reporting limits). The Kruskal-Wallis test (Helsel and Hirsch 1992) was used to test for spatial differences in the medians of two or more groups. The Wilcoxon signed-ranked test (Helsel and Hirsch 1992) was used to identify temporal trends by determining whether the median difference between paired observations equaled zero. A significance level of 0.05 was used for all statistical tests in this study. This acceptable probability of error ($\alpha = 0.05$) means that there is a 1 in 20 chance that the statistical test reported a significant relation when one did not exist. Thus, the smaller the p-value, the greater is the certainty that a reported statistical relation is real.

Results

Herbicide parent compounds were found in 17% of the 86 water samples collected for this study. Atrazine and metolachlor were the only herbicides detected in > 5% of the samples collected (Table 1). Herbicide degradates, however, were detected in 53% of the samples and were 12 of the 15 most frequently detected herbicide compounds (Figure 3). Metolachlor ESA and Alachlor ESA were the only compounds found in > 40% of the wells sampled (Table 1, Figure 3). The prevalence of herbicide degradates

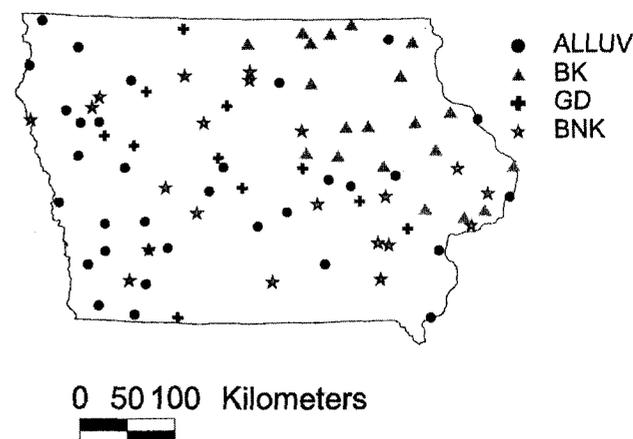


Figure 1. Location of 86 municipal wells sampled in Iowa during 2001 (ALLUV = alluvial, BK = bedrock/karst region, GD = glacial drift, BNK = bedrock/nonkarst region).

Table 1
Summary of Herbicide and Herbicide Degradate Results for 86 Wells Sampled in 2001

