HERBICIDES AND DEGRADATES IN SHALLOW AQUIFERS OF ILLINOIS: SPATIAL AND TEMPORAL TRENDS[1]

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ABSTRACT: During the fall of 2000, the occurrence was examined of 16 herbicides and 13 herbicide degradates in samples from 55 wells in shallow aquifers underlying grain producing regions of Illinois. Herbicide compounds with concentrations above 0.05 µg/L were detected in 56 percent of the samples. No concentrations exceeded regulatory drinking water standards. The six most frequently detected compounds were degradates. Water age was an important factor in determining vulnerability of ground water to transport of herbicide compounds. Unconsolidated aquifers, which were indicated to generally contain younger ground water than bedrock aquifers, had a higher occurrence of herbicides (73 percent of samples) than bedrock aquifers (22 percent). Temporal analysis to determine if changes in concentrations of selected herbicides and degradates could be observed over a near decadal period indicated a decrease in detection frequency (25 to 18 percent) between samplings in 1991 and 2000. Over this period, significant differences in concentrations were observed for atrazine (decrease) and total acetochlor (increase). The increase in acetochlor compound concentrations corresponds to an increase in acetochlor use during the study period, while the decrease in atrazine concentrations corresponds to relatively consistent use of atrazine. Changes in frequency of herbicide detection and concentration do not appear related to changes in land use near sampled wells.
(KEY TERMS: herbicides; degradates; ground water; fate and transport; monitoring; nonpoint source pollution; temporal analysis.)

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INTRODUCTION

Herbicides are used extensively in agricultural regions of the United States for control of competing weeds in crops. Substantial advances in agricultural production during the past 35 years are associated directly with the increased use of herbicides. However, this increased use has introduced concerns about their occurrence in water resources and their potential adverse effect on human health and the environment. More than 300 studies (USGS, 1996) have documented the occurrence of herbicides in the state (Risch, 1994; Mehnert *et al.,* 1995; Kolpin *et al.,* 1997a, 1998b), at the regional scale (Kolpin *et al.,* 1994, 1995, 1996, 1998a), and at the national scale (USEPA, 1990, 1992; Holden *et al.,* 1992; Kolpin *et al.,* 2000a). Concerns about contamination of ground water are high in many agricultural regions, particularly in the Midwestern United States, where ground water is the principal rural domestic source and a substantial rural public source of drinking water (Kay, 2002). The potentially toxic effects of herbicides on humans and animals and the disruption of reproductive cycles and food chains have been documented in various studies (Blaustein and Wake, 1990; Carbonell *et al.,* 1995; Nemes-Kosa and Cserhati, 1995; Bain and LeBlanc, 1996; Longley and Sotherton, 1997; Ribas *et al.,* 1997; Spawn *et al.,* 1997; Andersen *et al.,* 2002; Anderson and Lydy, 2002; Crump *et al.,* 2002).

Despite the number of studies regarding the occurrence of herbicides in ground water, understanding of their distribution and fate remains incomplete. Although the occurrence of many herbicides has been studied extensively, study of their degradates (transformation products) in ground water is comparatively limited. These degradates result from microbial,

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physical, and chemical processes that alter the field-applied (parent) herbicides. Previous research has shown that degradates frequently can be more prevalent and found at higher concentrations in ground water than their parent compounds (e.g., Kolpin *et al.,* 1998b, 2000b). Degradates can, in some cases, have toxicity similar to their parent herbicide compounds (Tessier and Clark, 1995; Belfroid *et al.,* 1998; Sinclair and Boxall, 2003). Study of long term temporal trends of herbicides and their degradates in ground water (USGS, 1996) also is limited. Applications of herbicides in Illinois over the past decade have not always been consistent. For example, acetochlor was not used prior to 1994 but by 2000 was one of the most heavily used herbicides (USDA, 2002). Conversely, alachlor and cyanazine use has decreased dramatically from heavy use in the early 1990s to limited use by 2000. Available research has suggested a relation between temporal changes in herbicide use and herbicide concentrations in ground water (Kolpin *et al.,* 1997b).

In an attempt to better understand the spatial and temporal occurrence of herbicide compounds in Illinois ground water, 55 wells completed in unconsolidated and bedrock aquifers (Figure 1) were sampled during October and November 2000; one of these wells was sampled in February 2001 because it was inoperable during fall 2000. These wells represent a subset of 68 Illinois wells that were sampled initially in 1991 as part of a regional study of herbicide compounds in ground water (Kolpin *et al.,* 1994, 1995, 1996, 1998a). Similar collection procedures and sample analyses allow for examination of the temporal trends of herbicide compounds on a near decadal scale. Numerous parent herbicides and degradates also were evaluated in the 2000 study using analytical methods that were not available in the 1991 study, thus providing a better understanding of the distribution and fate of herbicide compounds in Illinois ground water. This article presents the results of the 2000 study.

METHODS

Samples were collected from 55 wells selected by a weighted random protocol (Kolpin and Burkart, 1991). Selection protocol required the following criteria.

1. The top of the aquifers included in the study had to be 15 m or less below land surface; the relative number of wells representing the selected shallow unconsolidated and bedrock aquifers was based on percentage of the state underlain by these aquifer types.

