Bull. Environ. Contam. Toxicol. (1987) 39:807–814

Bulletin of Environmental Contamination and Toxicology

Groundwater Transport of the Herbicide, Atrazine, Weld County, Colorado

M. P. Wilson,[1] E. P. Savage,[1] D. D. Adrian,[2] M. J. Aaronson,[1] T. J. Keefe,[1] D. H. Hamar,[3] and J. T. Tessari[1]

[1]Colorado Epidemiologic Pesticide Studies Center, Institute of Rural Environmental Health, Colorado State University, Fort Collins, Colorado 80523; [2]Department of Civil Engineering, Louisiana State University, Baton Rouge, Louisiana 70803; and [3]Department of Pathology, Colorado State University, Fort Collins, Colorado 80523

The herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is one of the most widely used pesticides in the United States. The uses of atrazine include control of many annual broadleaf and grass weed species in corn, sorghum, sugarcane, pineapple, and certain other crops (Berg, 1986). Groundwater contamination by atrazine has been reported in Iowa (Richard et al., 1975) and in the Central Platte Valley of Nebraska (Wehtje et al., 1983; Junk et al., 1980). The toxicology of atrazine is not clearly understood and the data available are not adequate to make a well-founded safe drinking water level determination (National Research Council, 1977). Although atrazine is thought to degrade in nature within approximately 18 months (Klassen and Kadoum, 1979; Wagner and Chahal, 1966), groundwater downgradient from atrazine-treated fields may show seasonal concentration peaks which could exceed safe levels (Wehtje et al., 1983; Junk et al., 1980). These observations warrant further investigation into atrazine's impact on groundwater resources.

Atrazine is perhaps the most commonly used herbicide in the South Platte River Valley of Weld County, Colorado (Wilson and Nik Hussain, *unpublished*). The primary use of this compound in Weld County is to control broadleaf weeds in corn, one of the principal crops of the region. Many of the soils to which atrazine is applied are highly permeable and overlie unconfined groundwater at shallow depths. This groundwater is tapped by many domestic-use wells. The purpose of this study was to monitor groundwater at gradient points above, directly beneath, and below an atrazine-treated site in the South Platte River Valley of Weld County. This investigation permitted an evaluation of the potential health hazard, based on currently available toxicological data, posed by consumption of groundwater moving from beneath the selected study site.

Send reprint requests to M.P. Wilson at the above address.

MATERIALS AND METHODS

The study site, in the South Platte River Valley of Weld County, was selected because it was representative of the general conditions under which atrazine enters the agricultural environment of the Valley. Characteristics of hydrogeology, agriculture, and soils were considered. The site (Figure 1) is located approximately 2.5 miles east by north of Gilcrest, Colorado in Range 66 West, Township 4 North (6th principal meridian, 40th parallel base line). The site measures 1 by 3 miles with the long axis parallel to the underlying groundwater flow. The groundwater gradient slopes downward from south to north. At the south end of the site, groundwater gives way to an outcropping of bedrock; thus groundwater beneath the study site is hydrologically isolated from underflow from this direction (Smith et al., 1963). The water bearing formation consists of valley-fill deposits which include intertongued beds and lenses of gravel, sand, and clay (Smith et al., 1963). The depth to unconfined groundwater ranges between 10 and 18 feet (Colorado Division of Water Resources, 1985). Within the study site are 240 acres which are annually planted to field corn. Preemergent broadleaf weed control on this acreage has been managed for more than 20 years by the use of atrazine. All applications were made in aqueous solution by means of ground spraying equipment at a rate of 1.1 pounds per acre. Atrazine has not been applied to adjoining fields which lie to the north, south and west of these 240 acres during the past 10 years. Minor amounts of atrazine have been applied along fence rows to the east. The soils to which atrazine was applied are primarily sandy loams and loamy sands: level, deep, well drained, and moderately to rapidly permeable (Soil Conservation Service, 1980). Irrigation of the atrazine-treated fields is by center pivot sprinkler system. The water for this system is pumped from an irrigation ditch which originates at the South Platte River. The frequency and duration of irrigation was based on observations of soil moisture. Additional moisture was obtained from spring and summer precipitation. The combined contribution of precipitation and irrigation during the months May through September is estimated to be 20.5 to 34.0 inches (National Oceanic and Atmospheric Administration, 1955-1984; Baes and Sharp, 1983). Irrigation of the atrazine-treated fields ended 1 September, 1985.

