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Groundwater Analysis of Triazine Herbicide Using Solid Phase Extraction and High Pressure Liquid Chromatography

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ABSTRACT

The concentration of Triazine Herbicide in well water of the Arkansas River between Maize and Haven is determined through the use of High Pressure Liquid Chromotography and Solid Phase Extraction. The Samples were taken from shallow wells in cross sections of the river on December 9, 1998. The water samples were prepared using LC-18 Solid Phase Extraction tubes and then run on a Shimadzu HPLC equipped with an LC-8 DB Supelco Column with the detection set at 254 nanometers and the absorbance set to 0.8. There is evidence that there are small concentrations of triazine herbicide in the well water more than six months after crop sprayings.

Keywords: *triazine, atrazine, propazine, HPLC, well water contamination*

INTRODUCTION

In talking with Mike Dealy, General Manager of the Equus Beds Groundwater Management District 2, the concern over the amount of the triazine herbicide in the groundwater was brought to my attention. Triazine Herbicides are six membered rings containing three nitrogens and azine (a nitrogen containing ring) making up the heterocyclic nitrogens. Triazines are applied to the soil mainly for their postemergence activity. Their selectivity depends on the plants ability to metabolize the parent compound, where the susceptible plants do not. (Ware, 112) Atrazine, the most common of the triazines is one of the most common herbicides on the market today, used at the rate of 100 million pounds a year.

Such an abundance of atrazine has caused some problems. In Kansas, approximately 97 percent of all the rivers and streams are considered unsafe for swimming and for drinking. (Sierra , 18) The contamination levels of triazines, namely atrazine are very low due to the health concerns that the herbicide has. The EPA has set the contamination level at 3 parts per billion for atrazine. (Fawcett, 19)

The reason for the concern with the triazine herbicides is because of the effects the chemical has on the body. In addition to killing weeds, atrazine has been proven to "wreak havoc on the liver, kidneys, and cardiovascular system". (Holden, 902) When atrazine was fed at high doses to a particular strain of lab rats, the rats that were exposed to the triazine family herbicide grew more cancerous tumors then those who weren't exposed to the herbicide. (Fawcett, 19)

The above mentioned has led to my research on the amount of the triazine herbicide in four wells on the Arkansas River between Haven and Maize, Kansas. Samples were taken from the wells, extracted using Solid Phase Extraction, and then run through a High Pressure Liquid Chromatograph.

MATERIALS AND METHODS

In coordination with Mike Dealy (manager) and Tim Boese (Hydrologist Technician) of the Equus Beds Groundwater Management District 2 in Halstead Kansas, I obtained well water samples from four cross sections of the Arkansas River in Haven (well #EB 214-AA), Mount Hope (well #EB 209-A), Bentley (well #EB 203-A), and Maize (well #EB 220-A). These wells were selected due to their small ground level to water distance, the permeability of the soil, and the amount of agriculture in the immediate area. A minimum of 500 mL of each of the samples was taken to give accurate quantitative results. It was decided to use 2 Liters in each sample to increase the probability of a hit. The samples were then stored on ice in amber bottles and taken back to the lab for analysis.

To extract the triazines from the water samples, the samples were filtered through LC-18 3mL Supelco Solid Phase Extraction tubes which were treated with a 2mL methanol wash. The water was then passed through the filter gravimetrically for two minutes, and then vacuum filtrated the rest of the way. The water was measured for quantitative analysis and then discarded. The tube is then washed with 2mL of 4:3:1 water:acetonitrile:methanol solution. The sample is then eluded with 2 mL of methanol. This process should give 100% recovery of the triazine herbicide as well as better response and resolution. (Supelco).