2. The counties in which wells were to be located had to contain 25 percent of cropland in corn or soybean (grain) production (Gianessi and Puffer, 1988).

3. At least 25 percent of land use within 3.2 km of the well locations had to be in corn or soybean production (as determined by site inspection).

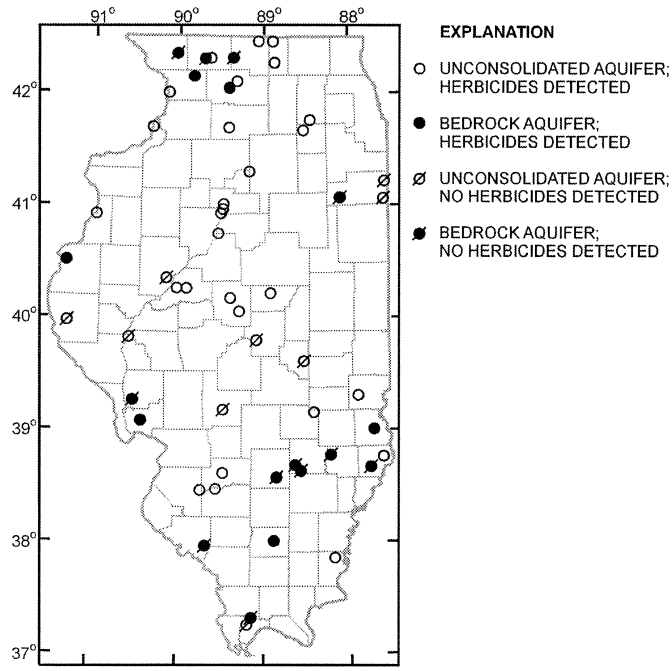

Figure 1. Occurrence of Selected Herbicides and Their Degradates in Ground Water Samples From 55 Wells Completed in Unconsolidated and Bedrock Aquifers in Illinois, October and November 2000.

Of the 55 selected wells, 37 were completed in unconsolidated aquifers and 18 in bedrock aquifers. Most of the aquifers to which the wells are open were expected to be either unconfined or partially confined. The wells included 33 for domestic supply, 13 for public supply, 6 for commercial, industrial, or irrigation use, and 3 monitoring wells. Well depths ranged from about 2 to 229 m, with 90 percent of the depths less than 66 m. Open intervals of the wells ranged from about 1 to 184 m, with 90 percent of the intervals less than 30 m. All of the wells were considered to be properly constructed and thus to provide representative ground water samples.

Samples were collected by procedures detailed in Kolpin and Burkart (1991). Prior to sampling, wells were purged 15 minutes or longer to remove water stored in the well casing, pressure tank, and (or) delivery piping. Field water quality indicators, including pH, water temperature, specific conductance,

dissolved oxygen, and at some sites, oxidation reduction potential (ORP), were monitored through a flow cell to ensure representative ground water samples. Supply wells were sampled before any treatment processes (e.g., softening, chlorinating, and fluoridating) were applied. Samples were passed through a 0.7 µ baked glass fiber filter at a rate of 0.25 gal/min (about 1 L/min) or less and collected in amber baked glass bottles. Sampling equipment was constructed of stainless steel and Teflon to avoid leaching or adsorption of the organic herbicides. The samples were shipped chilled (about 4°C) to the analytical laboratory within three days of collection. A quality assurance program that included field blanks and duplicates and laboratory control samples (each representing about 15 percent of the total number of ground water samples collected) further verified representative ground water samples.

Herbicides were analyzed by the U.S. Geological Survey (USGS) Organic Geochemistry Research Laboratory (OGRL) in Lawrence, Kansas. Samples were analyzed for 16 herbicides and three triazine degradates (Table 1) by gas chromatography/mass spectrometry following solid phase extraction (Zimmerman and Thurman, 1999; Kish *et al.,* 2000) and 10 chloroacetanilide degradates by high performance liquid chromatography/mass spectrometry following solid phase extraction (Zimmerman *et al.,* 2000; Lee *et al.,* 2001). The reporting limit for all herbicides and degradates was 0.05 µg/L.

For evaluation of temporal trends, data were compared for herbicides and degradates analyzed in both 1991 and 2000. In 1991, samples were collected in spring, before herbicide application, and in late summer (mid-July and August) after crop maturation. Analytical results from the summer sampling were used in this temporal analysis; those seasonal ground water conditions are expected to more closely approximate the conditions of the 2000 fall sampling than the conditions of the spring sampling (Kolpin *et al.,* 1994). Although herbicide concentrations in ground water may vary between seasons or over periods of a month or less (Detroy *et al.,* 1988; Risch, 1994; Dennis McKenna, Illinois Department of Agriculture, December 11, 2003, personal communication), this variability is assumed to be inconsequential in the analysis of near decadal changes in concentrations for a collective dataset (that is, the total concentration of an herbicide detected in samples from all wells in the study). To evaluate the contribution of land use change on herbicide detections and concentrations, various land uses (e.g., row crops, pasture, forest, and water) within a 3.2 km radius around each well were categorized in 1991 and 2000 and the percentage of the radial area for each land use was estimated (Kolpin *et al.,* 1994).

