Temporal Trends of Selected Agricultural Chemicals in Iowa's Groundwater, 1982–1995: Are Things Getting Better?

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ABSTRACT

Since 1982, the Iowa Groundwater Monitoring (IGWM) Program has been used to sample untreated groundwater from Iowa municipal wells for selected agricultural chemicals. This long-term database was used to determine if concentrations of select agricultural chemicals in groundwater have changed with time. Nitrate, alachlor [2-chloro-2'-6'-diethyl-*N*-(methoxymethyl)-acetanilide], atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine), cyanazine {2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile)}, and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide] were selected for this temporal analysis of the data. Conclusive temporal changes in frequency of detection and median chemical concentrations were found only for atrazine (decrease) and metolachlor (increase). The greatest temporal chemical changes occurred in the shallowest wells and in alluvial aquifers—both relating to groups of wells generally having the youngest groundwater age. The temporal patterns found for atrazine and metolachlor are consistent with their patterns of chemical use and/or application rates and are suggestive of a causal relation. Only continued data collection, however, will indicate if the trends in chemical concentrations described here represent long-term temporal patterns or only short-term changes in groundwater. No definitive answers could be made in regards to the question of overall improvements in groundwater quality with respect to agricultural chemical contamination and time, due to the inherent problems with the simplistic measurement of overall severity (summation of alachlor + atrazine + cyanazine + metolachlor concentrations) examined for this study. To adequately determine if there is an actual decreasing trend in the overall severity of contamination (improving groundwater quality), the collection of additional water-chemistry data and the investigation of other measures of severity are needed.

IOWA has some of the most productive farmland in the world. To maximize crop yields, agricultural chemicals (pesticides and N fertilizers) have become an integral part of farming in Iowa, where some of the most intensive applications of these chemicals in the USA occurs (Battaglin and Goolsby, 1995). Intensive chemical use has made Iowa a focus for research on the occurrence of agricultural chemicals in groundwater (e.g., Detroy et al., 1988; Glanville et al., 1995; Hallberg, 1989a; Hallberg, 1989b; Kross et al., 1990; Libra et al., 1987), documenting that alachlor, atrazine, cyanazine, and metolachlor have historically been the most frequently detected pesticides in Iowa's groundwater. This research has increased public awareness on the occurrence of agricultural chemicals in groundwater. A continuing public concern has been whether the severity of groundwater contamination from agricultural chemicals has changed over time (is water quality getting better or worse). Studies that have obtained long-term ground-

water chemistry data have documented that temporal changes in chemical use affect concentrations of agricultural chemicals in groundwater (Hallberg, 1987; Hallberg, 1989b; Hallberg et al., 1989; Libra et al., 1991; Rowden et al., 1995). Few studies to date, however, have exhibited the consistency and longevity required to adequately address this issue on a regional scale (Barbash and Resek, 1996). One of the few Iowa studies that could address the temporal issue on a statewide level documented a steady increase in nitrate concentration from 1949 to 1979 in groundwater from shallow municipal wells (<30 m deep) sampled in Iowa (McDonald and Splinter, 1982).

A monitoring program in Iowa that has provided long-term water-chemistry data is the IGWM Program, a joint effort by the University of Iowa Hygienic Laboratory (UHL); the Iowa Department of Natural Resources, Geological Survey Bureau; and the U.S. Geological Survey (USGS) (Detroy, 1985; Detroy et al., 1988). Since 1982, 2041 nitrate samples from 1024 municipal wells and 1375 pesticide samples from 730 municipal wells have been collected for the IGWM. Several features of the IGWM make it appropriate for an examination of temporal trends of agricultural chemicals in Iowa's groundwater. First, only water from municipal wells has been sampled for this study. Thus, the question of using water-chemistry results from differing well types is not an issue. Second, the sampling protocol has not changed during this study—eliminating the possibility of potential temporal changes in chemical concentrations being caused by changes in how the water samples were collected. Third, the same laboratory has been used to analyze all water samples. The use of multiple analyzing laboratories could have introduced variability in chemical concentrations based on differing analytical accuracy and precision. Fourth, the analytical method (and the corresponding analytical reporting limits) have remained unchanged for the duration of this project. Changes in the method of analysis or the analytical reporting limits would have to be taken into account for a temporal analysis of any data set. Research has shown an inverse relation between analytical reporting limits and the frequency of pesticide detection (Kolpin et al., 1995).

This paper describes the results of an investigation of the temporal variability in the concentrations of nitrite plus nitrate as nitrogen (N) (hereafter referred to as nitrate), alachlor, atrazine, cyanazine, and metolachlor in Iowa's groundwater from 1982 to 1995 using data collected for the IGWM. These compounds represent the most frequently detected agricultural chemicals in groundwater for the state (Detroy et al., 1988; Hallberg, 1989a).

D.W. Kolpin and D. Sneck-Fahrer, U.S. Geological Survey, 400 S. Clinton St., Box 1230, Iowa City, IA 52244; G.R. Hallberg, University of Iowa Hygienic Laboratory, 102 Oakdale Campus H101 OH, Iowa City, IA 52242; R.D. Libra, Iowa Department of Natural Resources, Geological Survey Bureau, 123 N. Capital, Iowa City, IA 52242. Received 28 June 1996. *Corresponding author (dwkolpin@usgs.gov).

Abbreviations: IGWM, Iowa Groundwater Monitoring; UHL, University of Hygienic Laboratory; USGS, U.S. Geological Survey; USEPA, U.S. Environmental Protection Agency.

METHODS

Field

All groundwater samples were collected by USGS personnel using protocol designed to obtain a water sample representative of the aquifer (Detroy, 1985). Thus, all samples were collected as close to the wellhead as possible and prior to any water treatment. All wells were pumped at least 20 min prior to sampling to allow for complete removal of stagnant water from the casing and for the sampled water to reach chemical stability (based on successive field measurements of water temperature, specific conductance, and pH). Water samples collected for the analysis of nitrate were filtered through a 0.45-μm cellulose acetate filter into opaque polyethylene bottles, preserved with sulfuric acid (1 mL), and immediately chilled. Water samples collected for pesticide analysis were unfiltered, stored in 1-L borosilicate glass bottles having polypropylene lids with teflon liners (specifically prepared for collecting samples for pesticide analysis), and immediately chilled. The chilled water samples for nutrient and pesticide analysis were sent to UHL (typically within 24 h), where all the analytical work was performed.