To monitor the study site groundwater for atrazine leached from overlying soils, four water wells were identified which allowed the collection of groundwater at gradient points above, beneath, and below the atrazine treated fields. These wells were numbered 1 through 4; their locations relative to the atrazine-treated fields are shown in Figure 1. At the time of sample collection each well was first pumped to allow flushing of at least three times its residual volume. Longer times were allowed when necessary to obtain a sediment-free sample. Water samples were collected from each of the four wells on nine occasions at two week intervals beginning 31 July, 1985 and

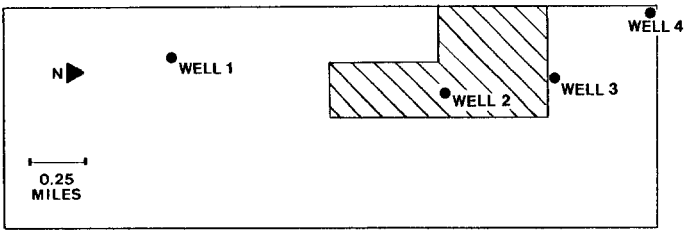

Figure 1. Map of study site showing principal features; hatching indicates atrazine-treated fields.

ending 20 November, 1985. Samples of ditch water used for center pivot irrigation were also collected to determine the atrazine contribution made by this source to the atrazine-treated fields. Since the potential exists for atrazine contamination of this water along its course due to surface runoff from bordering fields, ditch water samples were also collected at two week intervals, but only between 31 July and 23 October, 1985. The ditch water flow was inadequate for sampling after the latter date.

All water samples were collected and transported in hexane rinsed glass bottles with teflon-lined caps. Both field and laboratory spikes were prepared. Samples and spikes were extracted in the laboratory within three hours of sample collection. Extraction was performed in four steps of 175, 50, 50, and 50 ml of pesticide grade hexane, respectively. The resulting extracts were then reduced to a 5 ml volume by roto-evaporation and under a stream of nitrogen gas. Analyses of the extracts for atrazine was performed on a Tracor (Austin, TX) 222 gas chromatograph (GC) equipped with a Tracor 702 nitrogen-phosphorus detector. A 3 ft. x 5/32 inch I.D. glass column packed with three percent Reoplex 400 coated on 80/100 mesh 68 chrom WHP was employed (Iowa Institute of Agricultural Medicine, 1985). Inlet, transfer, column, and detector temperatures were set at 180, 190, 200, and 250^{o}C, respectively. Helium carrier gas flow rate was set at 75 cc/min. An atrazine standard was obtained from the Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. Confirmation of atrazine was achieved utilizing a Finnigan (San Jose, CA) 4023 gas chromatograph/mass spectrometer/data system (GC/MS) fitted with a 30 m x 0.25 mm I.D. DB5 (JW Scientific, Rancho Cordove, CA) glass capillary column (United States Environmental Protection Agency, 1985). Column temperature was programmed for 150 to 280 C (8^{o}C/min). Inlet and ionizer temperatures were set at 220 and 250^{o}C, respectively. Helium carrier gas flow was 30 cc/minute, electron energy, 70 eV., filament emission, 0.23 mA, and electron multiplier, -1475V. Confirmation of atrazine presence was based on a comparison to the gas chromatogram and mass spectrum of an atrazine standard and to spectra contained in the GC/MS library. The 5 ml water sample extracts which showed an apparent atrazine presence, above the detection limit of the GC analytical method, were

concentrated down to a volume of 0.1 ml for GC/MS analysis. Samples of similar origin which were just below the atrazine detection limit were pooled and also concentrated down to 0.1 ml. Those sample extracts which showed no apparent atrazine presence by GC analysis were not analyzed by GC/MS. Atrazine concentration data obtained from the analysis of the collected groundwater were analyzed, with respect to time, by linear regression and the standard test for slopes of the estimated regression (Kleinbaum and Kupper, 1978). Evaluation of the human health hazard posed by the atrazine concentrations measured in groundwater downgradient from the atrazine treated fields was made by comparing the measured values to currently available toxicological data. The suggested no-adverse-effect level, when one percent of the allowable daily intake of atrazine is obtained from drinking water, has been set at 7.5 ppb (National Research Council, 1977). The calculation of this value included the application of an uncertainty factor of 1,000. No conflicting data have been presented in studies which were not considered in the National Research Council's 1977 report (Binns and Johnson, 1970; Castano et al., 1982).