Nonparametric statistical tests were used for data analysis. Specifically, the Kruskal-Wallis test was used to test for differences in the medians of two or more groups. In addition, the Wilcoxon signed ranked test was used to determine if the median difference in paired observations (1991 concentration subtracted from the 2000 concentration) was statistically different (Helsel and Hirsch, 1992). Concentration changes of less than 10 percent were within the variability limits of the analytical methods used at the USGS lab and treated as no change in concentration. The Spearman's rank test was used to determine whether two variables covary, that is, whether as one variable increases the other variable tends to increase or decrease. A significance level of 0.05 was used for all statistical tests.

RESULTS

A summary of the herbicide and herbicide degradate results for the samples collected in 2000 are given in Table 1. Complete analytical results for these samples are given in Harris *et al.* (2002). As in previous ground water studies (Kolpin *et al.,* 1996, 2000b), herbicide degradates were found to be prevalent in Illinois ground water. The six most frequently detected compounds for this study, detected in 53 to 13 percent of samples, were degradates (Table 1; Figure 2a). For most herbicides, the frequency of detection and concentration both greatly increase when their degradates also are considered (Table 2; Figures 2a, 2b). Overall, herbicide parent compounds were detected in 11 percent of samples; herbicides and herbicide degradates were detected in 56 percent of samples. Occurrences of multiple herbicide compounds in water samples were common, with a median of four detected compounds. As many as 11 compounds were detected in one sample.

Concentrations of herbicide compounds ranged from detections at the reporting limit (0.05 µg/L) to almost 40 µg/L (metolachlor ESA, Table 1). No concentrations exceeded maximum contaminant levels (MCLs) or health advisory levels established by the USEPA for the protection of public water supplies (Table 1) (USEPA, 2003). However, these levels have not been established for some parent herbicides (e.g., acetochlor and prometon) or any of their degradates.

Factors Associated With Herbicide Occurrence

Atrazine was the most frequently detected parent herbicide and is the most frequently used herbicide in

TABLE 1. Herbicides and Their Degradates in Ground Water Samples From 55 Wells in Illinois, 1991 and 2000.[1]

Parent Herbicide (or) Degradate	Detection Frequency (percent)		Median Detected Concentration (µg/L)		Maximum Detected Concentration (µg/L)		Herbicide Use in Illinois[2] (1,000 kg)	
	1991	2000	1991	2000	1991	2000	1991	2000
Any herbicide Compound[3, 4]	–	56.4	–	–	–	39.7	–	–
Any Similar Compound[5]	25.5	18.2	–	–	1.81	0.86	–	–
Acetochlor	na	1.8	na	–	na	0.41	0	2,037
Acetochlor ESA	na	5.5	na	0.14	na	0.74	–	–
Acetochlor OA	na	12.7	na	0.10	na	0.23	–	–
Alachlor	1.8	1.8	0.45	–	0.45	0.07	4,263	80
Alachlor ESA	na	41.8	na	0.55	na	4.66	–	–
Alachlor OA	na	12.7	na	0.27	na	5.85	–	–
Atrazine	14.5	9.1	0.29	0.11	1.81	0.14	4,815	4,956
Deethylatrazine[6]	20.0	14.5	0.09	0.08	0.42	0.33	–	–
Deisopropylatrazine[7]	5.5	1.8	0.23	–	0.40	0.24	–	–
Cyanazine	1.8	0	0.68	–	0.68	–	1,936	0
Cyanazine amide8	na	1.8	na	–	na	0.47	–	–
Dimethenamid	na	0	na	–	na	–	0	761
Dimethenamid ESA	na	1.8	na	–	na	0.06	–	–
Dimethenamid OA	na	1.8	na	–	na	0.05	–	–
Metolachlor	3.6	1.8	0.44	–	0.71	0.86	4,208	1,688
Metolachlor ESA	na	52.7	na	0.74	na	39.7	–	–
Metolachlor OA	na	30.9	na	0.26	na	11.6	–	–
Metribuzin	1.8	0	0.09	–	0.09	–	179	40
Prometon	5.5	1.8	0.06	–	0.22	0.13	–-	–
Simazine	0	0	–	–	–	–	0	195

Notes: 1, µg/L is micrograms per liter; kg is kilograms; na is not analyzed in 1991; – is no data or not applicable; < is less than.
2. Analyzed for but not detected in 1991: ametryn, prometryn, propazine, and terbutryn; Reporting limit for herbicides and degradates was 0.05 µg/L.
3. Analyzed for but not detected in 2000: ametryn, flufenacet, flufenacet ethanesulfonic acid (ESA), flufenacet oxanilic acid (OA), pendimethalin, prometryn, propachlor, propazine, and terbutryn; ESA and OA are degradates of the associated herbicides. Reporting limit for herbicides and degradates was 0.05 µg/L.
4. Maximum contaminant levels (MCL) for atrazine, alachlor, and simazine are 3, 2, and 4 µg/L , respectively. Health advisory levels for cyanazine, metolachlor, and metribuzin are 1, 100, and 200 µg/L, respectively (USEPA, 2003).

