

Herbicides and herbicide degradates in shallow ground water and the Cedar River near a municipal well field, Cedar Rapids, Iowa

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ABSTRACT

Water samples were collected near a Cedar Rapids, Iowa municipal well field from June 1998 to August 1998 and analyzed for selected triazine and acetanilide herbicides and degradates. The purpose of the study was to evaluate the occurrence of herbicides and herbicide degradates following springtime application of herbicides to upstream cropland. The well field is in an alluvial aquifer adjacent to the Cedar River. Parent herbicide concentrations generally were greatest in June and decreased in July and August. Atrazine was most frequently detected and occurred at the greatest concentrations; acetochlor, cyanazine, and metolachlor also were detected, but at lesser concentrations than atrazine. Triazine degradate concentrations were relatively small (<0.50 micrograms per liter) and generally decreased from June to August. Although the rate of ground-water movement is relatively fast (about 1 meter per day) in the alluvial aquifer near the Cedar River, deethylatrazine (DEA) to atrazine ratios in ground-water samples collected near the Cedar River indicate that atrazine and DEA probably are gradually transported into the alluvial aquifer from the Cedar River. Deisopropylatrazine (DIA) to DEA ratios in water samples indicate most DIA in the Cedar River and alluvial aquifer is produced by atrazine degradation, although some could be from cyanazine degradation. Acetanilide degradates were detected more frequently and at greater concentrations than their corresponding parent herbicides. Ethanesulfonic-acid (ESA) degradates comprised at least 80 percent of the total acetanilide-degradate concentrations in samples collected from the Cedar River and alluvial aquifer in June, July, and August; oxanilic-acid degradates comprised less than 20 percent of the total concentrations. ESA-degradate concentrations generally were smallest in June and greater in July and August. Acetanilide-degradate concentrations in ground water adjacent to the Cedar River indicate acetanilide degradates are transported into the alluvial aquifer in a manner similar to that indicated for atrazine and DEA.

INTRODUCTION

Agriculture in the United States is most intense in the Midwest, where corn and soybeans are major row crops. Synthetic organic herbicides are applied to cropland to control a variety of broadleaf weeds and annual grasses. About two-thirds of the estimated 218 million kilograms of herbicides used for agriculture in the United States is applied to cropland in the Midwest (Barbash and Resek, 1996).

Triazine and acetanilide compounds are commonly used pre-emergent herbicides. Larson and others (1997) indicate that triazine and acetanilide compounds account for about one-half of the total herbicides used annually for agriculture in the

United States. Triazine compounds, such as atrazine and cyanazine, typically are applied to corn. Acetanilide compounds, such as acetochlor, alachlor, and metolachlor, typically are applied to corn and soybeans (Larson and others, 1997).

Triazine and acetanilide herbicides are moderately to highly soluble in water and have relatively low soil-sorption coefficients. Because of these properties, herbicides applied to cropland can be transported to shallow ground water by infiltration or to surface waters by storm-water runoff. Goolsby and Battaglin (1993) indicated that a relatively small fraction of the total amount of herbicides applied to cropland are transported to streams (less than 4 percent of triazines and less than 2 percent of acetanilides). Herbicides that

Table 1. Targeted constituents for chemical analyses of water samples collected from the alluvial aquifer and Cedar River, Cedar Rapids, Iowa, June-August, 1998.

[ESA, ethanesulfonic acid; OA, oxanilic acid]

Constituent	Chemical name
Parent compounds	
Acetochlor	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide
Alachlor	2-chloro-2'-6'-diethyl-N-(methoxymethyl)-acetanilide
Ametryn	2-(ethylamino)-4-isopropylamino-6-methyl-thio-s-triazine
Atrazine	2-chloro-4-ethylamino-6-isopropylamino-s-triazine
Cyanazine	2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-amino]-2-methylpropionitrile
Metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide
Metribuzin	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one
Prometon	2,4-bis(isopropylamino)-6-methoxy-s-triazine
Prometryn	2,4-bis(isopropylamino)-6-methylthio-s-triazine
Propachlor	2-chloro-N-isopropylacetanilide
Propazine	2-chloro-4,6-bis(isopropylamino)-s-triazine
Simazine	2-chloro-4,6-bis(ethylamino)-s-triazine
Terbutryn	2-tert-butylamino-4-ethylamino-6-methylthio-s-triazine
Degradate compounds	
Acetochlor ESA	2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)-amino]-2-oxoethanesulfonic acid
Acetochlor OA	2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)-amino]-2-oxoacetic acid
Alachlor ESA	2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid
Alachlor OA	2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid
Cyanazine-amide	2-chloro-4-(1-carbamoyl-1-methyl-ethylamino)-6-ethylamino-s-triazine
Deethylatrazine	2-amino-4-chloro-6-(isopropylamino)-s-triazine
Deisopropylatrazine	2-amino-4-chloro-6-(ethylamino)-s-triazine
Hydroxy-atrazine	2-hydroxy-4-(ethylamino)-6-(isopropylamino)-s-triazine
Metolachlor ESA	2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid
Metolachlor OA	2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid

runoff to streams present a concern because many municipal-water supplies in the Midwest are obtained from surface water or from shallow aquifers in which infiltration from surface waters can affect ground-water quality. Herbicide compounds have been associated with a variety of human-health and environmental problems including cancer, genetic diseases, reproductive disorders, and deformities. The U.S. Environmental Protection Agency (1996) has established a Maximum Contaminant Level in public drinking-water supplies for alachlor (2 micrograms per liter [$\mu\text{g/L}$], atrazine (3 $\mu\text{g/L}$), and simazine (4 $\mu\text{g/L}$).

