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ATRAZINE CONTAMINATION OF GROUNDWATER IN THE PLATTE VALLEY OF NEBRASKA FROM NON-POINT SOURCES.[1]

G. WEHTJE, J.R.C. LEAVITT, R.F. SPALDING, University of Nebraska-Lincoln.
L.N. MIELKE and J.S. SCHEPERS, U.S. Dept. of Agriculture, Lincoln, NE, U.S.A.

ABSTRACT

Groundwater under large portions of the corn (*Zea mays* L.) producing areas of the state of Nebraska is contaminated with trace levels of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine]. Concentrations generally range between 200 and 800 nanograms/liter (ppt), which is well below the levels that would damage even the most sensitive crops. Downward leaching appears to be the predominate route by which atrazine is entering into the aquifers. Studies with soil extractors, established beneath a corn field irrigated with a center pivot system, indicate that 0.07% of the atrazine applied to the soil surface leached to 1.5 m below the surface by the end of the growing season. Groundwater atrazine in wells increased by 0.7 ppb from the up gradient to the down gradient side of the treated field. Dissipation of atrazine, once it has entered into the aquifer is due to dilution and dispersion, and to a small amount of chemical hydrolysis resulting in the production of hydroxy-atrazine. Mathematical models indicate that the trace amounts of atrazine seasonally entering the aquifer are not cumulative since degradation is effectively keeping the level of contamination well below the levels of phytotoxicity.

INTRODUCTION

Nebraska has extensive geographical areas characterized by relatively level topography and sandy soil; the result of aeolian and alluvial processes. These areas are underlain with thick nonconfined aquifers, beginning 5 to 7 m below the soil surface. The combination of fertile topsoil and the good supply of groundwater for irrigation makes this area excellent for corn production. Furrow irrigation is commonly used in the flat areas, and center pivot irrigation is more typically used in recently developed areas with rolling topography. The Central Platte Valley is one such area where irrigation development has

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been extensive. Amount of irrigation water applied often is in excess of the needs of the crop. Excessive water permeates below the root zone and ultimately recharges the aquifer. Thus materials applied to the surface could be leached directly into the aquifer.

Atrazine is a preemerge herbicide effective in controlling broadleaf weeds and some grasses in corn and sorghum (*Sorghum bicolor* Moench). The use of atrazine is almost universal in the production of these grains in the United States, and it is the most widely used pesticide in the state of Nebraska, 3.5 million kg were used in 1978 (1). Atrazine has recently been detected in the groundwater of these corn producing areas (2, 3). The widespread, low level contamination suggests a non-point source origin, that is a result of direct leaching from the surface into the aquifer (4).

Objectives of this study were to (a) quantify the leaching of atrazine that results from normal agricultural usage, (b) evaluate the agricultural significance of low levels of atrazine contamination, and (c) establish whether atrazine is dissipated after entering the aquifer, thus decreasing the potential for long term accumulation.

Route of atrazine entry - leaching

A system of underground vacuum soil water extractors and groundwater sampling wells were used to investigate the possibility that atrazine could be leached through sandy soil. This system was established in 1972 in a field in the Central Platte Valley of Nebraska and had previously been used to examine nitrate leaching (5). The surface soil in this area is a sandy loam in texture and the percent sand increases to nearly 100% with depth. The surface soil was characterized as an Entic Haplustoll, sandy-skeletal-mixed, mesic. The eight vacuum extractors, placed 1.5 m below the surface, were a 3.25 m long 'V' shaped sheet metal container with a ceramic candle in the bottom. The candle was kept under constant tension. Water that passed through the ceramic candle drained into an adjacent reservoir. The vacuum on the system was maintained in the same range as the water tension of the soil. Therefore, the extractors served only to intercept potential aquifer recharge as it percolated through the profile below the root zone. The water table laid 5.5 m below the surface; dropping about 0.75 m during the irrigation season. Groundwater flowed from west to east at a velocity of approximately 20 cm per day, based upon calculations using the Darcian flow equation (6).

At the beginning of the 1979 growing season, atrazine was applied to the soil surface at a rate of 4.4 kg/ha. The application rate was reduced to 2.2 kg/ha during 1980. The two different rates represent the high and low to medium range of typical agricultural usage. Water in the extractor reservoirs was sampled on a weekly basis throughout the growing season. The field received a total of 44.2 cm of water (irrigation and precipitation) during the 1979 growing season; of which 4.2 cm (9.5%) was recovered in the extractors. A similar rainfall, irrigation and leaching water pattern was seen in 1980. Atrazine equivalent to 0.33 g/ha, or 0.075% of the amount applied, had been recovered in the extractors by the end of the 1979 growing season. The amount recovered in 1980 was 0.14 g/ha, or 0.065% of the amount applied. Groundwater recovered from observation wells on the downward hydraulic gradient direction (east side of the field) contained about 10 times the amount of atrazine as the west side. Presumably water was becoming enriched with atrazine as it flowed under the treated field.