[1]Data collected in July and August 1991 and October and November 2000 (one sample collected in February 2001).
[2]USDA (2002). Use data are not reported for herbicides used on less than 1 percent of corn and soybean row crop acreage or herbicides applied on sweet or processed corn acreage, which generally represents less than 1 percent of the total application on row crop acreage.
[3]Parent (field applied) herbicide and degradate.
[4]Comparison of statistics for 1991 and 2000 sample periods is inappropriate; 13 compounds were analyzed in 1991 and 29 in 2000.
[5]Eleven similar herbicide compounds analyzed in 1991 and 2000.
[6]Degradate of atrazine.
[7]Degradate of atrazine, cyanazine, and simazine.
[8]Degradate of cyanazine.

Illinois (Table 1). In 2000, about 5 million kg of atrazine were applied for weed control on corn and sorghum – almost double the amount of the next most frequently used herbicide, glyphosate. Detection frequencies of atrazine were more similar to those of its degradates (deethylatrazine, deisopropylatrazine) than were the detection frequencies of other herbicides to their degradates. This greater similarity in detection frequencies is related to the comparatively slower transformation rates for atrazine, particularly under hypoxic conditions (Agertved *et al.,* 1992; McMahon *et al.,* 1992; Nair and Schnoor, 1992; Klint *et al.,* 1993; Clay *et al.,* 1995). Slower transformation rates allow comparatively more parent atrazine compound to be transported to near surface ground water.

At first inspection, detection frequencies of herbicide degradates in ground water seem to have little relation to current herbicide use (Table 2; Figure 3). For example, in 2000, alachlor was used infrequently in Illinois, while alachlor ethanesulfonic acid

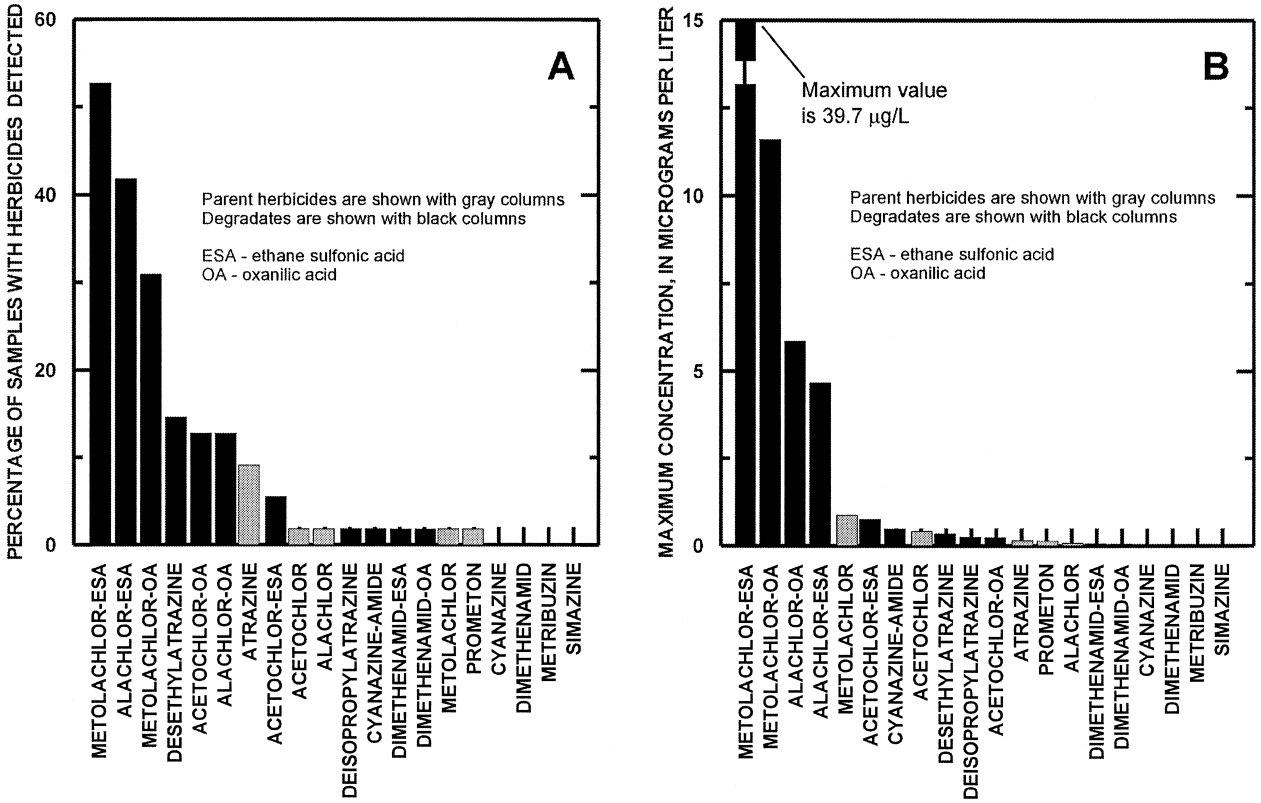

Figure 2. Frequency of Detection (A) and Maximum Concentration (B) of Herbicides and Their Degradates, Illinois, 2000 (reporting limit is 0.05 µg/L).