A number of compounds that are intermediate degradation products (degradates) have been isolated and detected in the environment. Triazine and acetanilide degradates primarily are produced by biological processes, but chemical

reactions such as hydrolysis, oxidation and reduction, and photolysis also can produce degradates. Larson and others (1997) indicated that acetanilides generally degrade faster than triazines. Degradates typically are more mobile in the environment than parent compounds. Recent studies, such as those by Thurman and others (1996), Kolpin and others (1996) and Kalkhoff and others (1998), have detected degradates in surface-water and ground-water samples at greater frequency and concentrations than the parent compounds. Data are lacking on toxicity and long-term human health and environmental effects associated with degradate compounds.

The City of Cedar Rapids, Iowa obtains its municipal water supply from four well fields along the Cedar River. The wells are completed in the Cedar River alluvium, an alluvial aquifer adjacent

to the Cedar River. The City of Cedar Rapids and the U.S. Geological Survey (USGS) are conducting a cooperative study of the ground-water-flow system and water-quality near the well fields. The purpose of this paper is to evaluate the occurrence of herbicides and herbicide degradates in the alluvial aquifer near the City's Seminole Well Field following springtime application of herbicides to upstream cropland. Analytical results from water samples collected from June 1998 to August 1998 were used in the study.

Description of Study Area

Cedar Rapids is in east-central Iowa (fig. 1) and has a population of about 110,000. The city is located along a flood plain of the Cedar River; the flood plain ranges in width from about 350 to 1,000 meters (m) near the study area. Upland topography is characterized by rolling hills of low relief. The upland area near the well field is used for rural housing. Land use surrounding the well field consists of a municipal park and riparian wetlands along the Cedar River. Upstream land use in the Cedar River basin is over 80 percent agricultural.

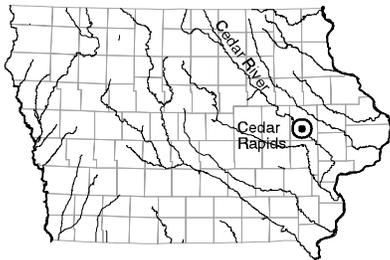


Figure 1. Location of Cedar Rapids, Iowa

Corn and soybeans are the major crops. Livestock raised in the area include beef and dairy cattle, hogs, and sheep. Iowa has a typical continental, subhumid climate, with relatively large seasonal variations in temperature (typically ranging between 40°C in summer to -30°C in winter). The average annual precipitation is about 84 centimeters (cm), with the greatest amounts occurring from May to August (Squillace and others, 1996).

Hydrogeology

Geologic units near the well field consist of an

unconsolidated surficial layer of glacial till, loess, and the Cedar River alluvium (alluvial aquifer), underlain by carbonate bedrock of Devonian and Silurian age (bedrock aquifer). The glacial till and loess form upland areas that bound the alluvial aquifer. The alluvial aquifer ranges in thickness from about 2 to 30 m near the well field. The alluvial aquifer consists of a sequence of coarse sand and gravel at the base, grading upward to fine sand, silt, and clay near the surface. The sand and gravel consist of carbonate, shale, and ferro-magnesium-rich rock fragments. The bedrock aquifer has a maximum thickness of about 210 m near the well field. The bedrock aquifer primarily consists of limestone and dolomite, but some interbedded shale and chert also occur. Joints and fractures are common in the bedrock aquifer (Hansen, 1970, Wahl and Bunker, 1986).

The alluvial aquifer is recharged by infiltration from the Cedar River induced by pumping of municipal wells, infiltration of precipitation, and flow from adjacent hydrogeologic units. In areas influenced by the pumping of municipal wells, the water-table gradient is from the Cedar River to the well field; in areas outside the influence of municipal pumping, the water-table gradient generally is toward the Cedar River (Hansen, 1970, Wahl and Bunker, 1986). Results from a regional ground-water-flow model constructed by Schulmeyer and Schnoebelen (1998) indicated that about 74 percent of water pumped from the alluvial aquifer is from the Cedar River, about 21 percent of the water is from adjacent and underlying hydrogeologic units, and about 5 percent of the water is from infiltrating precipitation. The bedrock aquifer is recharged by downward leakage from the alluvial aquifer and by infiltrating precipitation on outcrop areas distant from the study area. The bedrock aquifer is not used as a municipal water supply but is used for private residential and industrial water supplies.

Previous Studies

Herbicides have been most frequently detected in samples collected from the Cedar River and alluvial aquifer between mid-spring and mid-summer (Schulmeyer and Schnoebelen, 1998, Squillace and others, 1996). Atrazine is most frequently detected, but other herbicides such as acetochlor, alachlor, cyanazine, and metolachlor