RESULTS AND DISCUSSION

The detection limit of the GC analysis of atrazine was 0.80 ppb. The average percent recovery of atrazine from field spikes was 74.0 with a standard deviation of 6.8 percent. Recovery of atrazine from laboratory spikes averaged 75.0 percent and a standard deviation of 3.8 percent.

Atrazine concentrations which were measured in the collected ground and ditch water samples are presented in Table 1 wherein the value of "Sampling Day" is the number of days since the

Table 1. Ground and ditch water atrazine concentrations, uncorrected for recovery. Values given as <0.80 were below detection. All values given in ppb.

Sample Date	Sampling Day	Ditch	Well 1	Well 2	Well 3	Well 4
7-31-85	1	<0.80	<0.80	1.6	<0.80	2.3
8-14-85	15	<0.80	<0.80	1.6	<0.80	2.0
8-28-85	29	<0.80	<0.80	1.3	<0.80	2.2
9-11-85	43	1.0	<0.80	1.4	<0.80	1.7
9-25-85	57	<0.80	<0.80	1.6	<0.80	1.3
10-9-85	71	<0.80	<0.80	1.4	<0.80	1.4
10-23-85	85	ND*	ND*	1.8	<0.80	1.3
11-6-85	99	(no sample)	ND*	1.1	<0.80	1.4
11-20-85	113	(no sample)	ND*	1.3	<0.80	1.3

*ND--Not Detected

first sample date (7-31-85). The concentrations given in Table 1 have not been corrected for recovery because of the artificiality of assigning a corrected value to a sample whose concentration fell below the detection limit. All but one ditch water sample had atrazine concentrations below the GC detection limit. Only in this one sample (9-11-85, 1 ppb) could atrazine be confirmed by GC/MS. If 1.0 ppb is used to represent the concentration of atrazine in the irrigation water, an estimate of this water's contribution to the atrazine load of the treated fields can be calculated. Based on data for irrigation rates and the atrazine application rate cited above, the annual rate of atrazine contribution from irrigation would be 0.06 milligrams per square foot of field area. Compared with the rate of atrazine application at the study site, irrigation water would then account for only 0.52 percent, at a maximum, of the total atrazine load to the treated fields. Thus, the levels of atrazine detected in ditch water would have a very small relative impact on groundwater below the treated fields.

In groundwater samples collected from Well 1, atrazine concentrations were invariably below detection, as was also true of Well 3 samples. Atrazine could not be confirmed by GC/MS in pooled Well 1 samples; however, atrazine was confirmed in pooled Well 3 samples. The concentration of atrazine in Well 1 samples cannot be more precisely established than to say it was less than 0.8 ppb, the GC detection limit. The fact that pooled Well 1 samples could not be confirmed suggest that their concentration was very low or that the signal observed in the atrazine gas chromatogram was attributable to background interference. Whatever the actual levels, there did not appear to be measurable atrazine contamination in study site groundwater previous to its movement beneath the atrazine-treated fields. The low atrazine levels observed in Well 3 samples relative to those collected from Well 2 may be explained by the peripheral location of Well 3; water pumped from Well 3 quite likely included water from east of the atrazine-treated fields. Thus, dilution of the groundwater from beneath the treated fields would have occurred.