TABLE 2. Frequency of Detection of Herbicide Compounds in Ground Water Samples When Their Degradates Also Are Considered in the Frequency Analysis.*

Compound	Frequency of Detection (percent)	
	Parent	Parent and One or More Degradate
Acetochlor	1.8	18.2
Alachlor	1.8	43.6
Atrazine	9.1	23.6
Cyanazine	0	1.8
Dimethenamid	0	3.6
Metolachlor	1.8	54.5

*Data collected from 55 wells in Illinois, 2000.

(alachlor-ESA) was one of the most frequently detected compounds for this study. However, there is a time lag between application of herbicides at land surface and their subsequent degradation and transport to ground water. The fate and transport of herbicides to ground water are affected by many physical and chemical factors (e.g., hydrogeology, herbicide chemistry, and soil biochemistry). These factors, along with

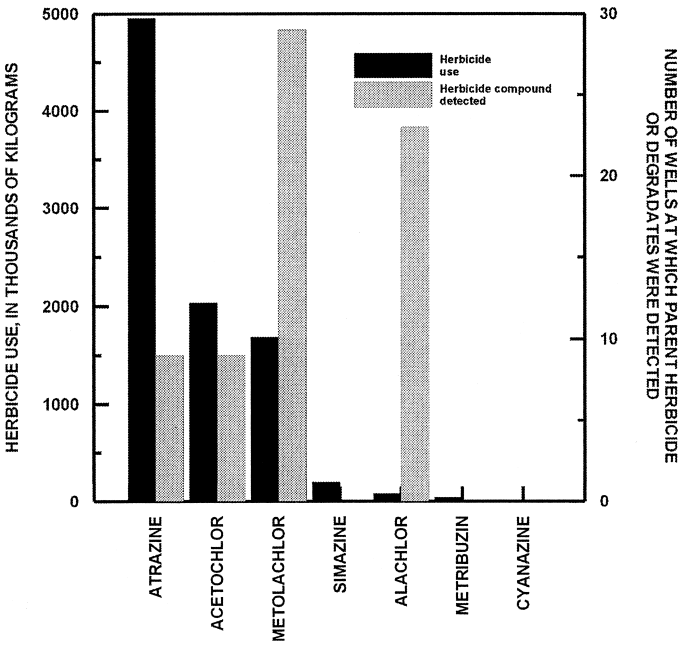

Figure 3. Relation Between the Number of Wells at Which Selected Herbicides and Their Degradates Were Detected and Annual Herbicide Use in Illinois, 2000. (USDA, 2002) (use data are not reported if herbicide was used on less than 1 percent of corn and soybean acreage).

historical trends in herbicide use, need to be examined to effectively determine relations between herbicide use and the subsequent occurrence of herbicide degradates in ground water.

The frequency of detecting herbicide compounds (parent compounds and/or degradates) were statistically greater ($p < 0.001$, Kruskal-Wallis test) in samples from unconsolidated aquifers (73 percent) compared to bedrock aquifers (22 percent). Previous research (Kolpin *et al.,* 1994), which included tritium analyses, suggests this difference in the occurrence of herbicide compounds relates to bedrock aquifers generally having older water (recharged before 1953 and the routine use of herbicides) than unconsolidated aquifers (recharged after 1953). Direct measures of ground water age (tritium data) were unavailable for most (all but four) of the sampled wells in this study; however, two indirect indicators of age were available – dissolved oxygen (DO) concentration and well depth. These data can be used as indicators of water age because oxygen tends to be consumed through biotic and abiotic processes as water travels from zones of recharge to deeper depths, and well depth provides a general indication of distance from a recharge zone (Kolpin *et al.,* 1997a). For this study, the sampled unconsolidated aquifers had higher DO (median DO = 0.5 µg/L concentrations) and shallower well depths (median well depth = 16 m) compared to the bedrock aquifers (median DO = 0.2 µg/L; median well depth = 53 m), supporting the hypothesis that unconsolidated aquifers sampled generally contained younger water than bedrock aquifers sampled. The two indirect estimates of ground water age were used to separate the sampled wells into vulnerability classes for herbicide contamination, as has been done in a study of Iowa ground water (Kolpin *et al.,* 2000b). Wells with a depth greater than 50 m and a DO concentration less than 0.5 µg/L equal low vulnerability. Wells with a depth greater than 50 m and a DO concentration greater than or equal to 0.5 µg/L or wells with a depth less than or equal to 50 m and a DO concentration less than 0.5 µg/L equal intermediate vulnerability. Wells with a depth less than or equal to 50 m and DO concentration greater than or equal to 0.5 µg/L equal high vulnerability. The results show that the frequencies of herbicide compound detection varied significantly ($p = 0.001$, Kruskall-Wallis test) among the vulnerability classes (Figure 4), again indicating that water age is an important factor in determining the transport of herbicide compounds to ground water.

