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A B S T R A C T

ANALYSES OF GROUNDWATER FOR TRACE LEVELS OF PESTICIDES

Agricultural production is a major source of revenue in Arkansas. In order to increase productivity, it has been necessary to rely increasingly on the use of pesticides and irrigation water. In the last 15 years several states have reported finding pesticides in groundwater as a result of normal agricultural practices. Since almost half of the population also relies on groundwater as their source of drinking water, it is necessary to conduct research as to ascertain the presence or absence of commonly used pesticides in groundwater.

Multiresidue analytical techniques were developed for the analysis of acifluorfen, alachlor, atrazine, cyanazine, diuron, fluometuron, linuron, metolachlor and propanil from groundwater, by either GLC or HPLC. Analytical sensitivities ranged from 1 to 5 ppb.

Groundwater samples were collected from three areas of southeastern Arkansas that are under heavy agricultural production. Samples were collected directly from irrigation wells just prior to and during the peak of the irrigation season and will be compared to determine whether any temporal differences exist. To-date, over 500 samples have been analyzed. No positive finding for any pesticide has been shown.

Terry L. Lavy

Completion Report to the U.S. Department of the Interior, Washington, D.C., September 1985.

Keywords -- Agriculture/Crop Production/Analysis/Detection/Pesticides/ Groundwater Contamination

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INTRODUCTION

Agricultural production in Arkansas provides a major source of revenue for the state as well as a significant amount of rice for world export. Large areas of land are devoted to the production of rice (Oryza sativa), soybeans (Glycine max), cotton (Gossypium hirsutum), timber and other commodities. An important factor that has contributed to an increased production level for these crops is the use of pesticides. Many water-soluble compounds are routinely used because most soil applied herbicides must be solubilized in order to be effective in weed control. A growing area of concern among agriculturalists, environmentalists and lay people is the possibility for contamination of groundwater by these highly water-soluble pesticides. This concern is of considerable importance because nearly one-half of the population of the U.S. relies on groundwater as their source of drinking water. Groundwater is also used for livestock consumption, irrigation and for other purposes. With the continued worldwide increase in the need for food and fiber, the use of pesticides is expected to increase. It is therefore necessary to conduct research to determine the presence or absence of pesticides in groundwater.

Indeed, there have been many findings of pesticides in groundwater. However, prior to the late 1970's, most monitoring studies were focused around either waste-dump sites or urban sites rather than with rural agricultural areas. Then, in 1979, came the finding of aldicarb and DBCP (1,2-dibromo-3-chloropropane) in agricultural

areas. Just as important, their presence was believed to be due to normal agricultural practices and not as the result of some accident. Since then, there have been many findings of pesticides in groundwater, 12 different pesticides in 18 different states. However, with a few exceptions, there has been little research conducted in this area in the southern United States.

It should be pointed out that frequency of use and water solubility are not the only criteria needed to qualify for selection. Cohen (1984) has presented some chemical parameter guidelines for predicting pesticides with potential for contaminating groundwater. Some of these important characteristics include:

1. Kd, the soil/water distribution coefficient. A value less than 5 is desirable.
2. Koc, the Kd divided by the soil organic carbon fraction. Should be less than 300-500.
3. Henry's Law Constant, a measure of the escaping tendency of dilute solutes from water. Value less than 10^{-2} atm-m^3/ml.
4. Hydrolysis Half Life, > 25 weeks.
5. Photolysis Half Life, > 1 week.
6. Mobility.

Table 1 lists the relevent chemical characteristics for the pesticides selected for examination.

A. Purpose and Objectives

The major objective of this study was to collect groundwater samples from irrigation wells in areas of southeastern Arkansas where pesticides are intensively used and to analyze these samples for trace levels of pesticides that are commonly used in these areas.

Table 1. Chemical parameters of selected pesticides (Cohen et al. 1984).

