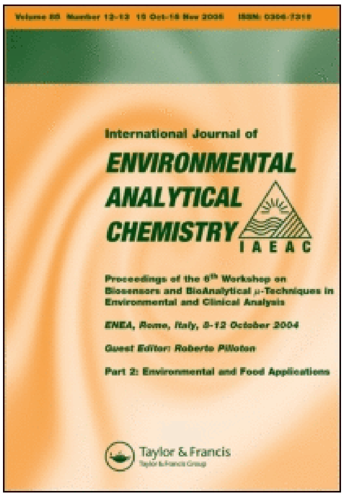

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ATRAZINE AND ITS METABOLITES AS INDICATORS OF STREAM-AQUIFER INTERACTION IN KANSAS, USA

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A survey of atrazine and its metabolites in Kansas ground water indicated that ground-water quality was impacted by stream-aquifer interaction between rivers in the Kansas River basin and their adjacent alluvial aquifers. Atrazine was detected in 19 of the 78 samples. The most common metabolite, deethylatrazine, was detected in 25 samples, 18 of which also had atrazine. The deethylatrazine/atrazine ratio (DAR) of < 1.0 indicates rapid movement of agricultural chemicals to ground water. In this study, 12 of 18 samples had DAR values < 1.0, suggesting rapid recharge to the aquifers. Hydroxyatrazine is seldom detected in ground water. In this study hydroxyatrazine was detected primarily in wells sited in alluvium of rivers. These rivers contain atrazine in varying concentrations. Results of the study suggest that stream-aquifer interaction is a process contributing to the presence of both atrazine and its metabolites in ground water in these areas.

Keywords: Atrazine; deethylatrazine; hydroxyatrazine; metabolites; stream-aquifer interaction

INTRODUCTION

Agricultural chemicals are major nonpoint source contaminants in the Midwestern United States. Atrazine is the dominant herbicide used in areas growing corn and grain sorghum in the region[1–2]. The most commonly studied compound is atrazine, however its metabolites deethylatrazine (DEA) and deisopropylatrazine (DIA) are attracting increasing attention. Atrazine and deethylatrazine are detected in both surface and ground waters but are present more frequently in surface water. Deisopropylatrazine is found in both surface and ground waters but less frequently than deethyatrazine. Recent research indicates that although hydroxyatrazine (HA) rarely occurs in ground water[3], its presence in surface water may be more common than previously known[4–5].

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Work by many researchers indicates that the deethylatrazine/atrazine ratio (DAR) may be a useful indicator of nonpoint or point source contamination[6–9]. Thurman and others[8] suggested that the DAR values found in surface water indicate seasonal stream-aquifer interaction with lower ratios occurring during the spring flush of high atrazine water and higher ratios occurring later in the year. Thurman and Fallon[7] used the change in DAR values in relation to atrazine concentrations to trace the movement of the atrazine during spring flush through Perry Reservoir in northeastern Kansas.

In Kansas much of the work evaluating the occurrence of herbicides has been done on surface water, particularly in northeastern Kansas where primarily corn and sorghum are grown. The topography, geology, soils, and annual precipitation of 90 cm/year in this area make it conducive for overland flow to streams and rivers to occur rather than infiltration to the ground water. As a result (and because atrazine is normally applied in the spring), atrazine concentrations are generally highest in streams after the spring flush and decrease with time[10,11]. Because much of the surface drainage feeds into reservoirs used for drinking water supplies, storage of the spring runoff with higher concentrations of atrazine can result in delayed release of water with atrazine concentrations above the 3 μg/L U.S. EPA drinking water limit[11].

Another result of spring runoff and high stream flows (or levels) can be the infiltration of surface water with higher atrazine concentration into adjacent alluvial aquifers. The excess surface water is stored as bank storage and then released as base flow as the surface-water level decreases[12,13]. Atrazine in bank storage can result in two conditions: (1) the continued detection of high atrazine concentration in the surface water and the possible use of this water by local or downstream municipalities that rely on surface water for drinking water, and/or (2) the mixing of bank-stored surface water with ground water and the movement of these contaminated waters to wells installed in the alluvial aquifer. Both of these scenarios could result in limitations on the use of the ground and surface water and affect the volume of potable water available to local and downstream watersheds.