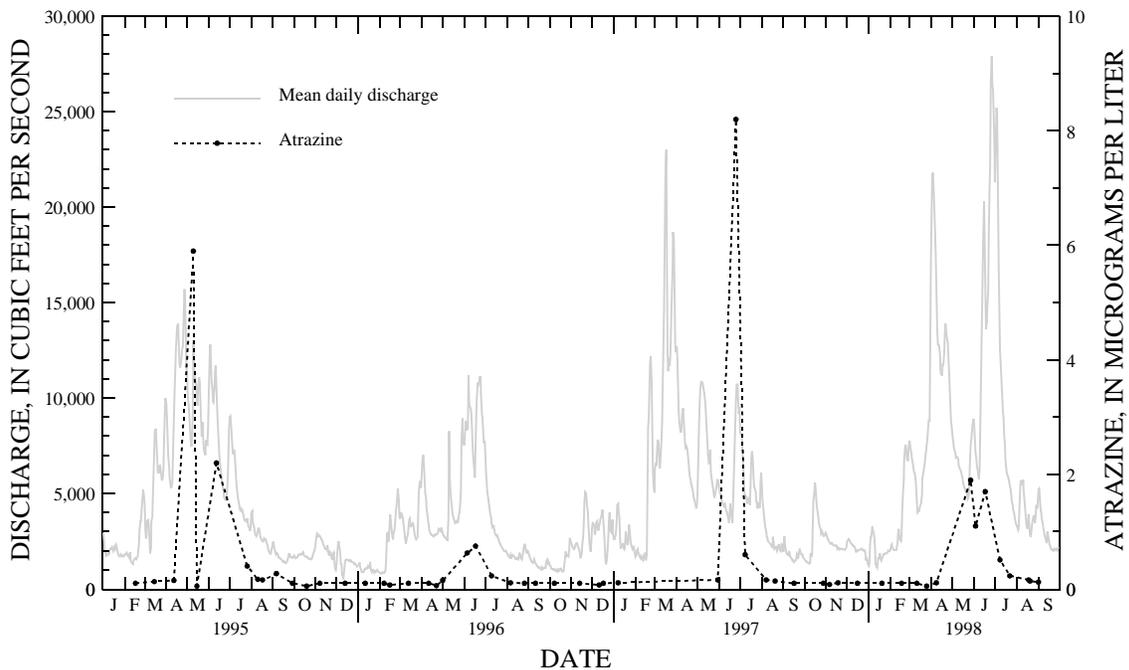


Figure 2. Mean daily discharge and atrazine concentrations in the Cedar River near Cedar Rapids, Iowa, 1995-1998.

also have been detected. Atrazine typically is detected at greater concentrations than the other herbicides. Figure 2 shows atrazine concentrations in the Cedar River near Cedar Rapids from 1995 to 1998 (Schnobelen and Schulmeyer, 1997, Tom Noth, City of Cedar Rapids Water Department, written commun., July 1998, and unpublished data maintained by the USGS). The seasonal increase in atrazine concentrations during the spring and summer corresponds to the timing of herbicide applications to cropland and the amount of surface runoff resulting from rain storms. The same compounds detected in the Cedar River have been detected in samples collected from the alluvial aquifer, but typically at smaller concentrations than the samples collected from the Cedar River (Schnobelen and Schulmeyer, 1997 and unpublished data maintained by the USGS).

Recharge from precipitation is a potential source for herbicides in the alluvial aquifer. Goolsby and others (1997) reported that triazine and acetanilide herbicides are frequently detected (with maximum concentrations detected from May to July) at relatively small concentrations in rainfall samples collected from National Atmospheric Deposition Program/National Trends Network sites. Ninety-nine percent of atrazine, alachlor,

metolachlor, and cyanazine concentrations were less than or equal to 1 $\mu\text{g/L}$. Herbicides detected in the alluvial aquifer near the well field are most likely from the Cedar River because most of the water pumped from the alluvial aquifer is from induced infiltration from the river (Schulmeyer and Schnobelen, 1998). In addition, herbicide concentrations in recharge from precipitation likely would be reduced by sorption onto surface soils and uptake by vegetation.

METHODS

Water samples were collected from 5.1-cm outer-diameter observation wells and 0.36-cm outer-diameter observation wells (see figure 3 for locations). The 5.1-cm diameter wells were installed using hollow-stem auger drilling techniques, completed with polyvinyl-chloride casing and slotted screen, and screened across a 76-cm interval above the bottom of the well. The 5.1-cm diameter wells at CRM-16, CRM-18, and CRM-19 were completed to a depth of about 13 m; the 5.1-cm diameter wells at CRM-15 and CRM-17 were completed to a depth of about 6 m. The 0.36-cm diameter wells were installed with a portable hammer-drill by advancing a stainless-

