

# Finding minimal herbicide concentrations in ground water? Try looking for the degradates

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## ABSTRACT

Extensive research has been conducted regarding the occurrence of herbicides in the hydrologic system, their fate, and their effects on human health and the environment. Few studies, however, have considered the degradates of herbicides. In this study of Iowa ground water, herbicide degradates were frequently detected. In fact, herbicide degradates were 8 of the 10 most frequently detected compounds. The total residue concentration (sum of parent compound plus degradates) was substantially greater than the concentration of just the parent compound for every herbicide examined.

The frequencies of herbicide detection and concentrations varied substantially among the major aquifer types sampled. These differences, however, were much more pronounced when herbicide degradates were included. Aquifer types having the most rapid recharge rates (alluvial and bedrock/karst region aquifers) were those most likely to contain detectable concentrations of herbicide compounds.

Two indirect estimates of ground-water age (depth of well completion and dissolved-oxygen concentration) were used to separate the sampled wells into general vulnerability classes (low, intermediate, and high). The results show that the frequencies of herbicide detection and concentrations varied substantially among the vulnerability classes regardless of whether or not herbicide degradates were considered. Nevertheless, when herbicide degradates were included, the frequency of herbicide compound detection within the highest vulnerability class approached 90 percent, and the median total herbicide residue concentration increased over an order of magnitude to 2 micrograms per liter. The results of this study indicated that obtaining data on herbicide degradates is critical in attempting to understand not only the fate of a specific herbicide but also its overall effect on human health and the environment.

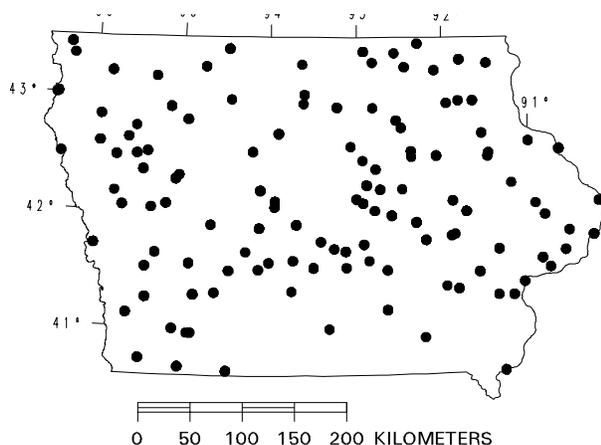
## INTRODUCTION

Extensive research has been conducted regarding the occurrence of herbicides in the hydrologic system (Holden and others, 1992; Walls and others, 1996), their fate (Bintein and Devillers, 1996; Kruger and others, 1997), and their effects on human health (Carbonell and others, 1995; Bain and LeBlanc, 1996; Ribas and others, 1997) and the environment (Longley and Sotherton, 1997; Pratt and others, 1997; Carder and Hoagland, 1998; Howe and others, 1998). However, the understanding of the total consequences from herbicide use are limited by the fact that most investigations have focused on the active ingredient (parent compound) and did not consider their transformation products (degradates).

Complete mineralization of most parent herbicide compounds has not been established (Stamper and others, 1997). However, relatively stable and persistent degradates can be formed during the transformation of many herbicides (Coats, 1993). These degradates can, in some cases, be more toxic than their parent compounds (La Clair and others, 1998; Belfroid and others, 1998).

This paper describes the results of a study to determine the relative transport of selected herbicide degradates to ground water compared to that of their parent compounds. Results from the sampling of 131 municipal wells from the major aquifer types in Iowa during 1995-98 are presented (fig. 1). The degradates analyzed include acetochlor ethanesulfonic acid (acetochlor ESA), acetochlor

oxanilic acid (acetochlor OA), alachlor oxanilic acid (alachlor OA), deethylatrazine (DEA), deisopropylatrazine (DIA), cyanazine amide, hydroxyatrazine, metolachlor ethanesulfonic acid (metolachlor ESA), and metolachlor oxanilic acid (metolachlor OA). This research is an extension of the multi-agency Iowa Ground Water Monitoring Program (IGWM) (Detroy 1985; Kolpin, Sneck-Fahrer, and others, 1997).