Results of the survey of Kansas ground water were used to evaluate the occurrence of atrazine in shallow ground water in areas of the state where corn and/or grain sorghum were frequently grown as part of the registration of atrazine by Novartis, Inc. (previously Ciba-Geigy). The study determined a number of factors that affect the occurrence of atrazine in the ground water in areas of Kansas[14]. In addition, use of the metabolite data, hydrologic data and evaluation of DAR values indicate that these chemicals are useful indicators of stream-aquifer interaction at certain sites in Kansas, which is the focus of this paper.

EXPERIMENTAL

The Kansas Geological Survey (KGS) collected ground water samples from fall 1993 to fall 1994 according to the protocols provided for the study by Novartis, Inc. Samples were sent to Novartis, Inc. for atrazine and atrazine daughter product analysis; the detection limit was 0.1 μg/L for atrazine and the daughter products. Final results from the laboratory were received in the summer of 1995. In addition to atrazine, deethylatrazine, deisopropylatrazine, and hydroxyatrazine were analyzed. The Kansas Geological Survey analyzed the samples for nitrate with a detection limit of 0.1 mg/L as nitrate.

Where possible, sites were selected on the basis of the following criteria: depth to ground water of less than 10 m; limited amount of clay in the subsurface; location near irrigated fields planted with corn or sorghum in recent years; domestic, municipal, or monitoring wells; availability of lithologic well log; and permission of well owner. Because of the quantity of clay present in alluvial aquifers in Kansas the amount of clay in the stratigraphic section was difficult to minimize.

Eighty-four samples (78 water samples plus 6 duplicates) were collected. Of the 78 wells sampled, 63 were domestic wells, 11 were municipal wells, and 4 were monitoring wells. Locations of sampled wells are shown in Figure 1.

RESULTS AND DISCUSSION

Atrazine

Evaluation of the atrazine data showed that 76% of the wells sampled had atrazine levels below the detection limit of 0.1 μg/L; 22% of the samples were between 0.1 and 3 μg/L (U. S. EPA drinking water limit for atrazine); and 2% were above 3 μg/L and are considered indicative of probable point sources. The factors that were statistically related to the concentration of atrazine in ground water in Kansas are: irrigation well density within a 3.2 km radius of the sampled well; depth of well; depth to the water table; and distance of application area from sampled well[14]. These factors are similar to findings from other studies[1,15,16]. Table I lists the values of atrazine, deethylatrazine, deisopropylatrazine, hydroxyatrazine, DAR and nitrate-N values for the sites where metabolites were detected.

Atrazine metabolites

Previous studies have shown that although atrazine may not be present in ground-water, detections of daughter products indicate that atrazine was present