The conclusion from this aspect of the study is that the usage of atrazine on sandy soil will result in a small percentage (<0.1%) of the applied amount reaching the underlying aquifer, assuming irrigation is sufficient in amount to result in deep percolation and thus provide recharge to the aquifer. This route is probably the predominant route by which atrazine is entering into the aquifer.

Biological significance of the contamination

Atrazine concentration in contaminated areas range between 200 and 800 ppt. The acute oral LD_{50} of atrazine to rats and mice is 3080 mg/kg and 1750 mg/kg, respectively (7). Experimental animals fed sublethal of atrazine for extended periods of time showed no adverse effects. The toxicological data indicates that the present levels of contamination pose no threat to man or to animals.

The worst consequence of this contamination would be if atrazine containing groundwater were to be used to irrigate atrazine sensitive crops. To assess this possibility, oats (*Avena sativa* L.) which are very sensitive to atrazine, were grown in sand in the greenhouse and watered daily with a nutrient solution containing 0, 1, 10, 25, 50, 75 and 100 ppb atrazine. The highest concentration of atrazine which had no detectable effect on either the total dry weight or the grain yield was 25 ppb. At present the levels of contamination remain well below the threshold level necessary to damage even the most sensitive of crops.

The fate of atrazine within an aquifer

Results indicate that continuous corn production under irrigation with yearly applications of atrazine will result in yearly additions of atrazine to the underlying aquifer. Concentrations will progress linearly upward and encroach upon the critical levels unless the atrazine is subject to some form of dissipation once it has entered into the aquifer. Possible routes of dissipation include degradation, adsorption onto aquifer material, and dilution, resulting from groundwater movements. The effectiveness of adsorption and dilution in dissipating atrazine once it has entered into the aquifer have not been quantified.

Degradation result in detoxification, thus it is the most effective means of dissipation. Atrazine is considered to be a long residual herbicide; residues can remain in the soil months after application (8). Atrazine degradation by microbial metabolism results in the removal of either the ethyl, or the isopropyl side chain (or both) (9, 10, 11). Chemical hydrolysis results in the removal of the chlorine (12). Both routes result in detoxification. However chemical hydrolysis occurs under a wider range of conditions, and is considered to be the predominate degradative pathway (13, 11, 14).

Atrazine degradation under similated aquifer conditions was studied by placing aquifer sand and water into a glass jar along with a precise amount of atrazine. Cultures of aquifer microbes, aseptically obtained by drilling and then probing into the aquifer, were also added. Jars were incubated for 3 months at 12 C (average aquifer temperature) at which time both the sand and the water were analyzed for parent atrazine plus the microbial and chemical hydrolysis breakdown products. Microbial degradation could not be detected. Approximately 2.5% of the atrazine had been converted to hydroxy-atrazine. Chemical hydrolysis is probably the only degradative pathway available under aquifer conditions; and 5% per year appears to be a reasonable, if not a conservative estimate, of the degradative activity.

Annual additions of atrazine into the aquifer, followed by partial degradation will result in either a slow increase in concentration, or an equilibrium situation. The following equation has been used to predict the residue that will remain after a specified number of years assuming yearly applications of the herbicide followed by partial degradation (15):

$$R = \frac{AX(1-X^n)}{(1-X)}$$

R = remaining residue
A = annual application rate
X = amount that remains after each year
n = number of years

For these calculations the amount of atrazine that annually enters into the aquifer is assumed to be 0.5 g/ha. This amount is four times higher than what was measured in the field under center pivot irrigation. However, much of the corn acreage is irrigated by furrow and the amount of deep percolation and aquifer recharge would be expected to be higher. The aforementioned equation indicates that an equilibrium situation will be reached in about 30 years after the initiation of applications. Atrazine has been used in the contaminated areas for approximately this length of time. The levels of groundwater contamination presently being detected may actually represent an equilibrium situation. Concentrations rise upon the arrival of 1 years leachate into the aquifer, and falls back to the original level with the ensuing dissipation. It appears unlikely that toxic levels will ever be reached.

CONCLUSIONS

The unique situation in Nebraska of corn production and atrazine usage with intense irrigation on a sandy soil with a fairly high water table results in conditions conducive for a small amount of atrazine applied to the soil surface (less than 0.1%) to be leached into the underlying aquifer. The resulting levels of contamination remain well below any critical threshold. Degradation to hydroxy-atrazine probably does occur within the aquifer, and at such a rate that long term accumulation appears unlikely.

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