Both Well 2 and Well 4 yielded groundwater samples with measurable atrazine concentrations ranging between 1.1 and 2.3 ppb. Atrazine was confirmed by GC/MS in all samples collected from these two wells. The concentration data for Wells 2 and 4 have been plotted against time (i.e., Sampling Day) in Figures 2 and 3, respectively. The linear correlation between atrazine concentration and time was not statistically significant for the data from Well 2 ($0.20 < p < 0.50$) but was highly significant for the data from Well 4 ($0.001 < p < 0.002$). Thus, groundwater samples collected from Well 2 failed to show a detectable atrazine concentration change with respect to time. At least within the time limits of this study, the cessation of irrigation of the atrazine-treated fields did not produce a

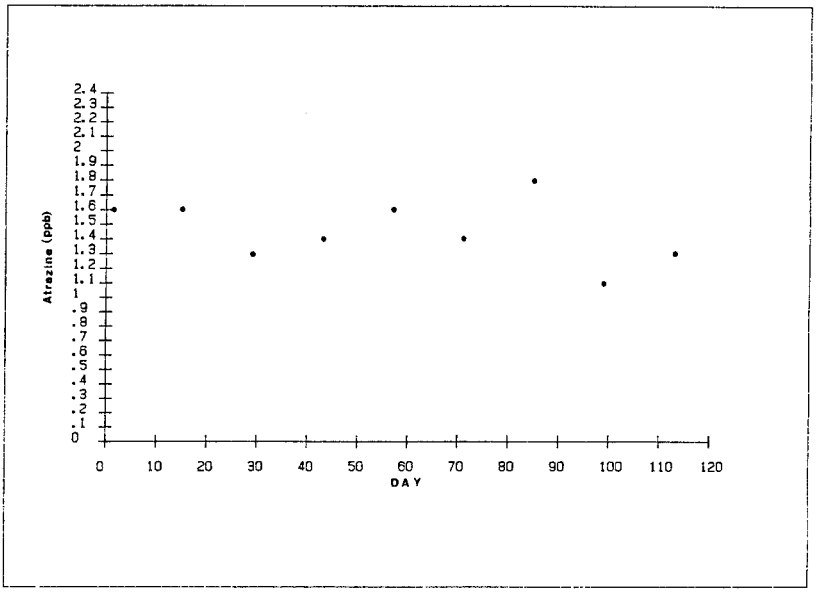

Figure 2. Groundwater atrazine concentration versus time, Well 2.

corresponding decrease in the groundwater atrazine concentration. The atrazine concentration in groundwater samples taken from Well 4 was estimated to decrease at a rate of 9.4 ppt per day and had a 95 percent confidence interval of 2.7 to 16.1 ppt per day. Seventy-seven percent of the variation in atrazine concentration at Well 4 was explained by the linear decrease over time.

Changes in irrigation of the atrazine-treated fields were not considered a question of importance in regards to the groundwater sampled at Well 4. The distance separating Well 4 from the atrazine-treated fields prevent such changes in management of these fields from having a direct or immediate impact on Well 4 sample concentrations. Atrazine levels in Well 4 samples are considered to be representative of points along the concentration gradient of a contaminant plume moving past the well. This gradient is the result of atrazine transport processes. The regression of Well 4 data described above suggests that the samples were collected from the tail of the contaminant plume and therefore higher concentrations may have occurred previous to the first sampling date.

A final goal of this study was to evaluate, based on presently available toxicological data, the hazard posed to human health by atrazine concentrations measured in groundwater downgradient from the treated fields, when used as a drinking water source. If 2.3 ppb, the maximum atrazine concentration measured at Well 4, is allowed to represent the maximum concentration achieved in downgradient water, this evaluation may be made. As previously noted, the suggested no-adverse-effect level, when one percent of