Laboratory

The laboratory methods used to obtain concentrations of the selected agricultural chemicals examined for this study have not changed significantly through the duration of the IGWM. Refrigerated water samples for nitrate were analyzed according to U.S. Environmental Protection Agency (USEPA) Method 353.3 (USEPA, 1983) employing copper-cadmium reduction and colorimetric quantitation with an automated analyzing system. The analytical reporting limit for nitrate using this method was 0.10 mg/L.

Refrigerated water samples for pesticide analysis were usually extracted within 2 to 3 d from sample collection but always within a 7-d holding period. These extracts were refrigerated until analyzed. Analysis of pesticides was performed using a USEPA multi-residue, gas chromatography method (USEPA, 1980, 1988; that is, USEPA Method 507, *Determination of Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector*). Laboratory established analytical reporting limits determined by USEPA Method 507 for alachlor, atrazine, cyanazine, and metolachlor are all 0.10 μg/L. Residues were extracted using methylene chloride and exchanged into hexane (adjusted to 10% acetone concentration to improve recovery of cyanazine). Varian 3400 gas chromatographs with capillary columns and N and P detectors were used for the analysis. Over the duration of the IGWM, minor improvements in methods and equipment have been made (e.g., changes from packed columns to capillary columns), but these have not substantively changed the precision or accuracy of the routine pesticide analyses. For confirmation, the laboratory used two dissimilar chromatographic columns for separation and quantitation of each compound. Instrument calibration was performed routinely using appropriate standards for these pesticides. For the pesticides included in this study, percentage recovery from laboratory spiked samples generally ranged from 84 to 110% during the period of study. Reported concentrations were not adjusted for percentage recovery.

As part of its quality-assurance effort, UHL participates in numerous interagency and interlaboratory proficiency and performance evaluation programs including: USEPA Water Supply Series, Water Pollution Series, Laboratory Proficiency Testing Program, and Solid Waste Series; the USGS Standard
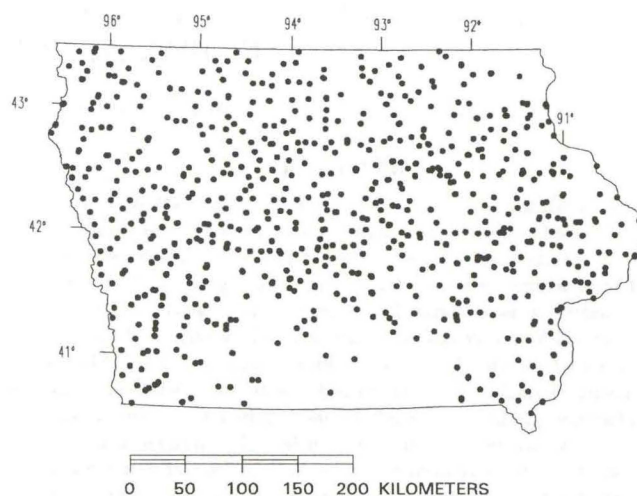

Fig. 1. Location of the 1019 Iowa municipal wells used for this study.

Reference Sample Program; and the American Industrial Hygiene Association programs.

Project Design

Because there could be some seasonal fluctuations in concentrations of agricultural chemicals in unconfined aquifers (Barbash and Resek, 1996; Kolpin et al., 1994), only IGWM samples collected during the months of April to September of each year were used for study. To eliminate potential bias in the data set, if an individual well had multiple water samples collected between April and September in a particular year, the water sample closest to the middle of this time period was selected. Even though problems of seasonality may not have been completely eliminated using this criterion (includes both spring and summer seasons), it was felt that further restrictions on the months of sample collection would have eliminated too many samples—decreasing the temporal nature of this dataset. A total of 1936 water samples from 1019 wells were obtained using these criteria (Fig. 1). The wells are distributed throughout the state except in portions of southern Iowa where surface-water supply systems are dominant. The data were divided into three roughly equal time periods (1982–1986, 1987–1991, and 1992–1995) to evaluate long-term patterns in chemical concentrations. The selected wells have a median well depth of 39.3 m. The wells are grouped into the following aquifer types: alluvial (34.2%), glacial-drift (19.6%), and bedrock (46.2%).

To ensure that the sampling design of the IGWM did not cause misidentifications of temporal trends in the data, a subset of all sampled municipal wells was selected for a more in-depth investigation of temporal patterns. Possible misidentifications may be caused by the changing population of wells sampled for a given year (not following the same set of wells through time). Furthermore, the selection of a portion of wells to be sampled during a particular year was not always completely random—during early years of the IGWM, specific aquifers were targeted because of suspected vulnerability, and some individual wells were sampled because of known water-quality problems. The criteria for selection were that a well have at least a water sample collected before 1988 and after 1991 for the analysis of agricultural chemicals. These criteria yielded 89 wells with the longest record of water-chemistry data available in the IGWM (Fig. 2) and assured that the same set of wells were examined through time. As with the entire IGWM data set, only the April to September samples for each well were used for this study. A median chemical concentra-
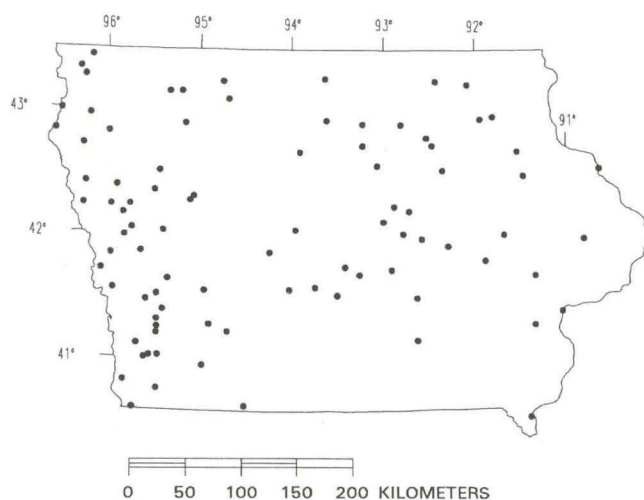
Fig. 2. Location of the 89 Iowa municipal wells having the longest record of agricultural-chemical data available for this study.

tion from samples for these wells was calculated for each time period under investigation. For these 89 wells, 69 had samples collected during 1982 to 1986; 76 had samples collected during 1987 to 1991; 89 had samples collected during 1992 to 1995; and 56 were sampled during all three time periods. These 89 wells have a median well depth of 17.7 m. The wells are grouped into the following aquifer types: alluvial (68.0%), glacial-drift (16.0%), and bedrock (16.0%). Thus, the subset of wells for in-depth study tended to be shallower and had a greater proportion of alluvial aquifers than the total IGWM data set.