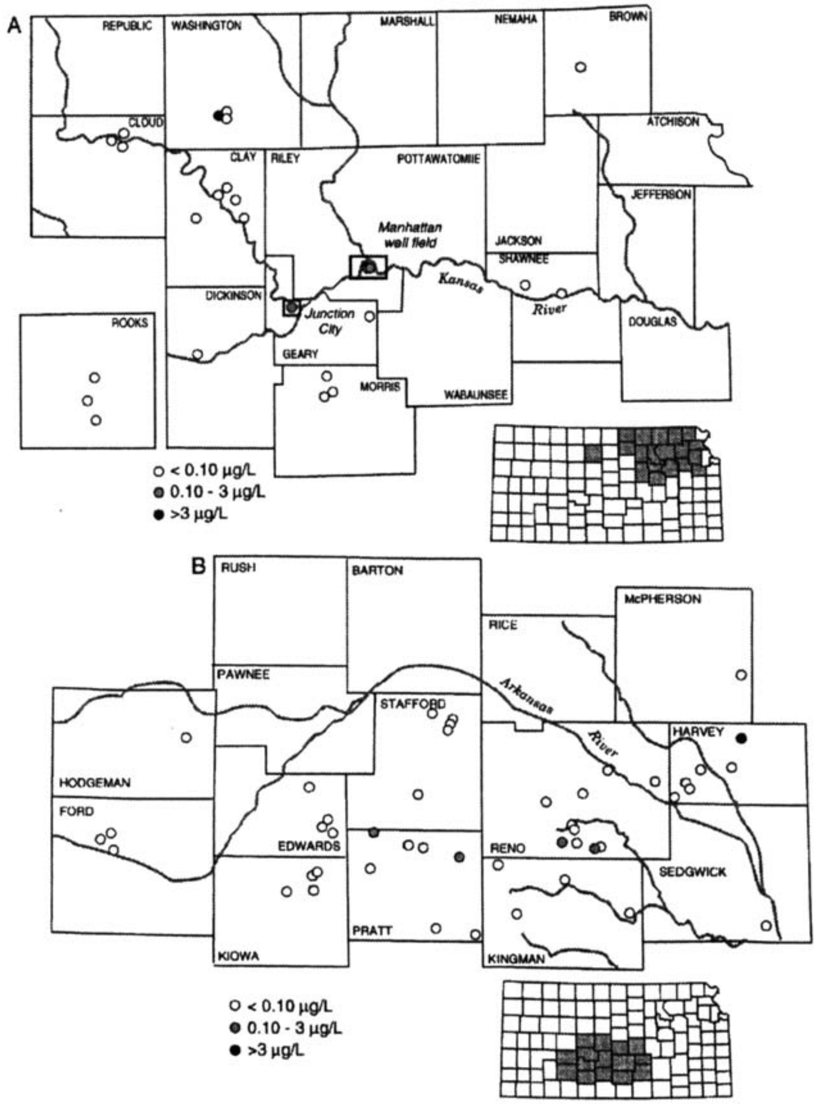

FIGURE 1 Atrazine sampling points in northeastern (A) and south-central Kansas (B). Manhattan and Junction City well fields (boxes in A) showed indications of stream-aquifer interaction

in the vadose zone or ground water at some point in time[8,15]. The percentage of wells with metabolite detections were: deethylatrazine 31%, deisopropylatrazine 10%, and hydroxyatrazine 9% (Table I). Figure 2 shows the distribution of atrazine and metabolite concentrations of deethylatrazine, deisopropylatrazine, and hydroxyatrazine.

TABLE I Atrazine, metabolites, DAR, and nitrate-N values for sites discussed in this study

ID	*Atrazine*	*DEA*[a] *(μg/L)*	*DAR*[b]	*DIA*[a] *(μg/L)*	*HA*[a] *(μg/L)*	NO_3*-N (mg/L)*	*Well Location (County)*	*Near Surface Water*
17	5.1	0.61	0.14	0.32		6.4	Harvey	No
68	3.3	0.51	0.18	0.12		32.1	Washington	Well Construction
11	1.1	0.59	0.62	0.3	0.77	0.2	Pottawatomie	91 m
21	1.1	0.72	0.75			16.8	Reno	No
14	1.0	0.59	0.68	0.28	0.41	0.3	Pottawatomie	91 m
13	0.87	0.32	0.42	0.15	0.77	0.2	Pottawatomie	91 m
16	0.74	0.23	0.36	0.12	0.44	0.2	Geary	91 m
15	0.64	0.28	0.50	0.13	0.54	0.2	Pottawatomie	91 m
12	0.51	0.22	0.49	0.1	0.31	0.5	Pottawatomie	91 m
61	0.48	0.23	0.55			9.9	McPherson	No
2	0.37	0.23	0.72			10.7	Morris	No
71	0.34	0.6	1.76			2.7	Kingman	No
42	0.28	1.1	4.52			13.7	Clay	No
18	0.22	1.1	5.75	0.19		6	Reno	No
25	0.22	0.18	0.94			11.7	Pratt	No
37	0.22	0.57	2.98			16.8	Pratt	No
27	0.13	0.4	3.58			0.7	Shawnee	No
28	0.1	0.2	2.29			1.4	Shawnee	No
29		0.12				2.9	Reno	No
47		0.19				15.3	Edwards	No
49		0.29				13.1	Kiowa	No
64		0.23				2.5	Cloud	No
72		0.39				27.8	Kingman	No
78	0.63				0.23	11.4	Rooks	Dug Well

a. DEA – Deethyatrazine; DIA – Deisopropylatrazine; HA – Hydroxyatrazine.
b. DAR – Deethyatrazine/Atrazine molar ratio. Blanks indicate values < 0.10 μg/L.

Deethylatrazine/Atrazine ratio (DAR)

Of the metabolites of atrazine, deethylatrazine is detected most often. Deethylatrazine is a microbial degradation product of atrazine in the soil and unsaturated zone. Because this type of degradation takes time, a significant microbe population, and nutrients for the microbes, calculation of the ratio of deethylatrazine/atrazine (DAR) has been suggested as a possible tracer for the pathway of atrazine and metabolite movement to ground and surface water and also as an indicator of possible point or non-point source contamination[8,9]. Work using DAR values suggests that a ratio > 1.0 indicates a longer residence time in the soil and ground water and thus greater opportunity for the atrazine to be broken down into its metabolites. A DAR ratio < 1.0 suggests rapid movement of atrazine via overland flow into a stream or by macropore flow to ground water and usually results in a larger atrazine concentration and a lower deethylatrazine concentration reflecting the rapid runoff of atrazine and the lack of time for degradation to occur[6]. Figure 3 illustrates these concepts for the sites in Kansas where both atrazine and deethylatrazine were detected.