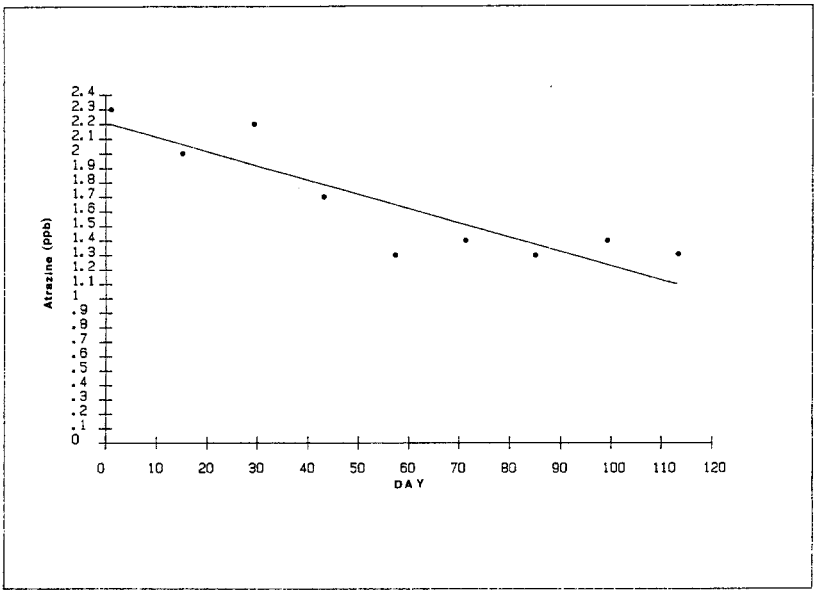

Figure 3. Groundwater atrazine concentration versus time, Well 3.

the allowable daily intake of atrazine is obtained from drinking water, has been set at 7.5 ppb (National Research Council, 1977). Thus, an exposure to drinking water concentrations of atrazine at 2.3 ppb, less than one-third of the suggested no-adverse-effect level, does not presently appear to pose a hazard to human health.

REFERENCES

Baes CF, Sharp RD (1983) A proposal for estimation of soil leaching and leaching constants for use in assessment models. J Environ Qual 12:17-28

Berg GL (1985) Farm chemical handbook. Meister Publ Co, Willoughby Ohio, p C3

Binns CW, Johnson AE (1970) Chronic and teratogenic effects of 2,4-D (2,4-dichlorophenoxyacetic acid) and atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) to sheep. Proc N Cent Weed Contr Conf 25:100

Castano P, Ferrario VF, Vizzotto L (1982) Sciatic nerve fibers in albino rats after atrazine treatment: A morphoquantitative study. Int J Tiss Reac 4:269-275

Colorado Division of Water Resources (1985) Ground Water Section, Master exact list. Office of the State Engineer, Denver, Colorado

Iowa Institute of Agricultural Medicine, Iowa National Hazard Assessment Project (1985) Personal communication

Junk GA, Spalding RF, Richard JJ (1980) Areal, vertical, and temporal differences in ground water chemistry: II. Organic constituents. J Environ Qual 9:479-483

Klassen HE, Kadoum AM (1979) Distribution and retention of atrazine and carbofuran in farm pond ecosystems. Arch Environ Contam Toxicol 8:345-353

Kleinbaum DG, Kupper LL (1978) Applied regression analysis and other multivariable methods. Duxbury Press, North Scituate, Mass, p 37

National Oceanic and Atmospheric Administration (1955-1984) Climatological data, Colorado. V 60-89. US Dept Commerce, Environ Data Service

National Research Council (1977) Drinking water and health. Report to the safe drinking water committee. Advisory Center on Toxicology, Assembly of Life Sciences. National Academy Press, Washington, DC, pp 533-537

Richard JJ, Junk GA, Avery MJ, Nehring NL, Fritz S, Svec HJ (1975) Analysis of various Iowa waters for selected pesticides: atrazine, DDE, and dieldrin--1974. Pest Monitoring J 9:117-123

Smith RO, Schneider PA, Petri LR (1963) Ground-water resources of the South Platte River Basin in Western Adams and Southwestern Weld Counties, Colorado. USGS Water Supply Paper 1658. US Gov Print Off, Washington, DC

Soil Conservation Service (1980) Soil survey of Weld County, Colorado, southern part. US Dept Agriculture, Soil Conservation Service, Washington, DC, pp 13, 34, 46

United States Environmental Protection Agency (1985) Semivolatile organic compounds by isotope dilution, GC/MS. Method No 1625, Revision B. United States Environmental Protection Agency, Washington, DC

Wagner GH, Chahal KS (1966) Decomposition of carbon-14 labeled atrazine in soil samples from Sanborn Field. Proc Am Soc Soil Sci 30:752-754.

Wehtje GR, Spalding RF, Burnside OC, Lowry SR, Leavitt RC (1983) Biological significance and fate of atrazine under aquifer conditions. Weed Sci 31:610-618

Received April 17, 1987; accepted August 1, 1987.