Ancillary data compiled for this study included statewide estimates of pesticide use for the years 1979, 1985, 1990, 1991, 1992, 1993, 1994, and 1995 (Hartzler and Wintersteen, 1991; USDA, 1995) and annual statewide estimates of N-fertilizer use for the period 1982 to 1995 (Vroomen, 1989; USDA, 1995) (Table 1). To obtain average pesticide application rate (intensity of use, mass per unit area), the estimated total mass applied was divided by total crop hectares planted. For atrazine and cyanazine, the divisor used was total corn (*Zea mays* L.) hectares planted; for alachlor and metolachlor, the divisor was total corn plus total soybean [*Glycine max* (L.) Merr.] hectares planted.

Nonparametric statistical techniques were used for this study. These methods were appropriate because the data were not normally distributed, and a large percentage of the data were censored; that is, many of the determinations were less than the analytical reporting limit. The Kruskal-Wallis test (Helsel and Hirsh, 1992) was used to test for differences in the medians of two or more groups. The Wilcoxon signed-ranked test (Helsel and Hirsh, 1992) was used to determine whether the median difference between paired observations

equaled zero. The long-term chemical use data (Table 1) were used to determine whether a one- or two-tailed Wilcoxon sign-ranked test was appropriate. If a continuous increasing or decreasing long-term trend in use was noted for an individual compound in Table 1, then a one-tailed Wilcoxon test was used. Otherwise a two-tailed Wilcoxon test was used. A significance level of 0.05 was used for all statistical tests in this study.

RESULTS

The overall frequency of detection for the agricultural chemicals under investigation for all groundwater samples collected for the IGWM during the months of April to September (1982–1995) is given in Table 2. Most reported concentrations were found to be below current USEPA's maximum contaminant levels or health advisory levels for drinking water, with nitrate by far having the most common exceedences (Table 2).

An examination of all groundwater samples collected for the IGWM during the months of April to September from 1982 to 1995, identified a significant ($P = 0.009$, Kruskal-Wallis test) temporal trend in frequency of detection only for metolachlor (Table 3). The frequency of detection for metolachlor progressively increased between the 1982 to 1986 and 1992 to 1995 time periods.

To determine if temporal patterns in the detection of agricultural chemicals were masked by confounding factors, the data also were grouped by well depth and aquifer type. For well depth, the wells were divided into three groups; shallow (≤ 15 m), intermediate (16–30 m) and deep (>30 m) wells. Well depth has been used in previous studies as a rough surrogate for groundwater age (e.g., Kalkhoff et al., 1992; Kross et al., 1990). The hypothesis relating to well depth is that temporal changes in detection frequency may be most evident in more recently recharged (younger) water. Grouping by well depth revealed significant temporal trends in the frequency of detection for the following: shallow wells (atrazine; $P = 0.027$, Kruskal-Wallis test), intermediate wells (metolachlor; $P = 0.006$, Kruskal-Wallis test), and deep wells (no significant temporal trends) (Table 4).

To evaluate the significance of aquifer type with respect to the detection of agricultural chemicals, the wells were divided into three groups representing alluvial, glacial-drift, and bedrock aquifers. Because of their differing geology, groundwater age likely differs significantly between these aquifers. The hypothesis relating to aquifer type is that temporal changes in detection frequency may be most evident for aquifer types having

Table 1. Estimated use of selected agricultural chemicals in Iowa, 1982–1995.

Compound	Average chemical use, in 1000 kg/yr of active ingredient			Average intensity of use, kg/ha		
	1982–1986	1987–1991	1992–1995	1982–1986	1987–1991	1992–1995
Nitrogen-fertilizer†	876 300	836 700	834 200	155	145	132
Alachlor‡	6 260	3 740	2 350	2.26	2.52	2.54
Atrazine‡	3 710	3 380	3 264	1.64	1.08	0.98
Cyanazine‡	4 282	2 654	3 170	2.31	2.38	2.53
Metolachlor‡	3 059	4 949	4 709	2.69	2.30	2.30

† Vroomen (1989), USDA (1995).
‡ Hartzler & Wintersteen (1991); USDA (1995).

Table 2. Summary of results for groundwater samples collected for the Iowa Groundwater Monitoring Program during the months of April to September (1982–1995) for selected agricultural chemicals.†

Compound	N	Reporting limit	Freq. of detection, %	Max. conc.	MCL or HA‡	Freq. of exceedence, MCL or HA, %
Nitrate	1929	0.10 mg/L	57.1	53.0 mg/L	10 mg/L	7.2
Alachlor	1485	0.10 µg/L	3.0	14.0 µg/L	2.0 µg/L	0.4
Atrazine	1485	0.10 µg/L	19.5	21.0 µg/L	3.0 µg/L	0.8
Cyanazine	1314	0.10 µg/L	3.6	4.5 µg/L	1.0 µg/L	0.3
Metolachlor	1309	0.10 µg/L	5.7	200 µg/L	100 µg/L	<0.1

† N, number of samples; Freq., frequency; Max. maximum; conc., concentration; MCL, maximum contaminant level; HA, health advisory level.
‡ USEPA (1996).

the youngest water. Significant temporal trends in the frequency of detection were identified for the following: alluvial aquifers (metolachlor; $P = 0.023$, Kruskal-Wallis test), glacial-drift (no significant temporal trends), and bedrock aquifers (cyanazine; $P = 0.023$, Kruskal-Wallis test) (Table 5).