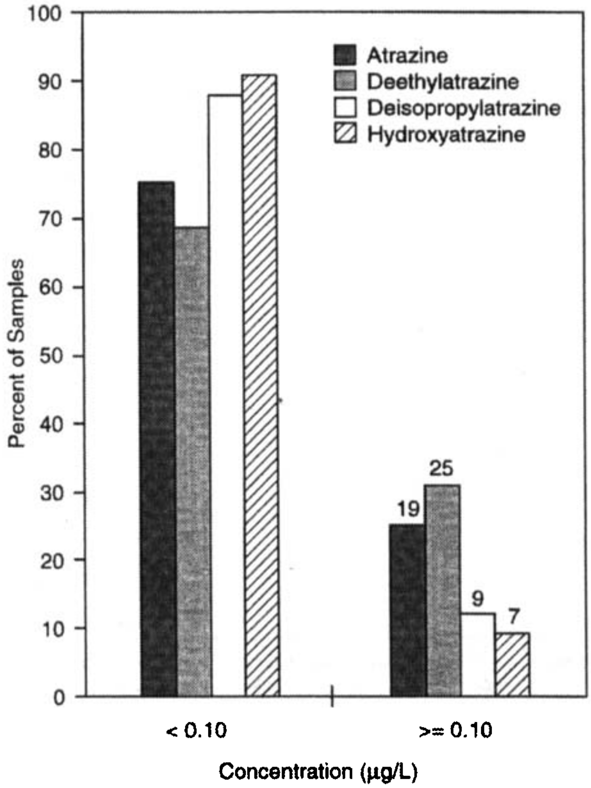

FIGURE 2 Distribution of atrazine and daughter products. The majority of samples are less than 0.10 μg/L (detection limit). Percentage of total samples (78) shown. Numbers above bars are actual number of samples with detections

Alluvial wells near the Big Blue and Kansas Rivers in Potawattomie County and the well near the Republican River in Geary County (Table I, wells 11–16) have DAR values of < 1.0 suggesting the possibility of atrazine contamination of the alluvial aquifer by stream-aquifer interaction as was noted by Squillace and Thurman[13]in their work in Iowa. Work by the Kansas Department of Health and Environment indicates that atrazine is the most often detected herbicide in surface water in Kansas, thus providing a potential source for the observed concentrations in alluvial wells sited near rivers[17].

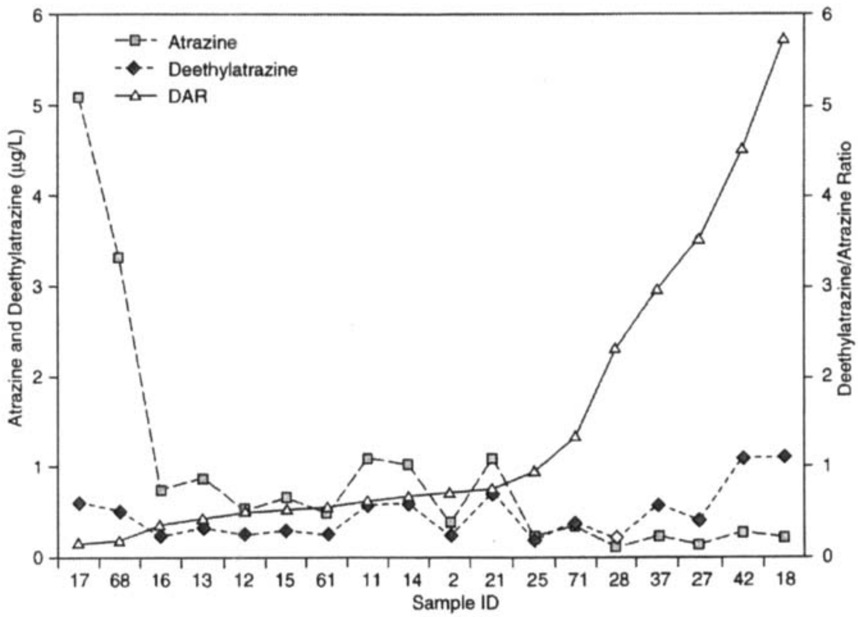

FIGURE 3 Increased DAR indicates breakdown of atrazine in unsaturated zone and probable non-point source for atrazine. Low DAR (<1.0) and measureable atrazine suggest overland flow to streams and/or macropore flow to ground water and little residence time for breakdown of atrazine to metabolites. Sample ID refers to Table I