Common Name	Chemical Name	Use or Origin	RL (µg/L)	% Detect	Max (µg/L)
Acetochlor	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide	Herbicide	0.05	1.2	0.58
Acetochlor ethanesulfonic acid (acetochlor ESA)	2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)amino]-2-oxoethane sulfonic acid	Herbicide degradate (acetochlor)	0.05	10.5	1.56
Acetochlor oxanilic acid (acetochlor OXA)	2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)amino]-2-oxoacetic acid	Herbicide degradate (acetochlor)	0.05	12.8	2.09
Alachlor	2-Chloro-2'-6'-diethyl-N-(methoxymethyl)-acetanilide	Herbicide	0.05	1.2	0.17
Alachlor ethanesulfonic acid (alachlor ESA)	2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethane sulfonic acid	Herbicide degradate (alachlor)	0.05	41.9	5.69
Alachlor oxanilic acid (alachlor OXA)	2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid	Herbicide degradate (alachlor)	0.05	11.6	4.17
Ametryn	2-(ethylamino)-4-isopropylamino-6-methylthio-s-triazine	Herbicide	0.05	0.0	ND
Amino methyl phosphonic acid (AMPA)	Aminomethyl-phosphonic acid	Herbicide degradate (glyphosate)	0.1	0.0	ND
Atrazine	2-chloro-4-ethylamino-6-isopropylamino-s-triazine	Herbicide	0.05	16.3	0.38
Cyanazine	2-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino-2-methyl propionitrile	Herbicide	0.05	0.0	ND
Cyanazine acid	2-(4-Chloro-6-ethylamino-[1,3,5]triazin-2-ylamino)-2-methyl-propionic acid	Herbicide degradate (cyanazine)	0.05	7.0	0.44
Cyanazine amide	2-chloro-4-(1-carbamoyl-1-methyl-ethylamino)-6-ethylamino-s-triazine	Herbicide degradate (cyanazine)	0.05	1.2	0.11
Deethylatrazine	2-amino-4-chloro-6-(isopropylamino)-s-triazine	Herbicide degradate (atrazine, propazine)	0.05	16.3	0.54
Deethylcyanazine	2-(4-Amino-6-chloro-[1,3,5]triazin-2-ylamino)-2-methyl-propionitrile	Herbicide degradate (cyanazine)	0.05	0.0	ND
Deethylcyanazine acid	2-(4-Amino-6-chloro-[1,3,5]triazin-2-ylamino)-2-methyl-propionic acid	Herbicide degradate (cyanazine)	0.05	17.4	2.19
Deethylcyanazine amide	2-(4-Amino-6-chloro-[1,3,5]triazin-2-ylamino)-2-methyl-propionamide	Herbicide degradate (cyanazine)	0.05	0.0	ND
Deethylhydroxyatrazine	4-Amino-6-isopropylamino-[1,3,5]triazin-2-ol	Herbicide degradate (atrazine)	0.1	1.2	0.09
Deisopropylatrazine	2-amino-4-chloro-6-(ethylamino)-s-triazine	Herbicide degradate (atrazine, cyanazine, simazine)	0.05	8.1	0.62
Deisopropylhydroxyatrazine	4-Amino-6-ethylamino-[1,3,5]triazin-2-ol	Herbicide degradate (atrazine)	0.1	0.0	ND
Demethylfluometuron	1-Methyl-3-(3-trifluoromethyl-phenyl)-urea	Herbicide degradate (fluometuron)	0.05	0.0	ND
3,4-dichloromethylphenylurea	1-(3,4-Dichloro-phenyl)-3-methyl-urea	Herbicide degradate (diuron)	0.2	0.0	ND
Didealkylatrazine	6-Chloro-[1,3,5]triazine-2,4-diamine	Herbicide degradate (atrazine)	0.05	23.2	2.68
Dimethenamid	2-Chloro-N-(2,4-dimethyl-thiophen-3-yl)-N-(2-methoxy-1-methyl-ethyl)-acetamide	Herbicide	0.05	1.2	0.8
Dimethenamid ethanesulfonic acid	[(2,4-Dimethyl-thiophen-3-yl)-(2-methoxy-1-methyl-ethyl)-carbamoyl]-methanesulfonic acid	Herbicide degradate (dimethenamid)	0.05	0.0	ND
Dimethenamid oxanilic acid	N-(2,4-Dimethyl-thiophen-3-yl)-N-(2-methoxy-1-methyl-ethyl)-oxalamic acid	Herbicide degradate (dimethenamid)	0.05	0.0	ND
Diuron	3-(3,4-Dichloro-phenyl)-1,1-dimethyl-urea	Herbicide	0.05	0.0	ND
Flufenacet	N-(4-fluoro-phenyl)-N-isopropyl-2-(5-trifluoro-methyl-[1,3,4]thiadiazol-2-yloxy)-acetamide	Herbicide	0.05	0.0	ND
Flufenacet ethanesulfonic acid	[(4-Fluoro-phenyl)-isopropyl-carbamoyl]-methanesulfonic acid	Herbicide degradate (flufenacet)	0.05	0.0	ND

Table 1 (continued)