Nitrogen fertilizers frequently are used in conjunction with pesticides to increase crop production (corn and wheat), and nitrate (as N) frequently is detected in aerobic ground water below areas where such fertilizers are used (Nolan *et al.,* 1997). Thus, nitrate concentration may be a useful indicator of the vulnerability of ground water to contamination by herbicides, their degradates, and other pesticides. In this study, the frequency of herbicide compound detection was related positively to nitrate concentrations; however, such a relation was not apparent when only parent herbicides were considered (Figure 5a). Similarly, there was a moderate positive relation between total concentrations of herbicide compounds (parents and degradates) and nitrate concentrations ($r = 0.49$, Spearman's rank test; $p = 0.0011$); yet such a relation was not apparent when only parent herbicides were considered ($r = 0.17$, $p = 0.47$) (Figure 5b). These relations between herbicide compounds and nitrate in ground water have been documented in other studies (Kolpin *et al.,* 1994, 2002).

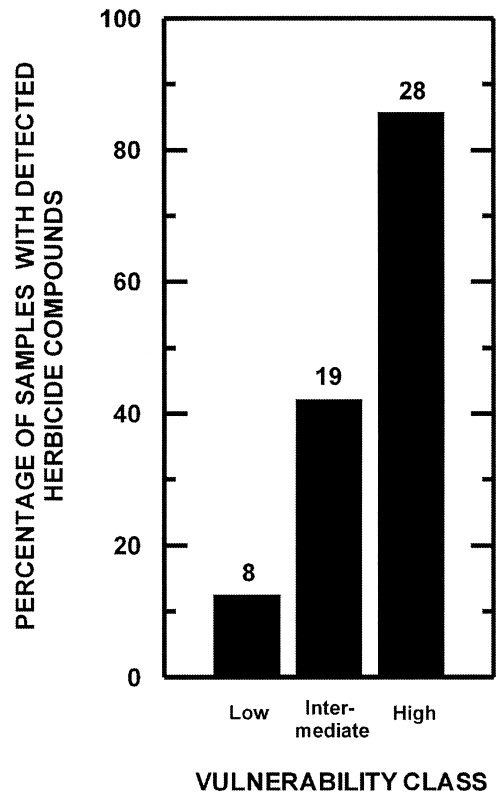

Figure 4. Relation of Frequency of Herbicide Compound Detection to Aquifer Vulnerability Class, Illinois, 2000 (total number of samples in vulnerability class is shown above bar).

The initial use of acetochlor in 1994 and subsequent sampling in 2000 provides useful insights into its transport and transformation rates. Acetochlor or its degradates were detected in 16 percent of sampled wells. None of these detections were in samples considered to represent older water (recharged before 1953; low vulnerability class); well depths where detections occurred ranged from about 11 to 31 m,

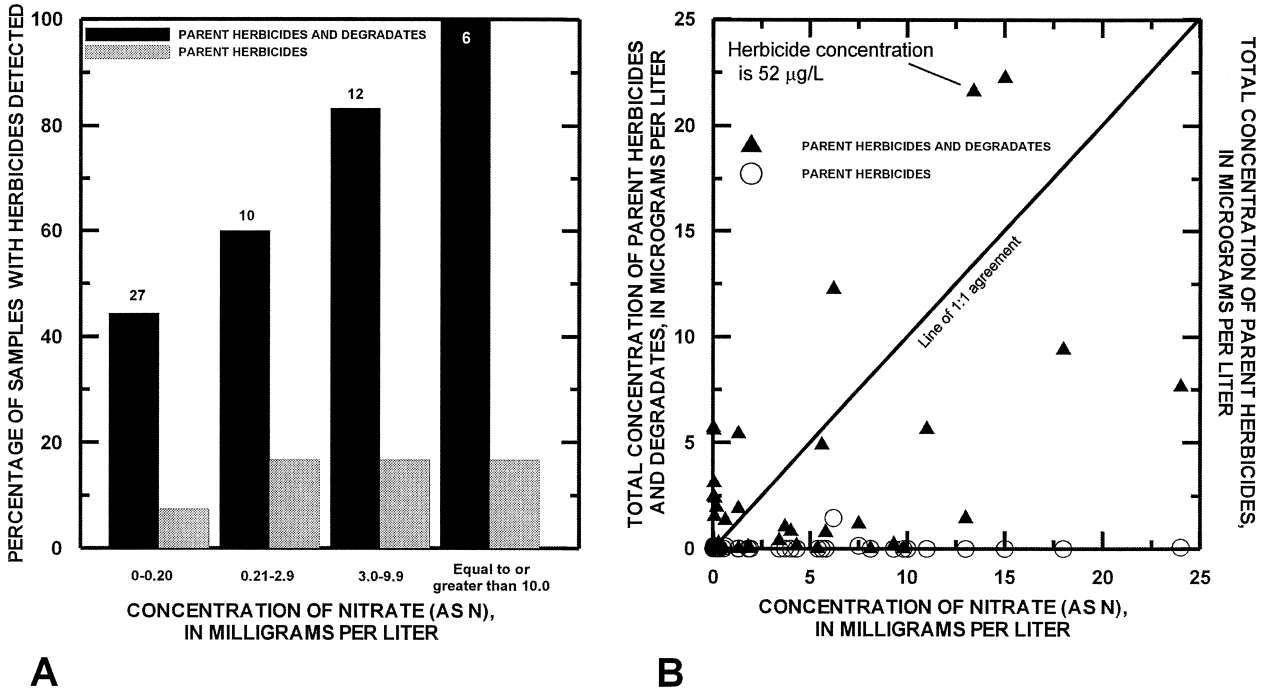

Figure 5. Relation of (A) Frequency of Herbicide Compound Detection to Concentrations of Nitrate (total number of samples in a concentration range is shown above or inside bar); and (B) Total Concentrations of Herbicide Compounds and Parent Herbicides to Nitrate Concentrations.