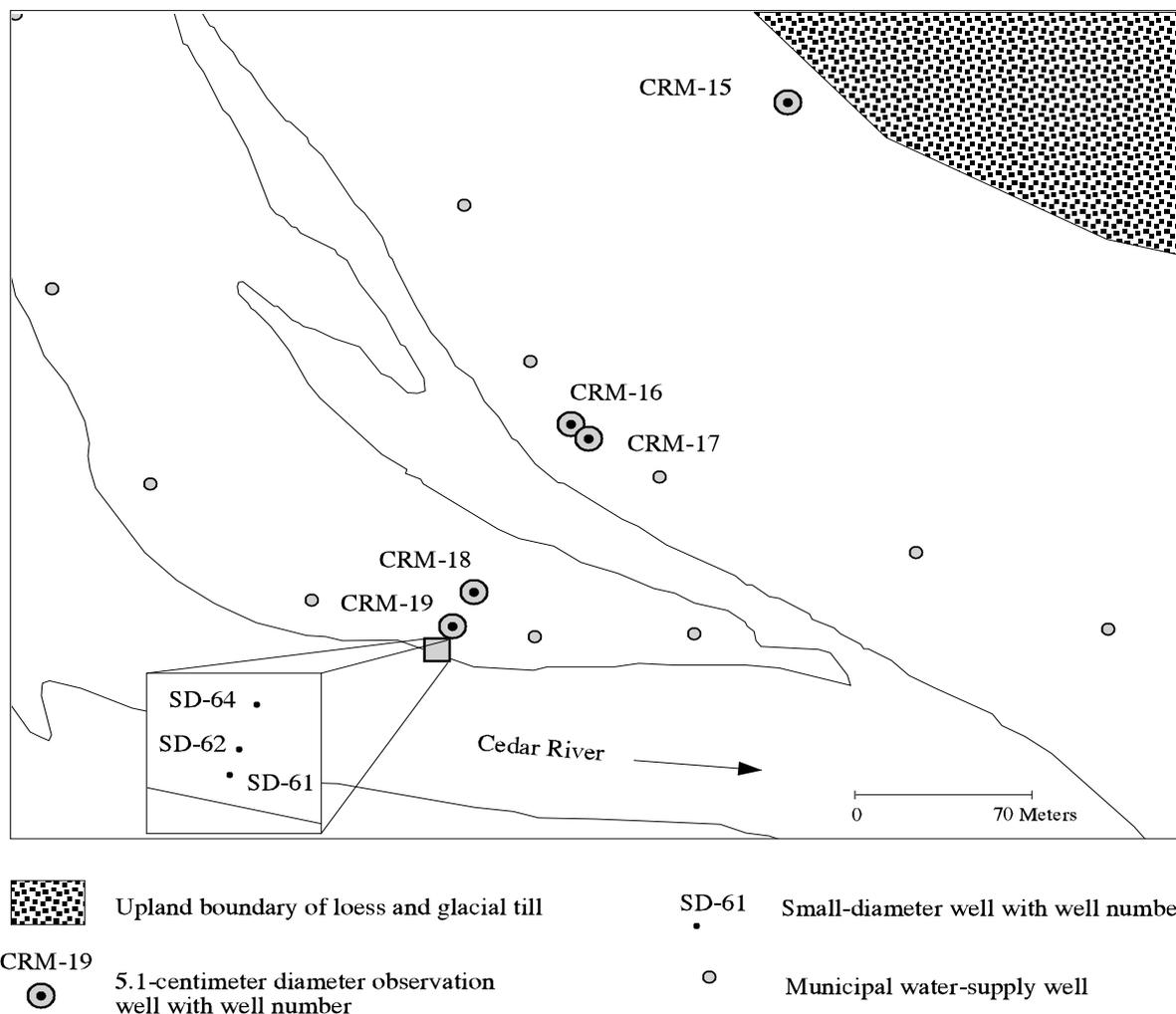


Figure 3. Observation wells in the Seminole Well Field sampled for selected herbicides and degradates, Cedar Rapids, Iowa, June-August, 1998.

steel sandpoint screen (7.6-cm long) attached to Teflon tubing (0.36-cm outer diameter) inside a 3.2-cm outer-diameter borehole. A total of five 0.36-cm diameter wells were installed at about 1-m intervals on the bank of the Cedar River (SD-60 was closest to the river and SD-64 was farthest from the river). During this study, only three of the 0.36-cm diameter wells were used (SD-61, SD-62, and SD-64). SD-61 was completed to a depth of about 3.8 m, SD-63 was completed to a depth of about 4.9 m, and SD-64 was completed to a depth of about 6.7 m.

Prior to collecting samples, each observation well was pumped to remove about three borehole volumes of water. Water samples were collected from 5.1-cm diameter wells with a submersible

pump and from 0.36-cm diameter wells with a peristaltic pump. Samples were filtered through a 0.7-micrometer, baked, glass-fiber filter. A set of three baked, amber glass, 125-milliliter bottles was collected from each observation well. Samples were shipped chilled to the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas. Samples were analyzed using gas chromatography/mass spectrometry (GC/MS) for the 13 parent herbicides listed in table 1 and three triazine degradates (cyanazine-amide, deethyl-atrazine [DEA], and deisopropylatrazine [DIA]). The minimum reporting limit for GC/MS analyses was 0.05 $\mu\text{g/L}$ for all constituents. Samples were analyzed with high-performance liquid chromatography (HPLC) for the six acetanilide degradates

Table 2. Concentrations of selected herbicides and triazine degradates detected in samples collected from the alluvial aquifer and Cedar River, Cedar Rapids, Iowa, June-August, 1998.

[All concentrations in micrograms per liter.]

Site name (figure 3)	Acetochlor	Atrazine	Cyanazine	Cyanazine- amide	Deethyl- atrazine	Deisopropyl- atrazine	Metolachlor
June 1998							
CRM-15	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
CRM-16	<0.05	0.05	<0.05	<0.05	0.07	<0.05	<0.05
CRM-17	<0.05	0.51	0.05	0.08	0.18	0.07	0.10
CRM-18	<0.05	0.06	<0.05	<0.05	0.08	0.05	<0.05
CRM-19	<0.05	0.22	<0.05	<0.05	0.14	0.08	0.11
SD-64	0.07	0.87	<0.05	0.19	0.21	0.10	0.14
SD-62	<0.05	0.95	0.09	0.23	0.22	0.12	0.11
SD-61	0.17	2.71	0.16	0.31	0.44	0.26	0.33
Cedar River	0.16	1.10	<0.05	<0.05	0.21	0.12	0.17
July 1998							
CRM-15	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
CRM-16	<0.05	0.08	<0.05	<0.05	0.16	<0.05	<0.05
CRM-17	<0.05	0.54	<0.05	0.08	0.18	0.06	0.19
CRM-18	<0.05	0.09	<0.05	<0.05	0.13	0.05	0.18
CRM-19	0.09	1.39	0.07	0.30	<0.05	0.12	0.23
SD-64	<0.05	0.48	<0.05	<0.05	0.14	<0.05	0.08
SD-62	<0.05	1.01	<0.05	<0.05	0.24	0.09	0.16
SD-61	<0.05	0.71	<0.05	<0.05	0.20	0.06	0.07
Cedar River	<0.05	0.23	<0.05	<0.05	0.15	0.08	0.05
August 1998							
CRM-15	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
CRM-16	<0.05	0.07	<0.05	<0.05	0.13	<0.05	<0.05
CRM-17	<0.05	0.59	<0.05	<0.05	0.17	<0.05	0.06
CRM-18	<0.05	0.12	<0.05	<0.05	0.14	0.06	0.13
CRM-19	<0.05	<0.05	<0.05	<0.05	0.22	0.11	0.15
SD-64	<0.05	0.38	<0.05	<0.05	0.08	<0.05	0.08
SD-62	<0.05	0.72	<0.05	<0.05	0.17	0.06	0.08
SD-61	<0.05	0.29	<0.05	<0.05	0.13	0.05	<0.05
Cedar River	<0.05	0.14	<0.05	<0.05	0.13	0.05	<0.05