Common Name	Chemical Name	Use or Origin	RL (µg/L)	% Detect	Max (µg/L)
Flufenacet oxanilic acid	N-(4-Fluro-phenyl)-N-isopropyl-oxalamic acid	Herbicide degradate (flufenacet)	0.05	0.0	ND
Fluometuron	1,1-Dimethyl-3-(3-trifluoromethyl-phenyl)-urea	Herbicide	0.05	0.0	ND
Glufosinate	2-Amino-4-(hydroxy-methyl-phosphinoyl)-butyric acid	Herbicide	0.1	0.0	ND
Glyphosate	(Phosphonomethyl-amino)-acetic acid	Herbicide	0.1	0.0	ND
Hydroxyatrazine	2-hydroxy-4-(ethylamino)-6-(isopropylamino)-s-triazine	Herbicide degradate (atrazine)	0.05	10.5	0.17
Linuron	1-Methoxy-1-methyl-3-(3,4-dichlorophenyl)urea	Herbicide	0.2	0.0	ND
Metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl ethyl)acetamide	Herbicide	0.05	9.3	3.2
Metolachlor ethane sulfonic acid (metolachlor ESA)	2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid	Herbicide degradate (metolachlor)	0.05	47.7	2.92
Metolachlor oxanilic acid (metolachlor OXA)	2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid	Herbicide degradate (metolachlor)	0.05	25.6	3.6
Metribuzin	4-Amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one	Herbicide	0.05	0.0	ND
Pendimethalin	N-(Ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline	Herbicide	0.05	0.0	ND
Prometon	2,4-bis(isopropylamino)-6-methoxy-s-triazine	Herbicide	0.05	3.5	0.13
Prometryn	2,4-bis(isopropylamino)-6-(methylthio)-s-triazine	Herbicide	0.05	0.0	ND
Propachlor	2-chloro-N-isopropylacetanilide	Herbicide	0.05	0.0	ND
Propazine	2-chloro-4,6-bis(isopropylamino)-s-triazine	Herbicide	0.05	0.0	ND
Simazine	2-chloro-4,6-bis(ethylamino)-s-triazine	Herbicide	0.05	0.0	ND
Terbutryn	2-tert-butylamino-4-ethylamino-6-methylthio-s-triazine	Herbicide	0.05	0.0	ND

RL: reporting level
 % Detect: frequency of detection
 Max: maximum concentration
 ND: not detected

in ground water is similar to previous investigations of Iowa ground water (Kolpin et al. 1996; Kolpin et al. 1998,

2000, 2001). This is the first time, however, that dideakylatrazine has been identified as a contaminant in Iowa ground water.

Table 2
Summary of Detection Frequencies for Select Herbicide Parent Compounds and Herbicide Parent, Plus Degradates for 86 Wells Sampled in 2001

Compound	Frequency of Detection (%)	
	Parent	Parent Plus Degradates
Acetochlor	1.2	16.3
Alachlor	1.2	44.2
Atrazine	15.3	29.1
Cyanazine	0	18.6
Dimethenamid	1.2	1.2
Flufenacet	0	0
Glyphosate	0	0
Metolachlor	9.3	48.8
Any herbicide	17.4	53.5

For most herbicides, both the frequency of detection and concentrations were greatly increased when their degradates were also considered (Table 2). Thus, the transport of herbicide compounds to ground water was substantially underestimated when herbicide degradates were not considered. The greatest increases were determined for alachlor and cyanazine (Table 2). Because herbicide degradates can have similar acute and chronic toxicity as their parent compounds (Tessier and Clark 1995; Belfroid et al. 1998; Tixier et al. 2001; Sinclair and Boxall 2003), these compounds have environmental significance as well as providing a more complete understanding of the fate and transport of a given herbicide. However, not all herbicide degradates measured were commonly found in ground water, with 11 degradates having few to no detections (Table 1). For example, glyphosate and its degradate (AMPA) were not found during this study (Tables 1 and 2), even though glyphosate use has rapidly increased since 1998 with the introduction of genetically altered glyphosate-resistant crops (Padgett et al. 1995).