**Figure 1.** Location of wells sampled in Iowa during 1995-98.

## MATERIALS AND METHODS

The 131 wells sampled were randomly selected within each major aquifer type (alluvial, glacial drift, bedrock/karst region, and bedrock/nonkarst region) for the IGWM from a population of over 2000 Iowa municipal wells. The 328 water samples collected from these 131 wells represent the annual sample collection carried out for the IGWM during 1995-98. The sampling protocol for this study was identical to that reported in previous discussion of these data (Kolpin, Kalkhoff, and others, 1997; Kolpin, Thurman, and Linhart, 1998). All wells were pumped a minimum of 30 minutes prior to obtaining measurements of dissolved oxygen, pH, specific conductance, and water temperature. Once the values for the above parameters stabilized, the water samples were collected. Water samples were filtered through a 0.7 micrometer glass-fiber filter into amber baked-glass bottles and immediately chilled.

All water samples were sent to the U.S. Geological Survey, Organic Research Laboratory in Lawrence, Kansas, to determine concentrations of

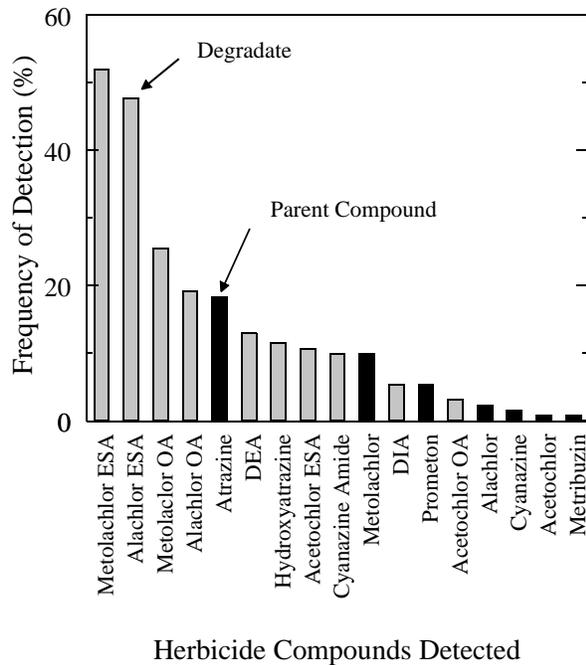
13 herbicides and 10 herbicide degradates (table 1). The 13 parent compounds and 3 of the triazine degradation products (table 1) were analyzed from 125 milliliter (mL) water samples by gas chromatography / mass spectrometry (GC/MS) following solid-phase extraction on C<sub>18</sub> cartridges (Thurman and others, 1990; Meyer and others, 1993). The analytical reporting limit for this method was 0.05 microgram per liter (µg/L) for all target compounds. The other seven herbicide degradates (table 1) were analyzed from 125-mL water samples by high-performance liquid chromatography (HPLC) with diode-array detection following solid-phase extraction on C<sub>18</sub> cartridges (Hostetler and Thurman, 1999). Complete separation of all analytes was achieved using this method. The analytical reporting limit for all target compounds was 0.2 µg/L for this method. Confirmation was achieved for alachlor OA, acetochlor OA, metolachlor OA, and metolachlor ESA by negative ion spray mass spectrometry (Ferrer and others, 1997).

The variation in the total number of samples collected per well for this study (from 1 to 4 samples) would have created a spatial bias in the dataset if left unmodified. Thus, average concentrations for each of the 23 compounds were calculated from all water samples collected from each well.