listed in table 1 and hydroxy-atrazine. The minimum reporting limit for HPLC analyses was 0.20 µg/L for all constituents.

HERBICIDES AND DEGRADATES IN THE ALLUVIAL AQUIFER AND CEDAR RIVER

Analytical results are summarized in table 2 and table 3. Table 2 lists concentrations of selected

herbicides and triazine degradates detected in water samples collected from the alluvial aquifer and Cedar River from June to August 1998. Table 3 lists the concentrations of acetanilide degradates and hydroxy-atrazine detected in water samples collected from the alluvial aquifer and Cedar River from June to August 1998. Results for some compounds listed in table 1 are not summarized because reported concentrations were all less than the minimum reporting limit.

Table 3. Concentrations of acetanilide degradates and hydroxy-atrazine detected in water samples collected from the alluvial aquifer and Cedar River, Cedar Rapids, Iowa, June-August, 1998.

[All concentrations in micrograms per liter; ESA, ethanesulfonic acid; OA, oxanilic acid.]

Site name (figure 3)	Acetochlor ESA	Acetochlor OA	Alachlor ESA	Alachlor OA	Hydroxy- atrazine	Metolachlor ESA	Metolachlor OA
June 1998							
CRM-15	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
CRM-16	0.39	0.20	1.02	<0.20	<0.20	2.27	0.45
CRM-17	1.26	0.85	1.62	<0.20	<0.20	4.83	1.22
CRM-18	0.71	<0.20	1.06	<0.20	<0.20	3.09	0.77
CRM-19	0.99	0.66	1.39	<0.20	<0.20	4.24	0.78
SD-64	1.72	1.04	1.43	<0.20	<0.20	5.27	1.20
SD-62	1.98	1.18	1.31	<0.20	<0.20	5.16	1.19
SD-61	2.06	1.66	1.32	<0.20	0.22	5.42	1.14
Cedar River	1.47	0.64	1.38	<0.20	<0.20	5.45	0.92
July 1998							
CRM-15	<0.20	<0.20	<0.20	<0.20	<0.20	0.38	<0.20
CRM-16	0.85	0.28	0.69	<0.20	<0.20	3.92	0.76
CRM-17	1.37	0.69	1.73	0.29	<0.20	4.51	1.25
CRM-18	1.14	<0.20	2.19	<0.20	<0.20	5.64	0.89
CRM-19	2.06	1.17	2.06	<0.20	<0.20	6.36	1.17
SD-64	2.48	1.34	1.97	0.25	<0.20	5.64	1.40
SD-62	3.32	1.75	2.20	0.31	<0.20	6.51	1.72
SD-61	2.90	1.08	2.36	0.20	<0.20	6.84	4.25
Cedar River	1.08	0.29	1.96	<0.20	<0.20	4.25	0.62
August 1998							
CRM-15	<0.20	<0.20	<0.20	<0.20	<0.20	0.37	<0.20
CRM-16	1.10	0.35	1.21	<0.20	<0.20	3.81	0.82
CRM-17	1.48	0.61	1.28	<0.20	<0.20	4.14	0.87
CRM-18	1.39	<0.20	2.50	<0.20	<0.20	6.49	0.81
CRM-19	1.58	0.20	2.35	<0.20	<0.20	5.48	0.69
SD-64	1.07	<0.20	2.15	<0.20	<0.20	4.75	0.59
SD-62	2.49	0.67	2.23	0.29	<0.20	6.47	1.04
SD-61	1.55	0.26	2.24	<0.20	<0.20	5.85	0.88
Cedar River	0.90	<0.20	2.13	<0.20	<0.20	4.15	0.54

Triazines

Atrazine was detected more frequently and at greater concentrations (<0.05 to 2.71 µg/L) than any other parent compound in samples collected during the study. Atrazine was detected in every sample except the three collected from CRM-15, the site representative of conditions least influenced by induced infiltration from the Cedar River, and one sample collected from CRM-19 in August.

Cyanazine was detected in four samples collected from the alluvial aquifer at relatively small concentrations (<0.05 to 0.16 µg/L). Cyanazine was not detected in samples collected from the Cedar River for this study, but cyanazine was detected in samples independently collected from the Cedar River by the City of Cedar Rapids on May 27 and June 17 at concentrations of 0.40 µg/L and 0.34 µg/L, respectively (Tom Noth, City of Cedar

Table 4. Ratios of selected triazine compounds in water samples collected from the alluvial aquifer and Cedar River, Cedar Rapids, Iowa, June-August, 1998.

[DEA, deethylatrazine; DIA, deisopropylatrazine; --, ratio not calculated because at least one compound was not detected above the minimum reporting limit.]