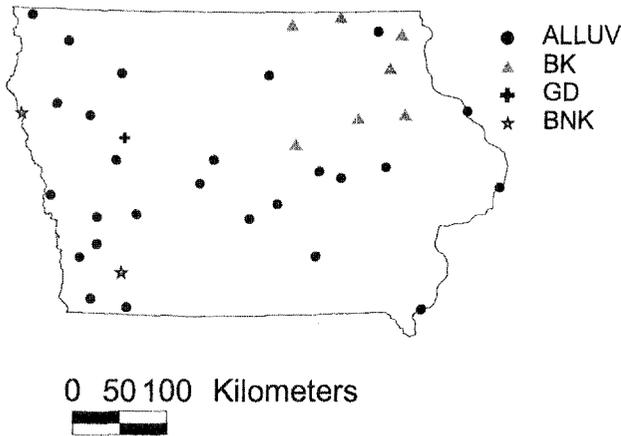


Figure 2. Location of 36 municipal wells containing post-1953 age water that were repeatedly sampled between 1995 and 2001 (ALLUV = alluvial, BK = bedrock/karst region, GD = glacial drift, BNK = bedrock/nonkarst region).

Discussion

Herbicide degradates not only provide a more accurate picture of herbicide occurrence, they also provide insight to the understanding of both the spatial and temporal distribution of herbicides in the environment. Specific examples follow.

Spatial

To determine if a spatial pattern exists in the herbicide concentrations from the 86 wells sampled in 2001 (Figure 1), the data were compared statistically among the four major aquifer types sampled (alluvial, bedrock/karst region, glacial drift, and bedrock/nonkarst region). When only herbicide parent compounds were considered, no statistical difference ($P = 0.277$, Kruskal-Wallis test) was found among the major aquifer types sampled. Few herbicides were

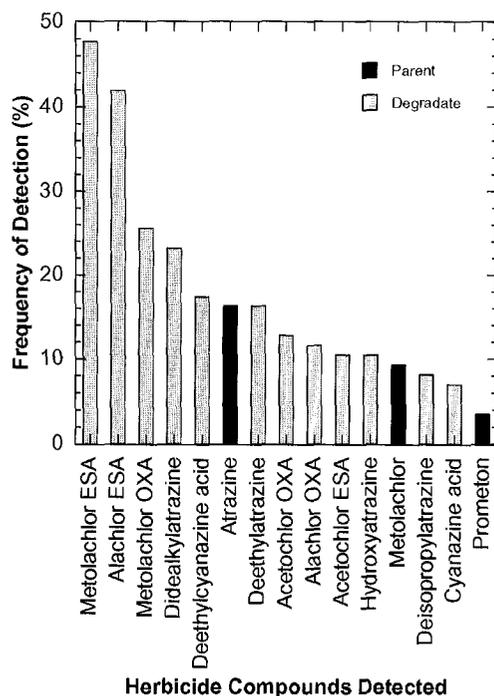


Figure 3. Frequency of detection for selected herbicide compounds.

found, with the frequency of detection being $< 25\%$ in all aquifer types (Figure 4). Based on this information, it could be concluded that the relatively uniform herbicide applications across Iowa (Kolpin et al. 1997a) translated into a relatively uniform and infrequent detection of herbicides in ground water. When herbicide degradates were included in the analysis, however, concentrations did vary significantly ($P < 0.0001$, Kruskal-Wallis test), thus highlighting a difference among the major aquifer types. Alluvial aquifers were found to have the highest detection levels and bedrock/nonkarst region aquifers to have the lowest detection levels for herbicide compounds (Figure 5). These patterns are likely due to factors such as age of the water since time of recharge and hydrogeologic characteristics of the aquifer. For example, alluvial aquifers have higher hydraulic conductivity and shorter residence times compared to those of bedrock/nonkarst aquifers. The herbicide results of this study are similar to that found in previous studies of ground water in the region (Kross et al. 1990; Burkart and Kolpin 1993; Kolpin et al. 1997a). Thus, data on herbicide degradates were instrumental in identifying a