## RESULTS AND DISCUSSION

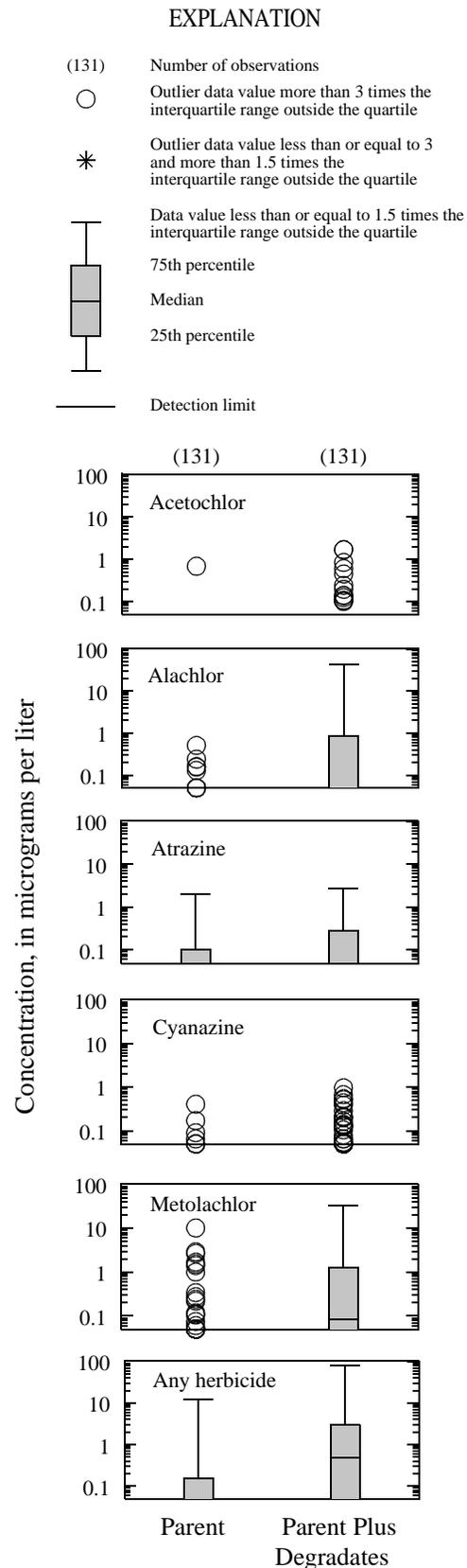
The most important finding of this study was that herbicide degradates were detected frequently. In fact, herbicide degradates were 8 of the 10 most frequently detected compounds (fig. 2). Atrazine was the only herbicide in which the parent compound was found more frequently than any of its degradates analyzed, perhaps because of the greater environmental persistence of atrazine compared to the other parent compounds under investigation (Wauchope and others, 1992; Stamper and others, 1997). However, the total residue concentration (sum of parent compound plus degradates analyzed) was substantially greater than the concentration of just the parent compound for every herbicide examined (fig. 3). Whereas previous investigations of herbicides generally found concentrations of the parent compounds to be less than 0.5 µg/L in ground water (Holden and

others, 1992; Kolpin and others, 1994; Kolpin, Barbash, and Gilliom, 1998), it was common for the total residue concentrations for this study to exceed this concentration (fig. 3).



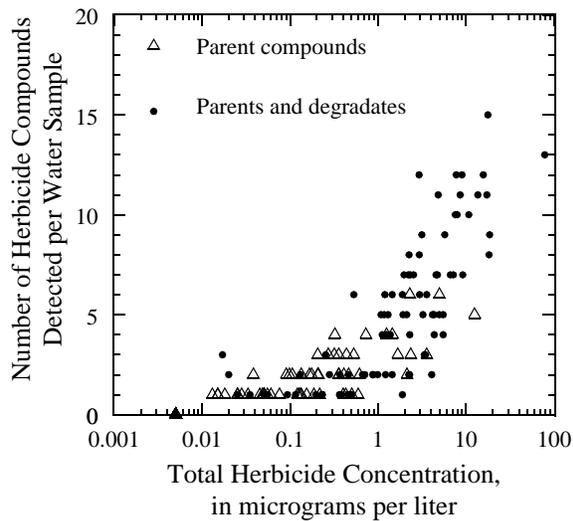
**Figure 2.** Frequency of detection for selected herbicide compounds (adjusted to a common detection threshold of 0.20 µg/L). See table 1 for compound abbreviation definitions.

Although no analyte concentrations exceeded their respective U.S. Environmental Protection Agency (USEPA) maximum contaminant levels or health advisory levels for drinking water (table 1), over half of the herbicide compounds under investigation had no such levels established. Furthermore, these drinking-water criteria only apply to individual compounds and do not consider the effects of more than one herbicide compound. Studies have shown that some combinations of compounds may exhibit additive or synergistic toxic effects (Marinovich and others, 1996; Thompson, 1996; Pape-Lindstrom and Lydy, 1997). The presence of multiple compounds in ground water was common during this study, particularly when herbicide degradates were included. An average of two herbicides was found in each ground-water sample in which a herbicide parent compound was detected. As many as 6 parent compounds were detected in a single sample; the



**Figure 3.** Distributions of concentrations of herbicide parent compounds and parent compound plus degradates.

maximum total herbicide concentration exceeded 12  $\mu\text{g/L}$  (fig. 4). When herbicide degradates were considered, the number of compounds detected and total concentrations greatly increase. An average of five herbicide compounds was found in each ground-water sample in which either a herbicide parent compound or one of its degradates was detected. As many as 15 herbicide compounds were detected in a single sample; the maximum total herbicide residue concentration exceeded 78  $\mu\text{g/L}$  (fig. 4).