Site name (figure 3)	DEA/atrazine			DIA/DEA		
	June	July	August	June	July	August
CRM-15	--	--	--	--	--	--
CRM-16	1.4	2.0	1.9	--	--	--
CRM-17	0.35	0.33	0.29	0.39	0.33	--
CRM-18	1.3	1.4	1.2	0.62	0.38	0.43
CRM-19	0.64	--	--	0.57	--	0.50
SD-64	0.24	0.29	0.21	0.48	--	--
SD-62	0.23	0.24	0.24	0.54	0.38	0.35
SD-61	0.16	0.28	0.45	0.59	0.30	0.38
Cedar River	0.19	0.65	0.93	0.57	0.53	0.38

Rapids Water Department, written commun., July 1998).

Triazine degradates detected in samples included cyanazine-amide, DEA, DIA, and hydroxy-atrazine. DEA and DIA were the most frequently detected triazine degradates. Triazine degradate concentrations were relatively small, ranging from less than the minimum reporting limit to a maximum DEA concentration of 0.44 µg/L.

Thurman and others (1994) used the DEA to atrazine ratio (DAR) in surface-water samples collected from Midwestern streams and rivers to relate parent herbicides and degradate concentrations to the period of herbicide applications. Thurman and others (1994) indicated that DAR values in runoff from cropland on which atrazine was applied increase with time after the initial herbicide application. Thurman and others (1994) reported DAR values less than 0.05 in runoff from field plots shortly after atrazine application and DAR values between 0.5 to 0.7 about 60 days after the atrazine application. The DAR values in samples collected from the Cedar River for this study (table 4) increased from June (0.19) to August (0.93). This is consistent with the results of Thurman and others (1994) for DAR values in runoff from cropland following the application of atrazine.

The DAR also is useful to evaluate atrazine transport in water infiltrating from the Cedar River into the alluvial aquifer because the DAR is not affected by dilution resulting from mixing.

Schulmeyer (1995) and Schulmeyer and Schnoebelen (1998) estimated the rate of infiltration from the river into the alluvial aquifer to be about 1 m per day. Because the infiltration rate is relatively rapid, DAR values in shallow ground water near the river (SD-61, SD-62, and SD-64) were expected to increase with DAR values in the river from June to August. SD-61, the site closest to the river, was the only site with DAR values that increased with DAR values in the river from June to August. DAR values in SD-62 and SD-64, located about 1 m and 3 m from SD-61, remained relatively constant (0.21 to 0.29) from June to August. Squillace and others (1996) studied the movement of herbicides between the Cedar River and alluvial aquifer in an area of the Cedar River alluvium (about 16 kilometers downstream of Cedar Rapids) that is not influenced by pumping of municipal supply wells. Their results indicated that herbicides enter the alluvial aquifer with bank-storage water during periods of high river stage, but are released as bank-storage water discharges to the river during periods of lower river stage. Infiltration induced by pumping of municipal wells during this study may have prevented the release of bank-storage water during periods of lower river stage, so atrazine and DEA remained in bank-storage water (rather than discharged back into the river) and were transported into the alluvial aquifer with induced infiltration from the river. As indicated by the DAR values from this study, atrazine and DEA likely are gradually transported into the alluvial aquifer away from

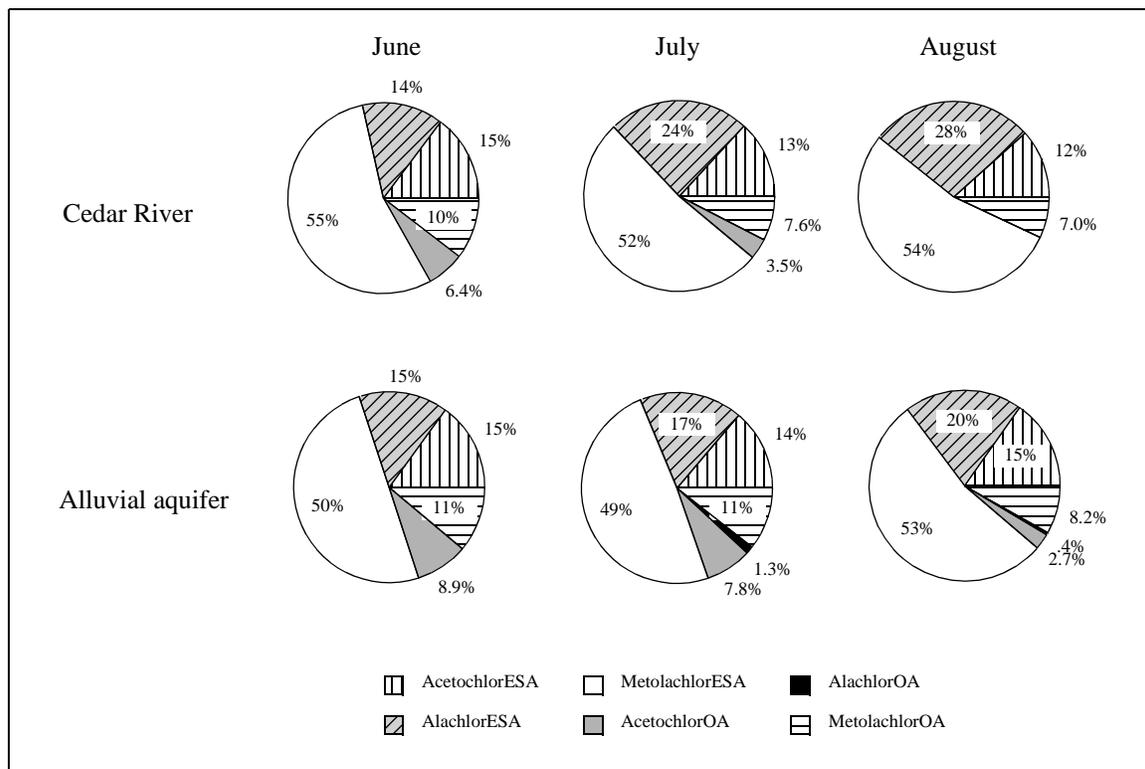


Figure 4. Distribution of acetanilide degradates in samples collected from the Cedar River and alluvial aquifer, Cedar Rapids, Iowa, June-August, 1998.