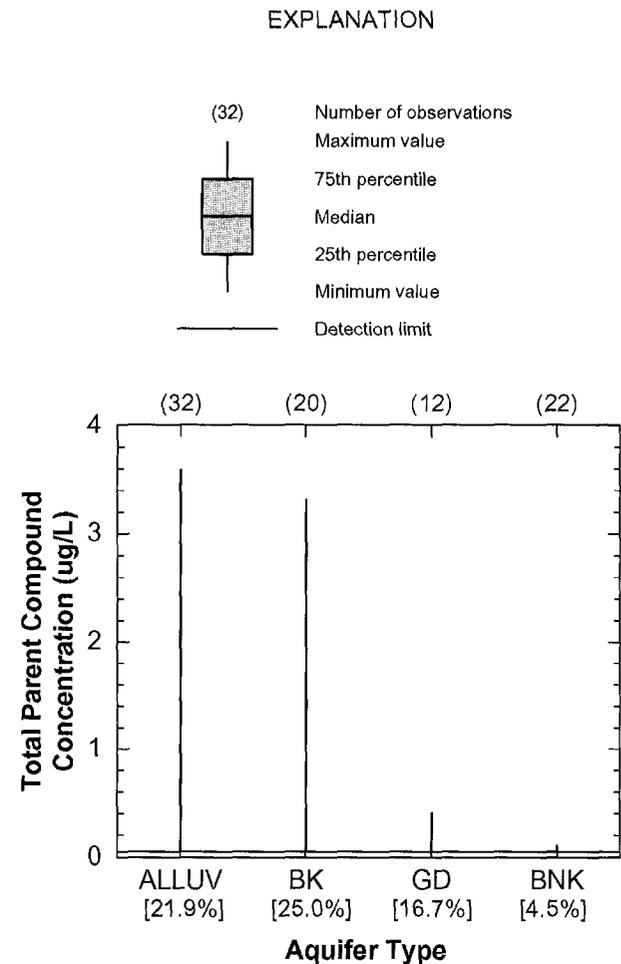


Figure 4. Total parent compound concentration (summation of detected concentrations of all parent compounds) by aquifer type (ALLUV = alluvial, BK = bedrock/karst region, GD = glacial drift, BNK = bedrock/nonkarst region). Numbers in brackets are the frequency of herbicide detection and the numbers in parentheses are the number of observations for that aquifer type. Because the frequency of detection is $< 25\%$ for all aquifer types, only maximum values can be shown in this graphical display of the data.

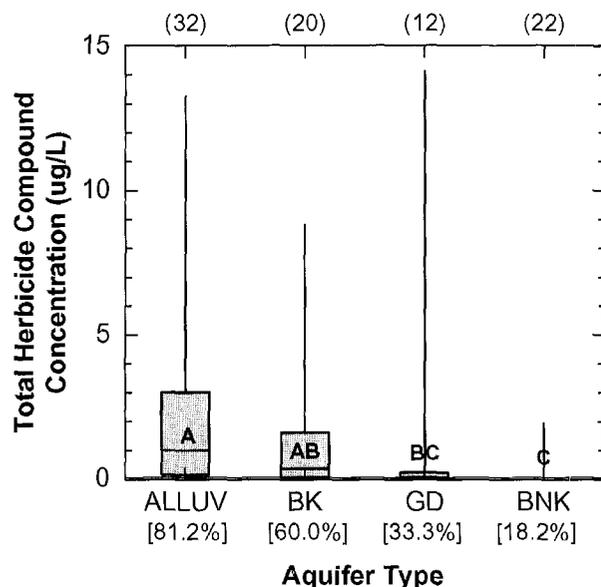


Figure 5. Total herbicide compound concentration (summation of detected concentrations of parent compounds plus degradates) by aquifer type (ALLUV = alluvial, BK = bedrock/karst region, GD = glacial drift, BNK = bedrock/nonkarst region). Numbers in brackets are the frequency of herbicide compound detection and the numbers in parentheses are the number of observations for that aquifer type. An explanation of a boxplot is provided in Figure 4. Boxes with same letter (for example, A and AB) are not significantly different (Kruskal-Wallis test).

spatial pattern in the transport of herbicide compounds based on hydrogeology.