The wells with low DAR values (<1.0) and nitrate-N values ≥ 3 mg/L indicate a possible anthropogenic source of contamination in the aquifers by rapid recharge to the aquifer either because of faulty well design (Table I and Figure 3, well 17), macropore flow, or rapid recharge through a very permeable unsaturated zone (Table I and Figure 3, wells 18, 21, 2, 25, 61, and 68). Well sample 68 is a shallow dug well which may explain the high nitrate and atrazine values and low deethylatrazine and DAR values.

Wells with DAR values > 1.0 indicate a long travel time for atrazine so that considerable degradation occurred before the soil water reached the ground water (Table I and Figure 3, wells 71, 42, 18, 37, 27, 28). However, the presence of high nitrate-N in some of these wells suggests that although conditions exist for the breakdown of atrazine because of the presence of lower permeable zones in the unsaturated and saturated zones, agrichemicals are still reaching the aquifer and can cause impairment of the water quality both by atrazine metabolites and nitrate.

Hydraulic characterization of sites

The wells that have low DAR values and hydroxyatrazine present (Table I wells 11–16), are all situated in city well fields adjacent to rivers. Wells 11–15 are in the Manhattan, KS well-field adjacent to the Big Blue River which is fed from Tuttle Creek Lake upstream (Figure 4). Well 16 (Table I) is situated in the Junction City, KS well-field near the Republican River and downstream from Milford Dam (Figure 5).

The geology of these two areas consists of alluvial and terrace deposits of Quaternary age. The alluvium consists of 24 to 27 m sequence of gravel, coarse-to-fine sand, and silt with inter-bedded clay layers, with the coarser sands and gravels at the base of the alluvial deposits. The alluvial and terrace deposits are underlain by Permian age shale and limestone.

From 1992 to 1994 the U.S. Geological Survey[18] worked on characterizing the effects of pumping municipal wells at Manhattan on stream-flow in the Big Blue and Kansas Rivers (Figure 4). The result of this study was that the municipal well-field has a significant impact on inducing recharge to the well-field from the rivers. The average hydraulic gradient between the river and the aquifer ranged from +0.21 to +0.29 with a plus value indicating flow from the river into the alluvial aquifer. Potentiometric surface maps for May, 1993 and December, 1994 at the Manhattan well-field show that a depression has formed with a steeper hydraulic gradient toward the well-field (Figure 4).

A MODFLOW simulation was used to estimate the percentages of induced recharge and captured base-flow that contributed to the pumpage of the well-field. Approximately 48% of the water pumped by the Manhattan well-field in May, 1993 was from induced infiltration from the rivers; in December the value increased to about 76%[18] (Table II). Intercepted ground-water base-flow was estimated from 2 to 31% (Table II).

A similar study was done at Junction City well-field adjacent to the Republican River[19] (Figure 5). At this site the average hydraulic gradient was found to be +0.07 with a plus value indicating flow from the river into the alluvial aquifer. In