bank-storage water. DAR values in samples from deeper observation wells (CRM-16, CRM-18, and CRM-19) were larger than DAR values in samples from shallower wells. Recharge requires greater time to flow to deeper zones of the alluvial aquifer, and atrazine entering the alluvial aquifer at the time of recharge probably degrades during transport.

Atrazine, cyanazine, and simazine degradation can produce DIA. DIA detected in samples during this study likely resulted from atrazine and cyanazine degradation because simazine is not used in significant quantities in the Midwest. Thurman and others (1994) used DIA/DEA ratios in samples collected from field-plot runoff studies to estimate amounts of DIA produced by the degradation of atrazine and cyanazine. Thurman and others (1994) reported DIA/DEA ratios of 0.4 ± 0.1 when atrazine was the only triazine applied to field plots; DIA/DEA ratios of 0.6 ± 0.1 were reported when both atrazine and cyanazine were applied. DIA/DEA ratios in samples collected from the Cedar River and alluvial aquifer (table 4) in June were between 0.39 and 0.62, indicating that some DIA could have resulted from cyanazine degradation. DIA/DEA ratios calculated for 9 of 10 samples collected in

July and August were less than 0.5, indicating that most DIA resulted from atrazine degradation.

Acetanilides

Acetochlor and metolachlor were the only parent acetanilide compounds detected in water samples collected during the study; alachlor was not detected in any samples. Acetochlor (<0.05 to $0.17 \mu\text{g/L}$) and metolachlor (<0.05 to $0.33 \mu\text{g/L}$) were detected at relatively small concentrations. Metolachlor was detected in more samples than acetochlor and was detected in June, July, and August; acetochlor only was detected in samples collected in June and July.

Acetanilide degradates generally were detected at greater concentrations than their respective parent compounds (table 2 and table 3). At least one acetanilide degradate compound was detected in every sample collected during the study except the sample collected from CRM-15 in June. Shallow ground water near CRM-15 most likely is not influenced by induced infiltration from the Cedar River; recharge is primarily from infiltrating precipitation and leakage across adjacent and