In an attempt to understand the variation in the occurrence of herbicide compounds among the major aquifer types, available tritium was examined. Previous research has shown a relation between tritium concentration and the frequency of pesticide detection (Domagalski and Dubrovsky 1992; Kolpin et al. 1995). The concentration of tritium in ground water can be used as a tracer to determine whether it was recharged before or after 1953. Because the first significant use of herbicides to control weeds in crops also roughly coincides with the start of atmospheric testing of nuclear weapons in 1953, ground water older than 1953 (i.e., < 0.8 TU) would predate the use of herbicides. When only herbicide parent compounds were considered, a statistical difference ($P = 0.012$, Kruskal-Wallis test) in tritium concentration was determined between water samples from wells that had a detection of a herbicide parent compound compared to those where no parent compounds were detected (Figure 6a). Only 40% of the ground water samples having no detectable herbicides, however, were derived from wells where the ground water age predated herbicide use. When herbicide degradates were considered, the number of wells having a detection increased compared to that for just parent compounds (Figure 6). Thus, a stronger statistical difference in tritium concentrations ($P < 0.001$, Kruskal-Wallis test) was determined between water samples from wells that had a detection of a herbicide compound (parent or degradate) compared to those where no herbicide compounds were detected (Figure 6b). In addition, the number of ground water samples having no

detectable herbicide compounds derived from wells where the ground water age predated herbicide use doubled from 40% (when only herbicide parents are considered) to 80% when herbicide degradates were also considered.

Temporal

In Iowa, rapid shifts in chemical use have occurred for acetochlor (increase) and alachlor (decrease) during the period 1991 to 2001 (Figure 7). In contrast, atrazine use has remained relatively stable over this same time period. To determine if these rapid changes in annual use for acetochlor and alachlor have translated into corresponding changes in ground water concentrations for these two herbicides, data from 36 wells containing post-1953 age water that were repeatedly sampled between 1995 (earliest date when data on alachlor and acetochlor degradates were obtained) and 2001 (Figure 2) were examined. Wells that contained pre-1953 age water were excluded from the temporal analysis because the ground water predates the use of herbicides.

If only the parent compounds for acetochlor and alachlor are considered, no statistical differences were determined with time (temporal comparisons were made between data collected during the years 1995 and 1997, 1995 and 1999, and 1995 and 2001). Thus, a conclusion that could be drawn is that infrequent detections of acetochlor and alachlor occur in ground water regardless of how much use occurs at the land surface—even though these herbicides have been among the most heavily used across the state (U.S. Department of Agriculture, National Agricultural Statistics Service 2002). However, when total concentrations are considered (defined as the summation of the parent compound plus ESA and OXA degradates: $T_{\text{acetochlor}} = \text{acetochlor} + \text{acetochlor ESA} + \text{acetochlor OXA}$, $T_{\text{alachlor}} = \text{alachlor} + \text{alachlor ESA} + \text{alachlor OXA}$)

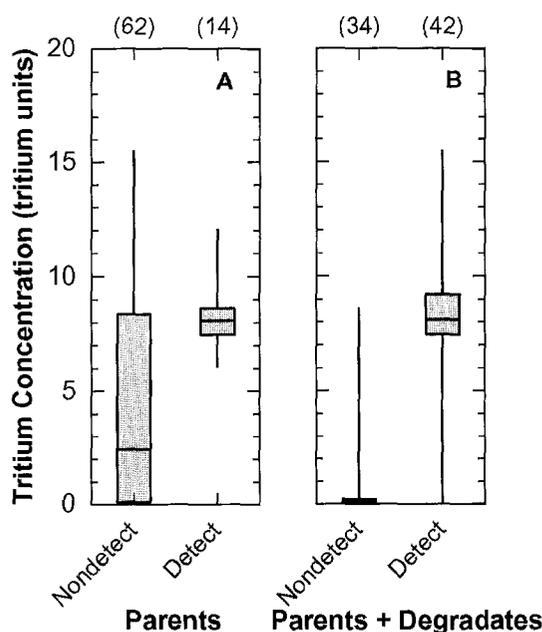


Figure 6. Relation between tritium concentration and the presence of herbicide compounds in ground water. Eight tritium sample bottles were broken prior to analysis. An explanation of a boxplot is provided in Figure 4.