To ensure that the sampling design (for example, changing population of wells sampled for a given year) of the IGWM has not caused misidentifications of temporal trends in the data, a subset of 89 municipal wells (Fig. 2) that were sampled repeatedly from 1982 to 1995 was selected for a more in-depth investigation of temporal patterns. The advantage of this subset of wells is that temporal changes in median chemical concentrations can be examined rather than just frequencies of detection because the same population of wells are examined through time. An examination of this subset of groundwater samples identified a significant temporal trend in median concentration only for atrazine, with a significant decrease ($P = 0.021$, Kruskal-Wallis test) being determined. This temporal pattern was caused by a substantial decrease in median atrazine concentration between the 1987 to 1991 and 1992 to 1995 time periods. There was no significant change ($P = 0.905$, Kruskal-Wallis test) in median atrazine concentration between the 1982 to 1986 and 1987 to 1991 time periods. About 80% (27 of 34) of the wells where atrazine was detected had decreases in median atrazine concentration between the 1987 to 1991 and 1992 to 1995 time periods.

Because of the availability of paired observations for this subset of 89 wells, the Wilcoxon signed-rank test also may be used to test for temporal changes in median concentrations. For this statistical test, the median 1992 to 1995 concentrations were subtracted from the median 1987 to 1991 concentrations for each well. If no data were available for the 1987 to 1991 time period for a particular well, the median 1992 to 95 concentration was subtracted from the median 1982 to 1986 concentration.

Examining these differences in paired observations identified a significant decrease in median atrazine concentrations ($P < 0.001$, one-tailed Wilcoxon signed-rank test) and a significant increase in median metolachlor concentrations ($P = 0.042$, one-tailed Wilcoxon signed-rank test) (Fig. 3). Those agricultural chemicals where no significant difference was identified had roughly equal positive and negative concentration differentials (Fig. 3).

The decreasing trend in median atrazine concentrations is consistent with results of other long-term research in groundwater and for streams in the midwestern USA. Concentrations of agricultural chemicals have been measured in groundwater from the 267 km² Big Spring basin (Libra et al., 1992; Rowden et al., 1995; Iowa Department of Natural Resources, Geological Survey Bureau, 1996, unpublished data) on a weekly basis since 1982. The flow-weighted mean atrazine concentrations from the Big Spring basin were 0.40 µg/L (1982–1986), 0.65 µg/L (1987–1991), and 0.20 µg/L (1992–1995). Bedrock aquifers in northeast Iowa (Floyd and Mitchell Counties) were sampled from a network of 25 wells in May 1986 and again in May to June 1994 (Quade et al., 1994). The frequency of atrazine detection decreased from 72 to 64% in these wells between the two sampling periods. The mean atrazine concentration,

Table 3. Temporal patterns in frequency of detection for selected agricultural chemicals in Iowa groundwater (1019 wells). A P value ≥ 0.05 is not considered statistically significant.

Compound	Median frequency of detection, %			Results of Kruskal-Wallis test (P value)
	1982–1986	1987–1991	1992–1995	
Nitrate	48.1	61.5	55.4	0.229
Alachlor	0.0	2.2	3.3	0.541
Atrazine	15.4	19.3	13.2	0.152
Cyanazine	0.0	3.3	4.1	0.096
Metolachlor	0.0	4.8	14.1	0.009

Table 4. Temporal patterns in frequency of detection for selected agricultural chemicals in Iowa groundwater (1019 wells) by well depth group. A P value ≥ 0.05 is not considered statistically significant.

Compound	Median frequency of detection, %			Results of Kruskal-Wallis test (P value)
	1982–1986	1987–1991	1992–1995	
	Shallow wells, ≤15 m			
Nitrate	77.1	81.1	76.1	0.292
Alachlor	0.0	1.4	4.0	0.248
Atrazine	20.0	29.7	16.4	0.027
Cyanazine	0.0	5.8	4.1	0.163
Metolachlor	0.0	6.2	6.8	0.480
	Intermediate wells, 16–30 m			
Nitrate	72.0	81.2	76.0	0.120
Alachlor	0.0	3.9	1.4	0.390
Atrazine	19.4	25.0	22.2	0.431
Cyanazine	0.0	6.4	8.8	0.108
Metolachlor	0.0	7.1	28.6	0.006
	Deep wells, >30 m			
Nitrate	36.8	40.7	27.8	0.254
Alachlor	0.0	2.4	1.9	0.344
Atrazine	6.9	10.6	7.6	0.361
Cyanazine	0.0	1.2	0.0	0.056
Metolachlor	0.0	1.3	3.4	0.130

however, showed an even more dramatic trend, decreasing from 1.8 μg/L in 1986 to 0.25 μg/L in 1994. A study of two areas in central and southeastern Wisconsin also found an apparent temporal relation between decreasing atrazine use and decreasing atrazine concentrations in groundwater (Saad, 1997). A study of 50 midwestern streams in the USA sampled during May to June for the years 1989, 1990, 1994, and 1995 found a statistically significant decrease in atrazine concentration between the 1989 to 1990 and the 1994 to 1995 sampling periods (Donald A. Goolsby, U.S. Geological Survey, 1996, written communication). Decreased concentrations in streams are important to aquifers having strong groundwater/surface water interactions (e.g., alluvial aquifers). Research has shown that streams can be a source of atrazine contamination to alluvial aquifers (Squillace et al., 1993; Wang and Squillace, 1994; Squillace, 1996).

As when the entire IGWM data set was examined, temporal patterns in concentrations of agricultural chemicals may be masked by confounding factors, such as well depth and aquifer type. Grouping by well depth revealed significant temporal trends in the median concentration for the following: shallow wells, atrazine—significant decrease ($P = 0.041$, Kruskal-Wallis test; $P < 0.001$, one-tailed Wilcoxon signed-rank test), metolachlor—significant increase ($P = 0.022$, Kruskal-Wallis test; $P = 0.031$, one-tailed Wilcoxon signed-rank test); intermediate wells, atrazine—significant decrease ($P = 0.049$, one-tailed Wilcoxon signed-rank test); and deep wells (no significant temporal trends). The temporal variability for atrazine and metolachlor decreased with increasing well depth (Fig. 4). Decreased chemical variability with increasing well depth is consistent with the literature (Hallberg, 1987; Hallberg, 1989b; Kolpin and Thurman, 1995). As expected, changes in chemical applications or climatic conditions at the land surface should be reflected by changes in chemical concen-

trations most rapidly in the shallowest (youngest) groundwater.