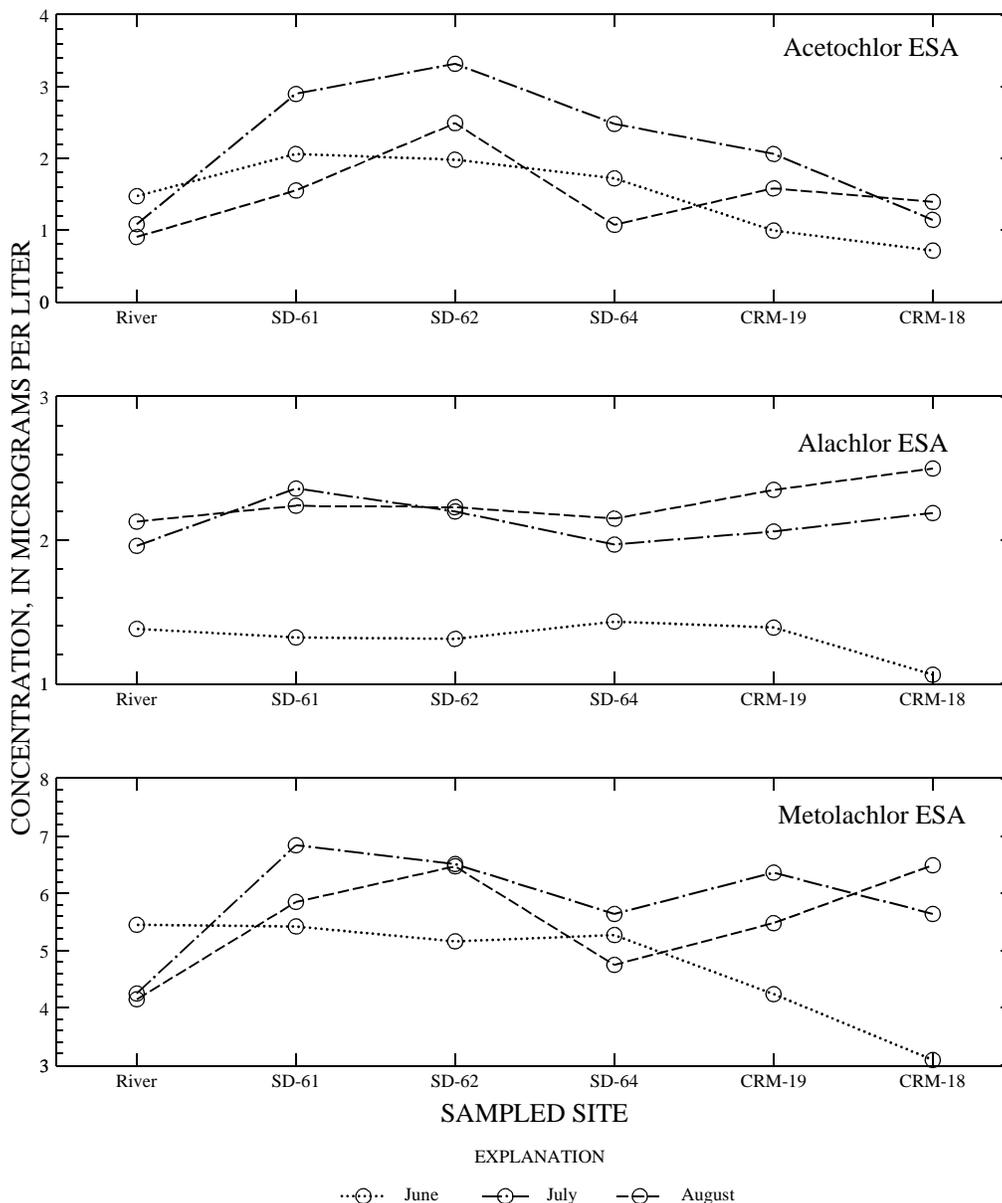


Figure 5. Ethanesulfonic-acid (ESA) degradate concentrations in samples from the alluvial aquifer and Cedar River, Cedar Rapids, Iowa, June-August, 1998.

underlying hydrogeologic units. Metolachlor ESA detected in ground-water samples from CRM-15 in July and August likely was from surface water that inundated the area near CRM-15 during a localized flooding event produced by unseasonably high stages in the Cedar River in early July.

Figure 4 shows the ratio of each acetanilide degradate to the total acetanilide degradate concentration in each round of samples collected from the Cedar River and alluvial aquifer. ESA degradates were detected at greater frequency and at greater concentrations than OA degradates. ESA-degradate concentrations represented at least 80 percent of the

total acetanilide-degradate concentration in each round of samples collected during the study. Kalkhoff and others (1998) noted similar results for ground-water and surface-water samples collected from eastern Iowa. Thurman and others (1996) and Aga and others (1996) indicated that acetanilide degradates are produced by dechlorination of parent compounds by glutathione conjugate reactions in plants, algae, and microorganisms. Eykholt and Davenport (1998) indicated acetanilide degradates also can be produced by abiotic reductive dechlorination in the presence of iron metal. Water-quality data collected near the wells sampled for this study

show that the shallow ground water is moderately reducing, likely has significant biological activity, and that minerals within the aquifer matrix contain iron. Even though conditions in the ground water are conducive to reductive dechlorination, results from this study do not indicate significant degradation of parent compounds because ratios of individual degradates to total degradate concentrations are similar in samples collected from the Cedar River and alluvial aquifer.

Figure 5 shows ESA-degradate concentrations in samples collected from observation wells near the Cedar River. ESA-degradate concentrations generally were smallest in June and greater in July and August. The differences in ESA-degradate concentrations between June and later in the summer probably result from the trend in the rate of formation of degradates from parent herbicides in cropland soils within the drainage basin. Aga and others (1996) observed the temporal variation of metolachlor and metolachlor ESA in soil samples collected from a field plot. Metolachlor decreased exponentially after application, with a half-life of about 25 days. Metolachlor ESA concentrations rapidly increased during the first five weeks after application, gradually increased to a maximum during the next 7 to 8 weeks, and then steadily decreased. Although data from field studies are lacking, similar trends probably occur for other acetanilide herbicides and corresponding ESA degradates. Most acetanilide-degradate concentrations in ground water at wells SD-61 and SD-62 were greater than concentrations in the Cedar River. Acetanilide-degradate concentrations in shallow ground water probably reflect concentrations in the river prior to sampling, assuming acetanilide degradates are transported in a manner similar to that indicated for atrazine and DEA.

SUMMARY

Triazine and acetanilide herbicides were detected in water samples collected from June to August 1998 from the alluvial aquifer and Cedar River near a Cedar Rapids, Iowa municipal well field. Atrazine was the most frequently detected compound and was detected at the greatest concentrations. Acetochlor, cyanazine, and metolachlor also were detected, but at smaller concentrations

than atrazine. Concentrations generally decreased from June to August.

Triazine degradates were detected at relatively small concentrations in water samples collected during the study. Concentrations generally decreased from June to August. DEA and DIA were detected more frequently than cyanazine-amide or hydroxy-atrazine. DAR values in samples from the Cedar River were consistent with degradation characteristics of atrazine from runoff from cropland on which atrazine was applied. Atrazine and DEA in the Cedar River probably are transported into the alluvial aquifer with infiltration induced by pumping of municipal wells, based on DAR values of samples collected during the study. DAR values in samples from observation wells in deeper zones of the alluvial aquifer were greater than those in shallower wells probably because of atrazine degradation during transport to the deeper zones of the alluvial aquifer. The DIA to DEA ratio in samples indicated that most DIA is produced by atrazine degradation, although some DIA might be produced by cyanazine degradation in June.

Acetanilide degradates were detected at greater frequency and at greater concentrations than their corresponding parent compounds. ESA degradates were detected more frequently and at greater concentrations than OA degradates. ESA degradates represented at least 80 percent of the total acetanilide-degradate concentration from each sampling date; OA degradates represented 20 percent or less of the total acetanilide degradate concentration. The composition of degradates detected in samples from the Cedar River was similar to the composition detected in samples from the alluvial aquifer, indicating that relatively little degradation occurs during transport from the river into the alluvial aquifer. Acetanilide-degradate concentrations in ground water adjacent to the Cedar River suggest that acetanilide degradates are transported into the alluvial aquifer in a manner similar to that indicated for atrazine and DEA.

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