with a median depth of 14 m. A study by Kolpin *et al.* (1997a) indicates that acetochlor can reach shallow ground water in detectable concentrations within the first year following application; this comparatively rapid transport rate seems to be supported by the findings of the present study. Of the 11 acetochlor compound detections, only one was of the parent compound (Table 1), thus indicating its comparatively rapid rate of transformation after field application, as observed in other studies (Barbash *et al.,* 1999).

Well type possibly was a factor in certain aspects of the herbicide detection results. Herbicide compounds were detected in about 45 percent of samples from domestic supply wells and 67 percent of samples from monitoring wells; detection frequencies for commercial/industrial/irrigation (CIR) and public supply wells were 83 percent and 92 percent, respectively. The higher detection frequencies for the CIR and public supply wells could be related to their comparatively higher withdrawal rates and often longer open intervals, which can result in comparatively larger areas contributing recharge to the wells. Coincidentally, the herbicide concentrations associated with CIR and public supply wells were comparatively low; the 11 highest total concentrations, ranging from 2.47 to 22.23 µg/L, were for samples collected from domestic supply wells. The presumably larger areas contributing recharge to the CIR and public supply wells possibly results in greater mixing with ground waters unaffected by herbicide contamination.

Temporal Trends in Herbicide Occurrence

Concentrations of selected herbicide compounds evaluated during the 1991 (Kolpin *et al.,* 1993) and 2000 studies were compared statistically to determine possible near-decadal temporal trends. Trends in herbicide occurrence and/or concentrations that were identified in ground water were compared with changes in herbicide and land use to assess possible causal relations. Analyses were limited to those compounds that were evaluated during both study periods and detected in at least one of the sample periods: alachlor, atrazine, deethylatrazine, deisopropylatrazine, cyanazine, metolachlor, metribuzin, and prometon (Table 1). Analysis also included acetochlor. Use of this herbicide began in 1994.

For the near decadal period, the frequency of detection for the nine herbicide compounds, as a group, decreased from 25 to 18 percent of samples. Total and maximum concentrations decreased (from 8.90 to 3.2 µg/L and from 1.81 to 0.86 µg/L, respectively). The decrease in detection frequency predominantly was the result of decreases in detection of atrazine and its degradates deethylatrazine and deisopropylatrazine

(Table 1). A significant difference in concentration only was indicated for atrazine (decrease in total concentration, from 4.26 to 0.51 µg/L; $p = 0.041$, Wilcoxon signed ranked test) and acetochlor (increase in total concentration, from 0 to 1.86 µg/L; $p = 0.002$). However, the temporal analysis was hampered by the lack of degradate data for most herbicides in the 1991 dataset (Table 1). Other research has shown that these degradate data are critical to determining temporal trends of herbicide compounds in ground water (Kolpin *et al.,* 2004).

Although a decrease in concentrations of atrazine and its degradates in ground water was indicated between 1991 and 2000, there was not a corresponding decrease in atrazine use (Table 1; Figure 6). This lack of relation could result because the available herbicide use data reflect trends in statewide rather than local use. Also, changes in other factors affecting chemical transport (e.g., application practices, crop management, and climate) could have affected the trend in atrazine concentrations. An evaluation of the possible influence of these temporally and spatially variable factors on the observed herbicide chemistry results was considered impractical because of the complexity of such an evaluation. However, cursory evaluation indicated that there were no substantial differences in atrazine application practices, crop management, or climate for the two sample collection periods. A similar lack of relation was found in a temporal study of Midwestern streams in which atrazine concentrations decreased during periods of relatively consistent atrazine use (Battaglin and Goolsby, 1999).

Because acetochlor was first used in the United States in 1994, it is apparent that concentrations of acetochlor and its ESA and oxanilic acid (OA) degradates would not be present (and therefore detectable) in the 55 samples collected in 1991. The significant increase in ground water concentrations of acetochlor or its degradates, as surrogates for acetochlor, observed between 1991 and 2000 corresponds to the substantial increase in acetochlor use in Illinois after 1993 (Table 1; Figure 6).

To further assess possible temporal trends in herbicide occurrence, results for 47 samples assumed to represent only ground water that was recharged after about 1953 were evaluated separately from the 55 samples that represented ground waters of various ages. Ground water that was recharged before about 1953 predates the routine use of herbicides and thus typically would be unaffected by herbicide contamination. Ground water age determinations were based on various direct (tritium) and indirect (well depth, DO concentration, ORP) indicators, as available. The 47 samples consisted of those previously determined as representing ground waters with high and intermediate vulnerability to herbicide contamination. Oxidation reduction potential values of +100 millivolts (mv) or greater were considered to support high-vulnerability classifications, and values greater than -100 mv and less than +100 mv were considered to support intermediate vulnerability classifications. The results of the evaluation of 47 samples were essentially the same as those of the 55 samples because all herbicide detections in the study but one (deethylatrazine, 0.13 µg/L) were from samples assumed to represent only ground water that was recharged after about 1953.