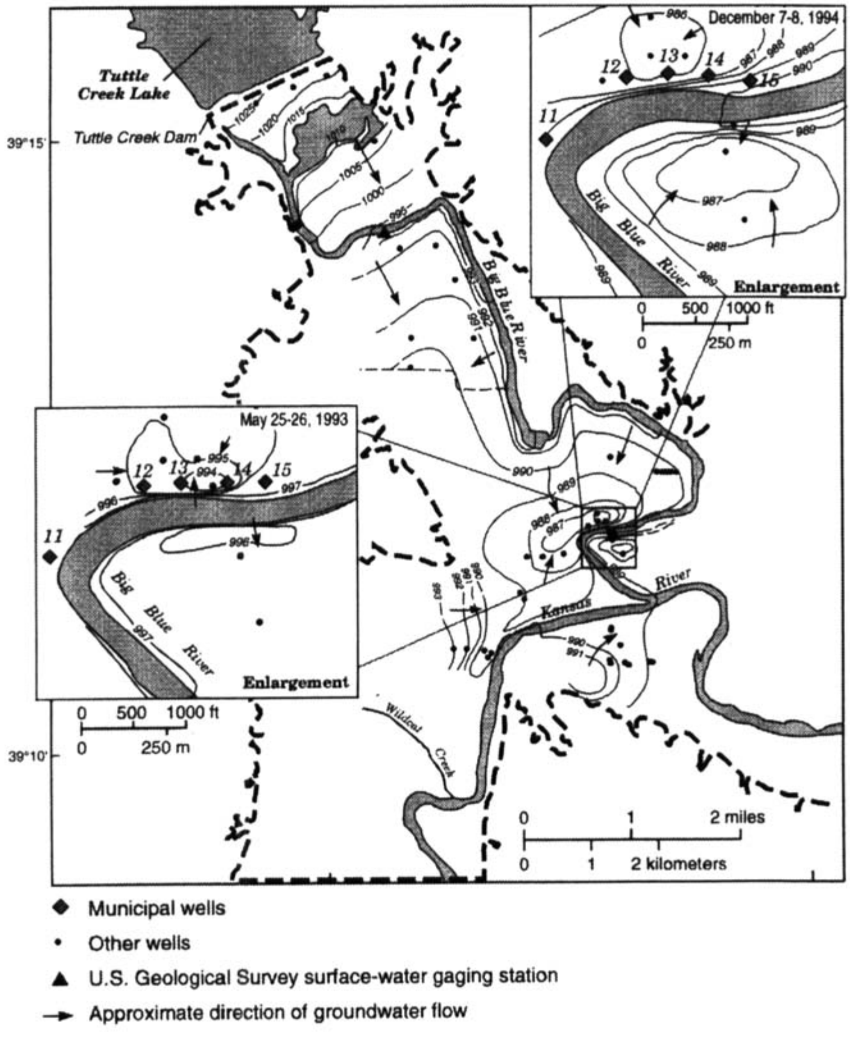

FIGURE 4 Potentiometric maps of drawdown cone from Manhattan, KS well-field adjacent to Big Blue River May, 1993 on left, December, 1994 on right. Both enlargements show the gradient of flow from the river to towards the well-field. Surface water flows from Tuttle Creek Dam to the southeast. Adapted from Jian and others[18]. Well numbers 11 – 15 refer to Table I

this area about 57% of the pumping in May, 1994 was estimated to be from induced river recharge, with 22% induced recharge occurring in November, 1994[19]. Intercepted ground-water base-flow was estimated between 13 to 48% (Table II). Potentiometric maps constructed for this well-field also indicate the contribution of induced recharge from the river to the well-field and the formation of a depression in the vicinity of the well-field[19] (Figure 5).