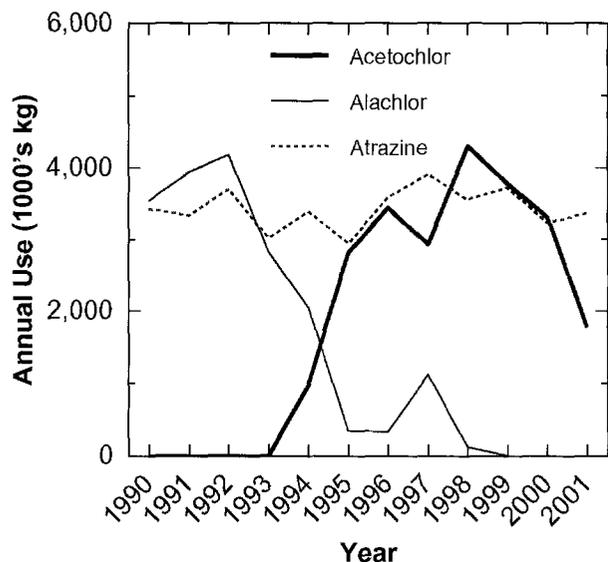


Figure 7. Temporal patterns in annual use for select herbicides in Iowa (U.S. Department of Agriculture, National Agricultural Statistics Service 2002).

ESA), a significant decrease in $T_{alachlor}$ ($P < 0.001$; one-tail Wilcoxon signed-rank test) was determined between the years 1995 and 1997, 1995 and 1999, and 1995 and 2001. This trend corresponds to the temporal decreases in chemical use that has occurred for alachlor (Figure 7). Although no statistically significant trends were determined for $T_{acetochlor}$ ($P = 0.078$; one-tail Wilcoxon signed-rank test), the frequency of detection did increase from 5.6% in 1995 to 16.3% in 2001. This increase in the frequency of detection matches the temporal increases in acetochlor use (Figure 7) and suggests that a significant temporal trend in $T_{acetochlor}$ may occur with continued acetochlor use.

Conclusions

Since 1995, a network of municipal wells in Iowa, representing all major aquifer types, has been repeatedly sampled for a broad suite of herbicide compounds yielding one of the most comprehensive statewide databases of such compounds currently available in the United States. This dataset is ideal for documenting the insight that herbicide degradates provide to the spatial and temporal distribution of herbicides in ground water. During 2001, 86 municipal wells in Iowa were sampled and analyzed for 21 herbicide parent compounds and 24 herbicide degradates. The frequency of detection increased from 17% when only herbicide parent compounds were considered to 53% when both herbicide parents and degradates were considered. Thus, the transport of herbicide compounds to ground water was substantially underestimated when herbicide degradates were not considered. Because herbicide degradates can have a similar acute and chronic toxicity as their parent compounds, these compounds have environmental significance as well as providing a more complete understanding of the fate and transport of a given herbicide.

A significant difference in the results among the major aquifer types was apparent only when both herbicide parent compounds and their degradates were considered. Thus,

without data on herbicide degradates, it could be erroneously concluded that the relatively uniform herbicide applications across Iowa translated into relatively uniform transport of herbicides to ground water. In addition, a temporal pattern of alachlor concentrations in ground water could only be identified when its degradates were considered. These concentration patterns corresponded to the dramatic decreases that have occurred in the annual use of alachlor between 1991 and 2001. Without data on alachlor degradates, it could be erroneously concluded that infrequent detections of alachlor occur in ground water regardless of how much use occurs at the land surface. This study clearly documents that obtaining data on both parent compounds and their primary degradates is critical for understanding the fate of herbicides in the hydrologic system.

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