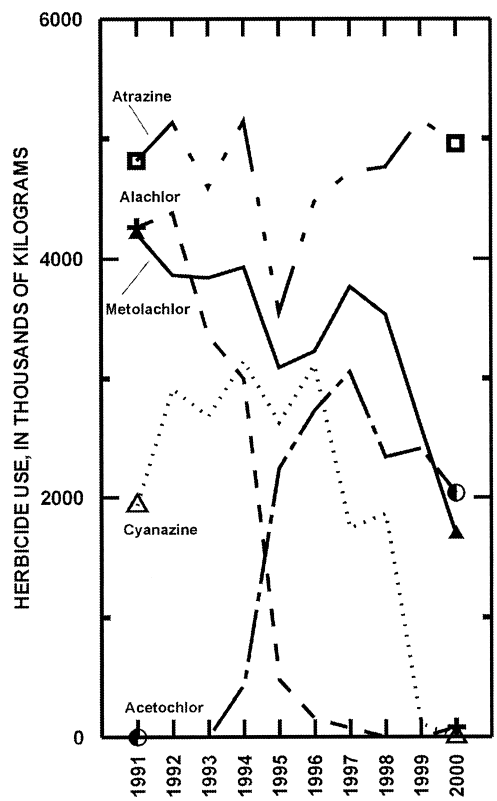

Figure 6. Herbicide Use in Illinois During 1991 Through 2000 (USDA, 2002) (use data are not reported).

Changes in frequency of herbicide detections and herbicide concentrations that may have occurred between 1991 and 2000 cannot be attributed to changes in land use. A review of land use patterns within 3.2 km of the 55 wells sampled in the study indicated essentially no change in land use during the period, particularly in the percentage and location of land used in production of corn or soybeans. A decrease in agricultural land use (about 25 percent at four sites and by 50 to 75 percent at two sites) was evidenced at only six (11 percent) of the sites. However, at each of these sites either herbicides were not detected or concentrations remained unchanged

(varied by less than 10 percent) or increased during the period.

SUMMARY AND CONCLUSIONS

During October and November 2000, the USGS studied the occurrence and distribution of 16 parent herbicides and 13 herbicide degradates in shallow aquifers (within 15 m of land surface) underlying the corn and soybean producing regions of Illinois. Results were compared with those for similar compounds in samples collected from the same wells in 1991. Herbicide compounds were detected at concentrations above 0.05 µg/L in samples from 56 percent of the wells. No concentrations exceeded current (2003) USEPA drinking water standards. However, standards are not established for some of the herbicides or any of the degradates, and standards or guidelines for the protection of aquatic ecosystems are established for only a few of the herbicides. No standards consider the toxicity or aquatic effect of multiple compounds in water. Aquatic standards are of concern in areas where contaminated ground water may discharge to surface water.

Analysis of herbicide degradates significantly increases the detection of the herbicide compounds present in shallow aquifers. Consideration of the degradates results in a fivefold increase in the frequency of detections. The six most frequently detected herbicide compounds, detected in 53 percent (metolachlor ESA) to 13 percent (acetochlor ESA) of samples, were degradates; five of these compounds were degradates of chloroacetanilides (acetolchlor, alachlor, and metolachlor). The frequent presence of degradates in this study confirms the importance of obtaining information on these compounds to better understand the distribution and fate of herbicides in the hydrologic environment. Water age and occurrence of nitrate are useful factors in assessing the vulnerability of Illinois ground water to the transport of herbicide compounds. Unconsolidated aquifers, which were indirectly indicated to contain younger ground water than bedrock aquifers, had a higher frequency of detection of herbicides (73 percent of samples) than bedrock aquifers (22 percent of samples). Awareness of the types of herbicides identified in statewide studies, such as this Illinois study, and factors that may be associated with their occurrence can aid in determining the potential for herbicide contamination of local ground waters and in developing more efficient strategies for sample collection.

For the seven parent herbicides and two degradates analyzed in both 1991 and 2000, the frequency of detection, as a group, decreased from 25 to 18 percent of samples; total and maximum concentrations decreased (from 8.90 to 3.2 µg/L and from 1.81 to 0.86 µg/L, respectively). Temporal differences in concentrations of specific herbicides only were observed for atrazine (decrease) and total acetochlor (increase), although the analysis was hampered by the lack of data for critical degradates for the 1991 sampling. The increase in acetochlor compound concentrations corresponds to the increase in acetochlor use following its introduction in 1994, while the decrease in atrazine concentrations corresponds to relatively consistent use of atrazine during this period. This lack of relation could result because the available atrazine use data reflect trends in statewide rather than local use. Changes in other factors affecting chemical transport (e.g., application practices, crop management, and climate) also could have affected the trend in atrazine concentrations, although there appear to be no substantial differences in atrazine application practices, crop management, or climate for the two sample collection periods. Changes in the frequency of herbicide detection or concentration during the period of study do not appear to be related to changes in land use near the sampled wells.

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