Grouping by aquifer type revealed significant temporal trends in the median concentration for the following: alluvial aquifers, atrazine—significant decrease ($P = 0.039$, Kruskal-Wallis test; $P < 0.001$, one-tail Wilcoxon signed-rank test), metolachlor—significant increase ($P = 0.039$, Kruskal-Wallis test); glacial-drift (no significant temporal trends); and bedrock aquifers (no significant temporal trends) (Fig. 5). In other investigations, alluvial aquifers have been determined to be more susceptible, in general, to contamination by agricultural chemicals than the generally deeper bedrock aquifers (Hallberg, 1989a; Kolpin et al., 1994; Kolpin and Goolsby, 1995). The relative absence of overlying low-permeability material, generally local flowpaths with surface-recharge areas in proximity to wells, and the relatively rapid rates of groundwater movement are all likely contributing factors to the temporal patterns found in alluvial aquifers. However, the relatively small number of wells completed in glacial-drift and bedrock aquifers for the subset of IGWM wells examined decreased our ability to adequately determine temporal patterns for these types of aquifers.

Although the temporal changes in median metolachlor concentrations determined for this study appear minor (fewer wells affected) in relation to those of atrazine (Fig. 3–5), the results are equally important. The increase in median metolachlor concentrations that occurred in water samples during the 1992 to 1995 time period might be the leading edge of an upward trend of metolachlor contamination in Iowa's groundwater.

Table 5. Temporal patterns in frequency of detection for selected agricultural chemicals in Iowa groundwater (1019 wells) by aquifer type. A P value ≥ 0.05 is not considered statistically significant.

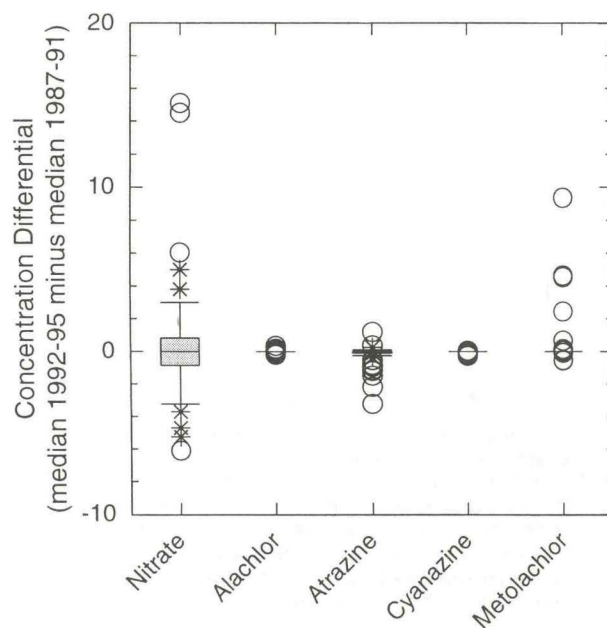| Compound	Median frequency of detection, %			Results of Kruskal-Wallis test (P value)
	1982–1986	1987–1991	1992–1995	
Alluvial aquifers				
Nitrate	73.8	79.0	74.2	0.309
Alachlor	0.0	1.7	3.1	0.797
Atrazine	19.2	28.3	21.0	0.150
Cyanazine	0.0	4.2	6.5	0.165
Metolachlor	0.0	7.4	16.5	0.023
Glacial-Drift aquifers				
Nitrate	46.9	57.5	34.8	0.214
Alachlor	0.0	3.4	0.0	0.470
Atrazine	6.7	17.2	0.0	0.094
Cyanazine	0.0	3.4	0.0	0.062
Metolachlor	0.0	0.0	0.0	0.927
Bedrock				
Nitrate	39.7	47.7	46.3	0.505
Alachlor	0.0	2.5	2.2	0.176
Atrazine	20.0	14.3	14.6	0.823
Cyanazine	0.0	1.8	0.0	0.023
Metolachlor	0.0	1.8	4.7	0.130

Fig. 3. Statistical summary of the concentration differential for selected agricultural chemicals. This concentration differential was calculated by a substraction of the median 1992 to 1995 concentration from the median 1987 to 1991 concentration for the 89 wells having the longest record of agricultural-chemical data. If a particular well had no chemical data for the 1987 to 1991 time period, the median 1992 to 1995 concentration was subtracted from the 1982 to 1986 concentration.
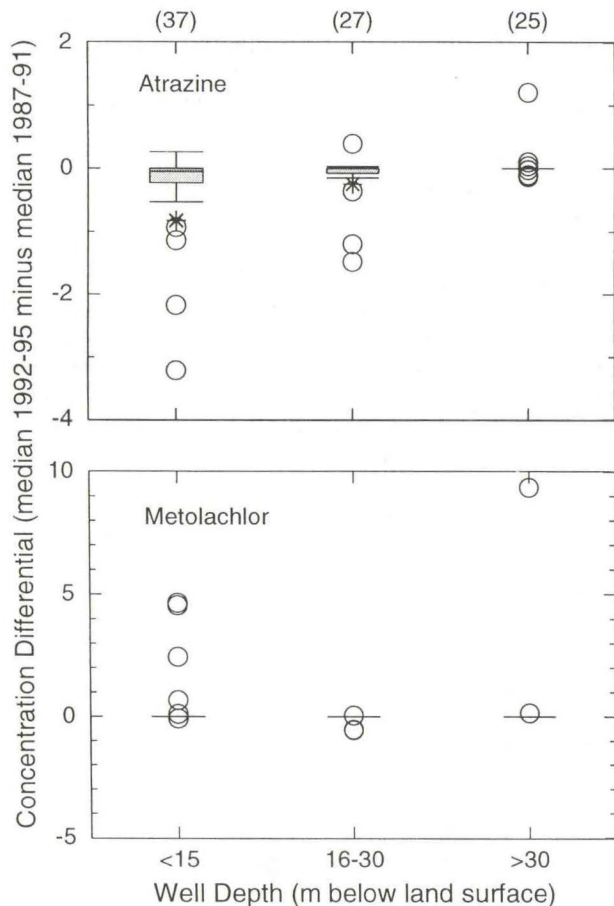
Fig. 4. Statistical summary of the concentration differential for selected agricultural chemicals by well depth. This concentration differential was calculated by a substraction of the median 1992 to 1995 concentration from the median 1987 to 1991 concentration for the 89 wells having the longest record of agricultural-chemical data. If a particular well had no chemical data for the 1987 to 1991 time period, the median 1992 to 1995 concentration was subtracted from the 1982 to 1986 concentration.