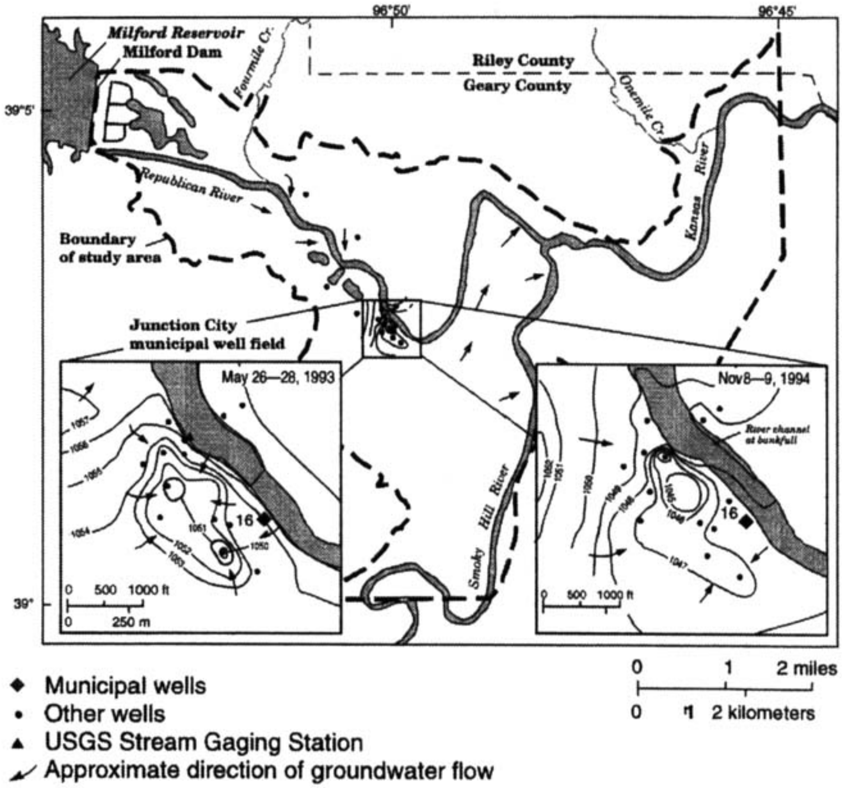

FIGURE 5 Potentiometric maps of drawdown cone from Junction City, KS well-field adjacent to Republican River. May 1993, on left, November, 1994 on right. Both enlargements show the gradient of flow from the river to towards the well-field. Surface water flows from Milford Lake Dam to the southeast. Adapted from Myers and others[19]. Well number refers to Table I

Agrochemicals as tracers for stream-aquifer interaction

Work by Duncan and others[20] and Spalding and Snow[21]showed by use of atrazine concentrations that the Platte River in Nebraska recharges the Lincoln well-field. Other metabolites were not evaluated in these studies. Pathways of atrazine and deethylatrazine to surface waters include overland flow of the chemicals in the dissolved phase with runoff water during the spring flush[8] and ground-water flow into a river system either from the bank storage or regional ground-water discharge.

TABLE II Summary of Hydrologic Information from USGS Studies[18–19]

Site	*Average Hydraulic Gradient*[a]	*Flow Direction*	*Mean Well-field Pumping Rate*	*Percent Induced Recharge*[b]	*Intercepted Ground Water Base Flow*[b]
Manhattan	0.21 to 0.29	Toward well-field	0.20 to 0.22 m^3/sec	48 to 76%	2 to 31%
Junction City	0.05 to 0.07	Toward well-field	0.13 m^3/sec	22 to 57%	13 to 48%

a. April 1993 through Dec. 1994.
b. Estimates from MODFLOW model of systems.

Thurman and others[8] and Thurman and Fallon[7] showed that use of DAR values can indicate the source of surface water in relation to the spring flush or later recharge events. Use of this ratio permitted Thurman and Fallon[7] to trace the movement of runoff water through a reservoir in Kansas and determine the flux of surface water and herbicides through the system.

Work by Squillace and others[9] indicates that atrazine behaves conservatively once it reaches surface water. The results of their study did not show changes in concentrations of atrazine or deethylatrazine in the Cedar Creek basin in Iowa when discharge was constant. They did not observe an increase in DAR values along the length of the stream which indicates that atrazine does not further degrade to deethylatrazine once it reaches surface water. This also suggests that the use of atrazine concentration as a tracer in surface water is a viable idea.

Atrazine, deethylatrazine and DAR values at alluvial sites in Kansas

The relationship between atrazine, deethylatrazine and the calculated DAR values with discharge at gauging stations located near the Manhattan and Junction City well fields indicate that although the nearby reservoirs act as flood regulators for downstream flow, daily mean discharge and chemical concentrations in the water still vary seasonally. Atrazine concentrations in particular vary directly with discharge. Figure 6 illustrates the measured agchemical concentrations at the stream gauging and water quality monitoring site near the Manhattan, KS. In addition, the figure shows the measured concentrations of atrazine and DEA found in the river by KDHE studies, and the ground-water samples collected during this study. As can be seen, the ground-water concentrations fall in the range of observed values for the river near the sample site, further supporting the hydrologic evidence of river recharge to this well-field (Figure 4; Table II). Data collected at the Junction City well-field showed similar results of agchemical recharge from the river to the well-field (Figure 5; Table II).

Hydroxyatrazine as an indicator of stream-aquifer interaction

At the Manhattan well-field, hydroxyatrazine was measured at 5 of the wells during the initial sampling (May, 1994) and 4 wells were resampled in December, 1994 (Table III). At the Junction City site only one sample was collected.