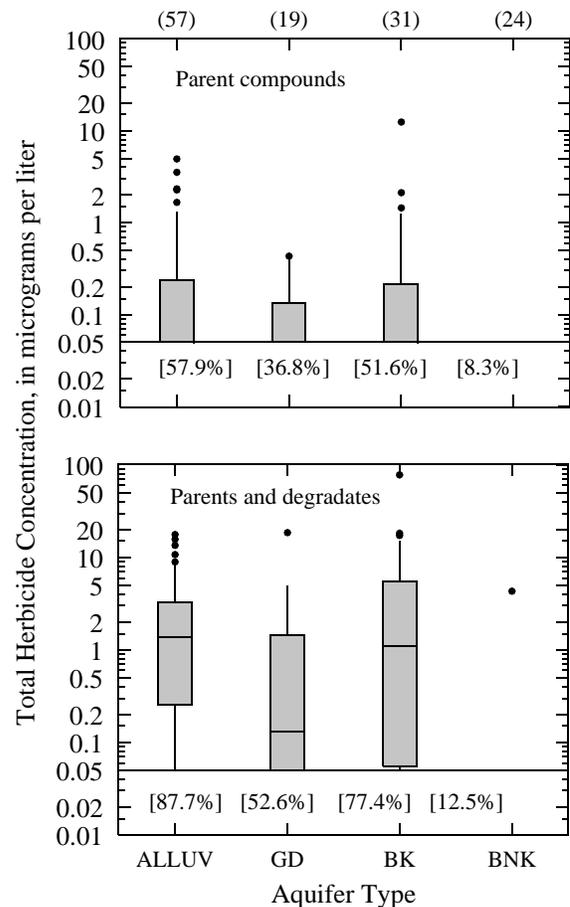


**Figure 4.** Relation between total herbicide residue concentration (parent plus degradates) and number of herbicide compounds detected per water sample.

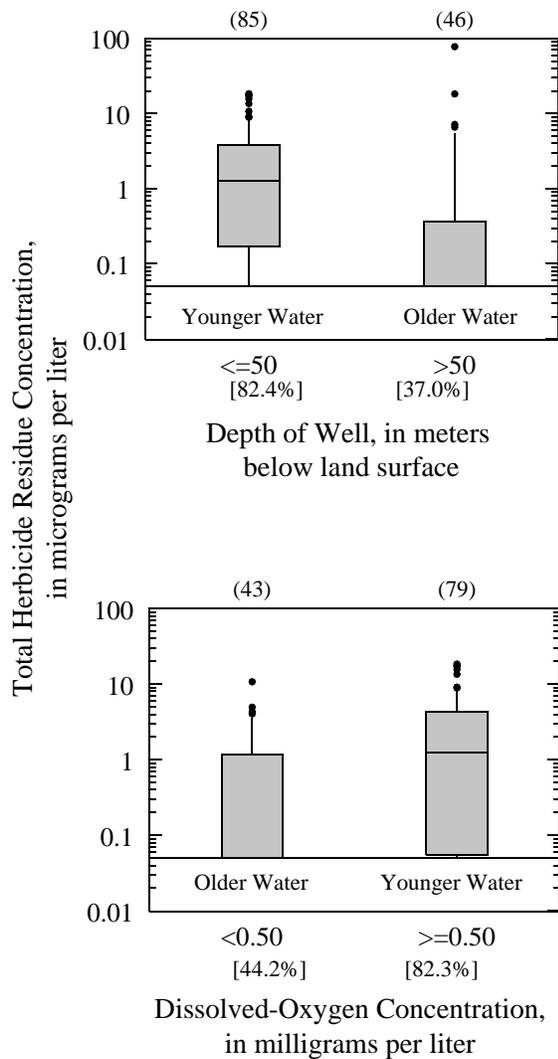
Although herbicides were commonly detected in ground water across Iowa during this study, their frequencies of detection and concentrations varied substantially among the major aquifer types sampled (fig. 5). These differences were much more pronounced when herbicide degradates were included (fig. 5). Aquifer types having the most rapid recharge rates (alluvial and bedrock/karst region aquifers) were those most likely to contain detectable concentrations of herbicide compounds, indicating that ground-water age could be an important factor in explaining these variations in herbicide contamination.