Continued collection of water-chemistry data for the IGWM is required to determine if this represents a long-term increase in metolachlor concentrations in groundwater.

Precipitation and Chemical Use

Two major factors that can have a temporal effect on chemical concentrations in groundwater are variations
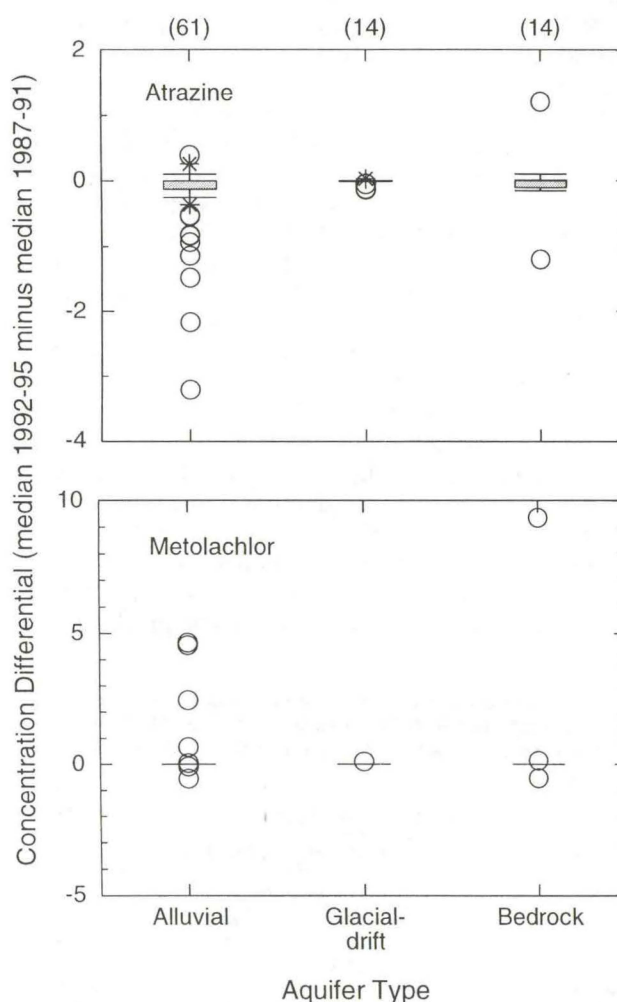

Fig. 5. Statistical summary of the concentration differential for selected agricultural chemicals by aquifer type. This concentration differential was calculated by a substraction of the median 1992 to 1995 concentration from the median 1987 to 1991 concentration for the 89 wells having the longest record of agricultural-chemical data. If a particular well had no chemical data for the 1987 to 1991 time period, the median 1992 to 1995 concentration was subtracted from the 1982 to 1986 concentration.

in precipitation (recharge) and chemical use patterns (Hallberg and Keeney, 1993; Hallberg et al., 1993; Lucey and Goolsby, 1993; Barbash and Resek, 1996). There is no apparent relation between precipitation and the

temporal patterns in median concentrations found for atrazine and metolachlor. In general, 1982 to 1986 was a time of relatively normal precipitation, 1987 to 1991 included the driest consecutive 2-yr period on record (1988–1989) in Iowa (Kross et al., 1990), and 1992 to 1995 included the single wettest year on record (1993) in Iowa (Kolpin and Thurman, 1995; Wahl et al., 1993). An improved understanding of the relation between precipitation and chemical concentrations in groundwater may be obtained if data on rainfall and/or recharge in proximity to sampled wells were available. Water level measurements from sampled wells also would be useful in determining possible changes in recharge for an individual well. However, all the wells in this study are municipal wells. Few municipalities allowed access for water-level measurements to be made or collected data on water levels themselves.

Although there appears to be a slight decrease in the statewide total mass applied and intensity of use for N fertilizer (Table 1), no significant temporal trends were noted in either the frequency of detection or median nitrate concentrations in groundwater. There are several possible explanations for this: (i) the general decrease in N-fertilizer applications are not large enough to cause a significant decrease in groundwater concentrations, (ii) more time is required for this decrease in applications to be reflected by groundwater concentrations, (iii) other sources of nitrate contamination, such as animal manure, are not taken into account, (iv) the statewide application data may not adequately characterize actual changes in fertilizer applications around the sampled wells, and (v) nitrate occurrence and concentrations in shallow groundwater are sensitive to changes in precipitation and recharge because of the mobility of nitrate (Hallberg and Keeney, 1993; Hallberg et al., 1993). Other studies in Iowa have suggested that nitrate concentrations increased in the 1992 to 1995 period, in part, because of pre-existing drought conditions that allowed considerable N to accumulate in the soil even though fertilizer applications had been reduced (Lucey and Goolsby, 1993; Rowden et al., 1995).