For the analysis of the herbicides, a Shimadzu LC-6A High Pressure Liquid Chromatographer was used. This consists of two LC-6A Shimadzu pumps (pump A and pump B), an SPD-6AV UV-Vis Spectrophotometer, and a C-R6A Chromatopac. The system was controlled by an SCL-6A System controller which controlled the rate of flow, the start time, and all of the system configurations. The UV-Vis was set at 254 nanometers for detection with the absorbance set at 0.8. The output was printed on the Chromatopac, which printed the peaks of the chromatogram and also did the calculations and integration's of the peaks. The mobile phase was a solution of 45:55 acetonitrile:water.

The machine was calibrated using at first 100 part per million standards. This was done by dissolving 5 mg of the standard in 50 ml 45:55 acetonitrile:water. After acquiring this initial 100ppm standard, it was

Table 1. Well Depth and Soil Content.

Well Number	Depth of Well	Depth of Water	Soil Content	Permeability	Content (ug/L)
EB 220-A	25.0 feet	8.7 feet	Elandco silt	0.6-2.0 in./hr.	No detection
EB 203-A	43.0 feet	5.95 feet	Naron Fine Sand	0.6-6.0 in./hr	No detection
EB 209-A	77.0 feet	10.74 feet	Naron Fine Sand	0.6-6.0 in./hr	No detection
EB 214-AA	50.0 feet	5.08 feet	Carwile Fine Sand	0.2-1.0 in./hr.	279.6 (atrazine)

possible to get 1ppm by a 1:100 dilution. With this 1ppm standard, it was possible to get 100 part per billion and 10 part per billion standards by using a 1:10 dilution. The machine was calibrated and would give accurate results down to ten parts per billion.

RESULTS

After all the standards were run and the machine was calibrated, I ran my samples through the same procedure. The samples were run through at 1.5 ml/minute with the detection at 254 nanometers. The resulting peaks were then integrated by the Chromatopac, which gave the area under the peaks. Well #EB-214AA showed a peak at 3.06 (atrazine) with an average area of 2220.33. All values then had to be divided by two to reduce the original sample which was taken from 2 Liters down to 1 Liter to get the ug/L which is the desired parts per billion.

The content was found using the formula for the calibration curve method (External Standard Method) as described in the instruction manual for the C-R6A Chromatopac. This equation is:

$$\text{Content} = (F1Ai+F2)W \times 100$$

where:

F1: Response factor for slope
F2: Response Factor for constant term
Ai: Area under peak
W: weight of sample

With this information, it was possible to find the content of the herbicide in my well water samples (Table 1).

DISCUSSION

Peaks were found on well #EB-214AA which has a depth of 5.08 feet from ground to water. Well #EB-214 AA was the shallowest well of the wells sampled. This is the result that I thought would happen. It makes sense to think that if there is going to be seepage, it will be more prevalent in the more shallow wells. Still I wanted to look at the soil content of all the wells to see whether or not the permeability of the soil had something to do with the fact that the deeper wells had no trace of the herbicide. EB-220A is made up of Elandco silt with a permeability rate of 0.6-2.0 inches per hour. EB-203A and EB-209A both consist of Naron fine sandy soil with a permeability rate of 0.6-6.0 inches per hour. EB-214AA is made up of Carwile-Farnum fine sandy with a permeability of 0.2-1.0 inches/hour.

According to this, the permeability doesn't really seem to have an effect on the amount of the herbicide that leaches into the groundwater. If permeability was a factor, I would have expected to find atrazine or propazine in well #EB-203A due to the fact that it was the one of the shallowest wells and the permeability rate was the greatest for the soil content above the well.

I was not expecting to find results in any of the wells for two different reasons. The first reason being the fact that the samples were taken in the first week of December, a good eight months from the original crop spraying. The second reason being the heightened concern on the effects of such chemicals being used in excess. The results may seem quite small, where the only well that had any trace of herbicide only showed 279.6 ppb atrazine, but it must be taken into account that the EPA has set drinking water contamination level at 3 ppb for atrazine.

If I were to do the experiment again, I would take into consideration the time of the year that the sample was taken and do a comparison study. The study would be taken throughout a year to see if the time of year the sample was taken mattered, or if the chemicals were at a constant throughout the year in the underground aquifer.

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