Although no direct measures of ground-water age were obtained for this study, two indirect estimates of age were available -- dissolved-oxygen

concentrations and well depth. These two factors can be used as general indicators of water age because oxygen tends to be consumed through biotic and abiotic processes as water travels from zones of recharge to greater depths, and well depth provides a general indication of distance from the recharge zone (Kolpin, Kalkhoff, and others, 1997). The detection and concentration of herbicides for this study were significantly related to these indirect estimates of ground-water age (fig. 6). In general, these indicators of younger ground water corresponded to more frequent detections and higher concentrations of herbicide compounds.



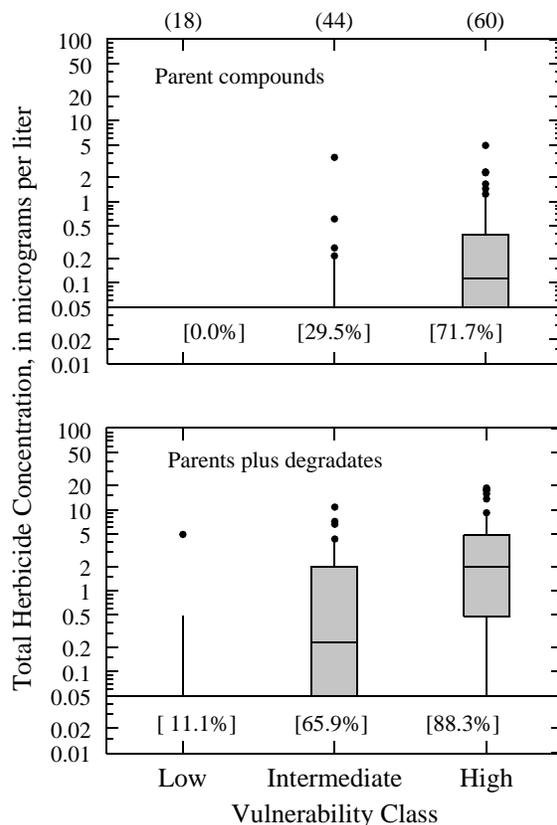
**Figure 5.** Total herbicide concentration by aquifer type (ALLUV = alluvial, GD = glacial drift, BK = bedrock/karst region, BNK = bedrock/nonkarst region). Numbers in brackets are the frequency of herbicide detection for that aquifer type. An explanation of a boxplot is provided in figure 3.



**Figure 6.** The relation between total herbicide residue concentration (parent plus degradates) and the two indirect estimates of ground-water age. Numbers in brackets are the frequency of herbicide compound detection for that group. Dissolved-oxygen concentrations could not be measured in water from nine of the municipal wells sampled. An explanation of a boxplot is provided in figure 3.

The two indirect estimates of ground-water age were used to separate the sampled wells into general vulnerability classes (low = well depth >50 m and dissolved-oxygen concentration < 0.5 mg/L; intermediate = well depth >50 m and dissolved-oxygen concentration  $\geq 0.05$  mg/L, or well depth  $\leq 50$  m and dissolved-oxygen concentration <0.5 mg/L; and high = well depth  $\leq 50$  m and dissolved-

oxygen concentration  $\geq 0.5$  mg/L). The results show that the frequencies of detection and concentrations varied substantially among the vulnerability classes regardless of whether or not herbicide degradates were considered (fig. 7). Nevertheless, when herbicide degradates were included, the frequency of herbicide compound detection within the highest vulnerability class approached 90% and the median total herbicide residue concentration increased over an order of magnitude to 2  $\mu\text{g/L}$  (Figure 7).



**Figure 7.** The relation between total herbicide concentration and vulnerability class (Low = well depth >50 m and dissolved-oxygen concentration <0.5 mg/L; Intermediate = well depth >50 m and dissolved-oxygen concentration  $\geq 0.05$  mg/L, or well depth  $\leq 50$  m and dissolved-oxygen concentration <0.5 mg/L; High = well depth  $\leq 50$  m and dissolved-oxygen concentration  $\geq 0.5$  mg/L). Numbers in brackets are the frequency of herbicide detection for that group. The nine wells where dissolved-oxygen data were not available were not used for this analysis. An explanation of a boxplot is provided in figure 3.

This study documents that obtaining data on herbicide degradates is critical in attempting to

understand not only the fate of a specific herbicide, but also its overall effect on human health and the environment.

## ACKNOWLEDGEMENTS

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