No significant temporal trends were noted in either the frequency of detection or median alachlor concentrations in groundwater, even though statewide alachlor use has decreased about 60% (Table 1) from 1982 to 1995. There are possible explanations for the absence of a temporal trend in median alachlor concentrations in groundwater. First, alachlor was found relatively infrequently in the wells having the longest record of water-chemistry data (7 of 89). Thus, because 92% of the wells did not have alachlor concentrations above analytical reporting limits the identification of a significant temporal pattern becomes more difficult. Alachlor has been found to degrade rapidly in the soil zone (Clay et al., 1995; Potter and Carpenter, 1995; Thurman et al., 1996), with a major degradation product being alachlor ethanesulfonic acid (alachlor-ESA; 2-[(2,6-diethylphenyl) (methoxymethyl)amino]-2-oxoethanesulfonic acid). Alachlor-ESA is a much more persistent compound and has been detected in groundwater almost 10 times as frequently as alachlor (Kolpin et al., 1996a, 1997). If long-term data on alachlor degradation products were available, a more definitive relation between alachlor use and chemical concentrations (parent + degradation products) in groundwater might have been identified. Second, alachlor has recently shown a dramatic decrease in statewide use. The statewide use of alachlor has decreased from first among all herbicides in 1985; to fourth in 1994; to 12 in 1995 (George R. Hallberg, University of Iowa Hygienic Laboratory, 1996, written communication). This sharp decrease in alachlor use that has occurred in recent years may take additional time to be reflected in measured concentrations from the few wells that were found to have alachlor in groundwater.

The temporal pattern of decreasing median atrazine concentrations determined for the subset of 89 wells examined for this study appear coincident with the changes in statewide atrazine use (Table 1), and are suggestive of a causal relation. The estimated mass of atrazine being used in Iowa has remained relatively constant from 1982 to 1995, with only a slight decrease (about 12%) in use occurring (Table 1). However, there has been about a 40% decrease in the intensity of use (Table 1) that also could affect the amount of chemical transport to groundwater. Research has shown that application rate can be an important factor in determining the amount of chemical transport (Cheng and Koskinen, 1986; Ng et al., 1995; Rhode, 1981). The decrease in the intensity of atrazine use can be attributed to several factors: (i) the increased use of product mixes/tank mixes containing atrazine that reduce the mass of atrazine applied (per unit area) by using it in combination with other herbicides, (ii) the increase in postemergent applications that use lower rates of atrazine application (Hartzler and Wintersteen, 1991), and (iii) State restrictions of the rate, per hectare, at which atrazine can be applied within selected areas in northeast and north-central Iowa (Iowa Department of Natural Resources, 1994). The relatively slow degradation rate for atrazine (Nair and Schnoor, 1992; Kruger et al., 1993; Clay et al., 1995; Widmer and Spalding, 1995) allows more parent compound to be transported to groundwater, and thus, may cause more apparent relations between chemical use and chemical concentrations in groundwater (more data above analytical reporting limits available for the temporal analysis).

No significant temporal trends were noted in median cyanazine concentrations in groundwater, even though cyanazine use has decreased about 25% (Table 1) from 1982 to 1995. Similar to alachlor, cyanazine has been found to degrade rapidly in the soil zone (Muir and Baker, 1976), and is found infrequently in Iowa's groundwater (Detroy et al., 1988; Kross et al., 1990). A major degradation product of cyanazine is cyanazine amide [2-chloro-4-(1-carbamoyl-1-methylethylamino)-6-ethylamino-s-triazine]. Cyanazine amide is a much more persistent compound and has been detected in groundwater about two to three times more frequently than cyanazine (Kolpin et al., 1996a, 1997). If long-term data on cyanazine degradation products were available, a more significant relation between cyanazine use and chemical concentrations (parent + degradation products) in groundwater might have been identified.

The temporal pattern of increasing frequency of met-

olachlor detections and increasing median metolachlor concentrations identified through this study appear coincident with the changes in statewide metolachlor use (Table 1), and are suggestive of a causal relation. The mass of metolachlor used has increased more than 50% from 1982 to 1995 (Table 1). The combination of the large mass of metolachlor used in Iowa (Table 1) and its relative mobility (Bowman, 1990; Wietersen et al., 1993; Kruger et al., 1996) may have contributed to the temporal trends identified for metolachlor in this study.

The agricultural-chemical data summarized for this study are the basis for continued assessment of the identified temporal trends to evaluate their significance. An improved understanding between chemical use and chemical concentrations in groundwater may be obtained if data on actual chemical use in proximity to sampled wells were available.

DISCUSSION

In this study, we have demonstrated that a general decrease in median atrazine concentrations and a general increase in median metolachlor concentrations has

EXPLANATION

(69)   Number of observations

○   Outlier data value more than 3 times the
            interquartile range outside the quartile

✳   Outlier data value less than or equal to 3
            and more than 1.5 times the
            interquartile range outside the quartile

            Data value less than or equal to 1.5 times the
            interquartile range outside the quartile

            75th percentile

            Median

            25th percentile
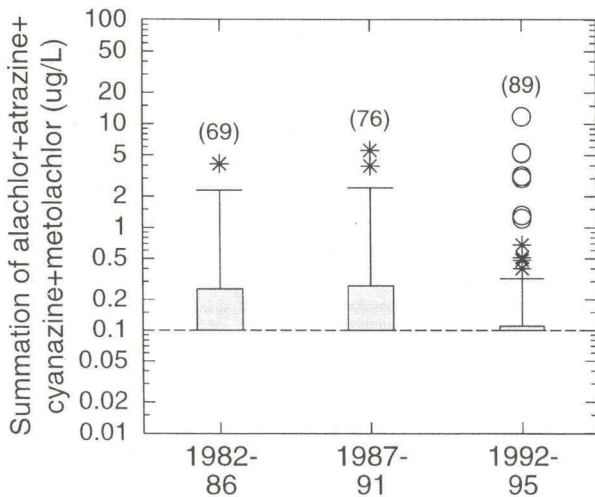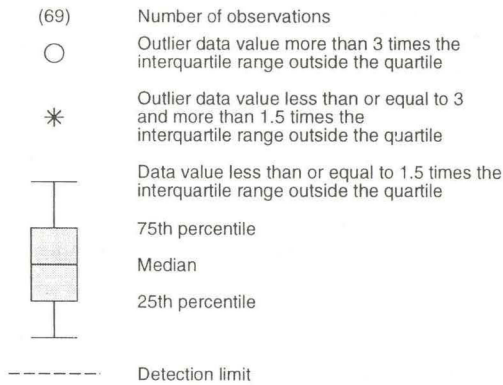
- - - - -   Detection limit

Fig. 6. Summation of alachlor + atrazine + cyanazine + metolachlor (SUM) for the 89 Iowa municipal wells having the longest record of agricultural-chemical data available for this temporal study.

occurred (particularly between the 1987–1991 and 1992–1995 time periods) in a subset of IGWM wells that had the longest record of water-chemistry data. These temporal concentration changes appear to coincide with their corresponding trends in long-term chemical use. A fundamental question that remains to be answered, however, is whether the severity of groundwater contamination by combined agricultural chemicals is increasing or decreasing through time. In other words, are the overall groundwater quality conditions improving (is the problem getting better or worse), or is there a simple replacement of chemicals in groundwater (decreasing concentrations of one chemical is balanced by an increase for another).