The similarity of the hydroxyatrazine values and the presence of the metabolite at different times of the year suggests that this is not an unusual occurrence. Although hydroxyatrazine was not analyzed from surface water samples, the work of Lerch and others[4,5]strongly indicates that hydroxyatrazine is more

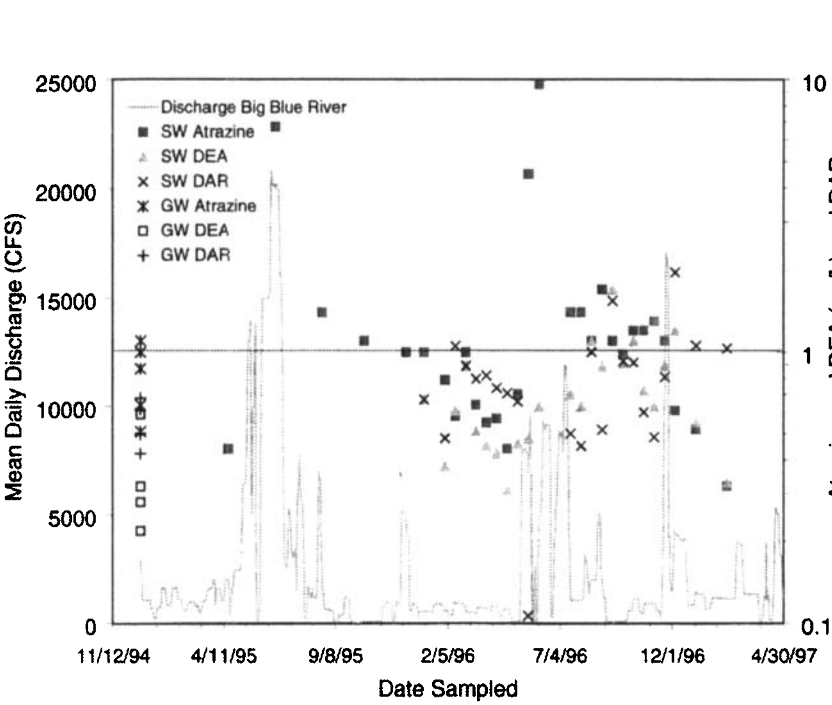

FIGURE 6 Atrazine, deethylatrazine (DEA), DAR values and mean daily discharge values from surface water sampling site (SW in graph) near Manhattan, KS on Big Blue River and ground-water (GW in graph) values from well-field samples 11–15 (Table I) collected in 1994. Ground-water atrazine values are within the concentration range of the surface water samples. DAR values are generally less than one (as shown by line), indicating rapid runoff of atrazine and DEA to surface water

common in surface water than previously thought. The presence of this daughter product at the Manhattan and Junction City well-fields strongly suggests that the source of atrazine in these wells is due to induced recharge from the river because of the change in gradient caused by the well pumping. More importantly, because hydroxyatrazine is rarely found in ground water, the source for this daughter product is most likely from the rivers, which at both well-fields are only about 90 meters from the wells.

CONCLUSIONS

The results of the reconnaissance ground-water quality survey showed that atrazine is not present in the majority of wells tested. Of the 78 samples collected, 76% were below the detection limit, 22% had detections above 0.10 µg/L (detection limit) but below 3 µg/L, and 2% were above the drinking water limit of

3 μg/L. Several of the samples that had atrazine or metabolites occurred in wells that are in the alluvium of rivers in the Kansas River basin. These samples had DAR values of <1.0. The low values may indicate that these wells are influenced by stream-aquifer mixing, and the atrazine and metabolites are from surface water sources rather than from regional ground water. Hydrologic characterization of the Big Blue River near Manhattan and the Republican River near Junction City by the U.S. Geological Survey indicate that both city well-fields have caused induced recharge from the rivers towards the well-fields.

TABLE III Atrazine and metabolites from alluvial wells adjacent to two major rivers in Kansas

Site ID	*Date Sampled*	*Atrazine (μg/L)*	*DEA (μg/L)*	*HA (μg/L)*
11	5/1994	0.37	<0.10	0.53
11B[a]	12/1994	1.1	0.59	0.77
12	5/1994	0.51	0.22	0.31
13	5/1994	1.3	0.45	1.4
13B[a]	12/1994	0.87	0.32	0.77
14	5/1994	0.31	0.13	0.32
14B[a]	12/1994	1.0	0.59	0.41
15	5/1994	0.48	0.21	0.51
15B[a]	12/1994	0.64	0.28	0.54
16	5/1994	0.74	0.23	0.44

a. Samples with B are duplicate samples collected to verify atrazine detections.

This discussion of the occurrence of atrazine and its metabolites in surface and ground water suggests that herbicides plus their metabolites may have a future greater impact on water quality than previously envisioned. If this is indeed the case, then future water-quality studies will have to address the metabolite issue as well as the major herbicides and nitrate sources as possible threats to the usability of the water.

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