One measure of the overall severity of contamination by agricultural chemicals is the total combined concentration in groundwater. For this study, a summation of alachlor, atrazine, cyanazine, and metolachlor concentrations (SUM) was used. Concentrations below the 0.10 μg/L analytical reporting limit were set to zero for the calculation of SUM.

No significant difference ($P = 0.065$) in median SUM through time was identified in the subset of 89 wells using a Kruskal-Wallis test, but a significant decrease ($P = 0.002$) in median SUM through time was found using a one-tailed, Wilcoxon signed-rank test. A substantial decrease in the median SUM concentration occurred during the 1992 to 1995 time period (Fig. 6). Thus, a decreasing trend in the overall severity of groundwater contamination from pesticides might be occurring. This decreasing trend appears coincident with progressive decreases in the overall combined use of alachlor, atrazine, cyanazine, and metolachlor in Iowa (Table 1)—with over a 20% decrease occurring during this study. There is, however, an offset between the greatest period of change in the combined chemical use (1982–1986 and 1987–1991, Table 1) and the greatest period of change in the median SUM concentration (1987–1991 and 1992–1995, Fig. 6). This suggests that, as noted in the literature (e.g., Hall, 1992), a lag time likely exists between changes in chemical use at the land surface and measured concentrations in groundwater.

This simplistic measure of severity, however, has various shortcomings. First, it does not take into account differences in toxicities between these four compounds (all chemicals have equal weighting). Currently, maximum contaminant levels are only determined for alachlor (2 μg/L) and atrazine (3 μg/L); with nonregulatory health advisory levels set for cyanazine (1 μg/L) and metolachlor (100 μg/L) (USEPA, 1996). Second, this measure of severity does not take into account the presence in groundwater of other pesticides that are known to be used in Iowa. Other pesticides beyond the four examined for this study have been found in Iowa's groundwater (e.g., Kross et al., 1990; Kolpin et al., 1995, 1996b). Third, this measure of severity does not take into account the presence in groundwater of pesticide degradation products, some of which have been found to be prevalent in groundwater (Barrett, 1996; Kolpin et al., 1996a, 1997; Potter and Carpenter, 1995; Roy and Krapac, 1994). If degradation products are not quanti-

fied, the total concentration in groundwater is substantially underestimated. Finally, this measure of severity assumes the toxicological interactions between all combinations of agricultural chemicals are additive and not synergistic. Research has shown that some combinations of pesticides have synergistic toxicity (Marinovich et al., 1996; Thompson, 1996). Thus, to adequately determine if there is an actual decreasing trend in the overall severity of contamination, the collection of additional water-chemistry data and the investigation of other measures of severity are required.

CONCLUSION

The IGWM has been used to collect water-chemistry data for selected agricultural chemicals from municipal wells in Iowa since 1982. Besides its duration, several features of the IGWM make it appropriate for an examination of temporal trends of agricultural chemicals in Iowa's groundwater including the consistency in well type, sample collection protocol, analyzing laboratory, analytical methods, and analytical reporting limits.

This study determined a significant decrease in median atrazine concentration and a significant increase in median metolachlor concentration in Iowa's groundwater. These temporal patterns in median concentration are consistent with their pattern of statewide chemical use and are suggestive of a causal relation. There is, however, an apparent offset between the greatest period of change in chemical use (1982–1986 and 1987–1991) and that for median concentration (1987–1991 and 1992–1995). This suggests a lag time likely exists between changes in chemical use at the land surface and measured concentrations in groundwater.

The temporal variability for atrazine and metolachlor decreased with increasing well depth, documenting that changes in chemical concentrations occur most rapidly in the shallowest (youngest) groundwater. The temporal variability for atrazine and metolachlor was found to be significant only for alluvial aquifers. The relative absence of overlying low-permeability material, generally local flowpaths with surface-recharge areas in proximity to wells, and the relatively rapid rates of groundwater movement are all likely contributing factors to the temporal patterns found in alluvial aquifers. However, the relatively small number of wells completed in glacial-drift and bedrock aquifers for the subset of IGWM wells examined decreased our ability to adequately determine temporal patterns for these types of aquifers.

The identification of temporal patterns in median agricultural chemical concentrations in groundwater and their apparent relation to changes in chemical use, demonstrates the importance and benefits of a program, such as the IGWM, to collect long-term water-chemistry data. Only through continued data collection can it be determined if the trends described here represent long-term temporal trends or only short-term changes in groundwater concentrations.

It is also important, however, that such a monitoring program have the flexibility to add compounds to its suite of constituents analyzed as new pesticides are introduced into farming and additional pesticide degradation products are identified. For example, imazethapyr (2 -[4,5-dihydro-4 -methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid), a soybean herbicide first registered for use around 1988, quickly obtained widespread use in Iowa within several years of registration (Hartzler and Wintersteen, 1991). An even more dramatic example is acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methyl-phenyl) acetamide], a herbicide first registered for use on corn in 1994. In a mere 2 yr, acetochlor went from zero use to the third most heavily used pesticide in Iowa (USDA, 1995). Thus, if these additional compounds are not examined in groundwater, a major part of the contemporary pattern of chemical use will be missed.

Furthermore, recent research has shown that pesticide degradation products commonly occur in groundwater, often being detected more frequently than their parent compounds (Kolpin et al., 1996a, 1997; Potter and Carpenter, 1995; Roy and Krapac, 1994). These degradation products also may contribute to concerns for deleterious effects on human health and the environment (Barrett, 1996; Coats, 1993; Tessier and Clark, 1995) and are requisites for understanding the environmental fate of pesticides. Consequently, if long-term data on pesticides and all their major degradation products are not available, an understanding of the environmental fate of pesticides will remain incomplete.

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