Pesticide	Koc	Kd	Water Solubility (ppm)	Hydrolysis Half-life (wks)	Presence in Groundwater
Acifluorfen	490		>250,000	>8	No
Alachlor	213	0.6-8.1	240	NA	Yes
*Aldicarb	36	<4	6,000	10-650	Yes
Atrazine	51	0.4-8	33	10-106	Yes
Cyanazine	200	3.4-4.6	171		Yes
Diuron	383	0.2-8.3	42	-	No
Fluometuron	175	-	90	110-144	No
*Hexazinone	-	0.2-1.0	33,000	stable	No
Linuron			75		No
Metolachlor	-		530		Yes
*Picloram	17	0.03-4.6	440		No
Propanil		500			

*Pesticides not investigated in this study.

B. Related Research or Activities

The vast majority of research on pesticide contamination of groundwater has been conducted either in California, the upper mid-western parts of the United States, or in the southern parts of Canada. Other than in Florida, very little research on this problem has been conducted in the southern sections of the United States. To our knowledge, there has been no previous research in this area in Arkansas.

Although the areas where pesticides have been found generally have more shallow groundwater depths and soil types that are more conducive to the movement of pesticides to groundwater, that does not mean that researchers in this area can feel safe that our groundwater will not become contaminated. Many of the pesticides found in groundwater elsewhere are also being heavily used in Arkansas. It may take pesticides years to pass through the soil profile to reach an aquifer, but the compounds have been shown to persist long enough to do so. It is, therefore, imperative that we continue to monitor the quality of this important natural resource.

METHODS AND PROCEDURES

Due to the fact that rice, soybeans and cotton are the most common field crops in Arkansas, certain herbicides have been selected on the basis of their frequency of use with these crops and on their solubility in water. The herbicides are: acifluorfen, alachlor, atrazine, cyanazine, diuron, fluometuron, linuron, metachlor and propanil.

Three locations in southeast Arkansas were selected for sampling. Criteria for selection included:

1. Location where pesticides are applied in an intensive farming operation.
2. Good field history and records of pesticide use over the past five years.
3. Repeated applications of at least one pesticide.
4. Several irrigation wells readily accessible for sampling.

The areas chosen were a) the Althiemer-Lake Dick region, b) the Dumas-Pickens region and c) Kelso. A map is attached to show the location of these sites.

The soil in the Altheimer-Lake Dick region consists primarily of a well-drained silt loam of the Rilla-Herbert-McGehee association. It is on bottom land of the Arkansas River. The crops grown in this region are mainly cotton and soybean. In the last few years, however, significant amounts of corn and milo have been planted.

The Dumas-Pickens region has cotton, soybeans and rice as the major crops. As at Altheimer, corn and milo have recently been planted. The soil varies from well-drained silt loams formed on bottom lands (Coushatta and Lonoke associations) to poorly drained clays of the Perry-Portand association.

The Kelso site also grows primarily rice, soybeans and cotton. The soil is primarily poorly drained Perry clay.

Samples were collected at different times of the irrigation season. A small number of wells in the Altheimer area were sampled in March, prior to the beginning of the irrigation season. All locations were then sampled at the approximate beginning of the irrigation season (mid-May to early June) and again during the height of

the irrigation season (in August). Results from these samples will be compared in an attempt to determine if the amount of water taken from the well was related to any pesticide concentration found.

Well depth in these areas are generally around 100 feet, while the depth to the groundwater varied depending on the site and the time of the irrigation season. An average range would be 40-70 feet.

Samples were collected directly from irrigation wells. If the wells were not already running, the pumps were allowed to operate for a few minutes. In this manner, the water collected was assured of being "fresh groundwater" as opposed to water that may have been sitting in the pipes or casing. Also, if the pump had been idle and is subsequently turned on, the first water coming out of the pump appears to contain high levels of soluble Fe or other metals. Letting the pump run for a few minutes eliminates the appearance of this rusty-looking water from the system.

The samples were collected in amber-colored glass bottles with teflon cap liners. Approximately four liters of water was collected from each well. Samples were immediately stored in ice chests and were kept cold until returning to the lab until analysis one-four weeks later. In the field, at the time of sampling, one liter subsamples of each sample were fortified with a mixture of the pesticides to be analyzed. The fortification level was either 10 or 20 ppb. At the laboratory, fortified samples were prepared at the 1.0, 5.0, 10.0, or 25 fortification levels and were interspersed with the actual samples. All samples were kept refrigerated at 4-6^{o} C until the time of analysis.

Samples were analyzed by either HPLC or GLC. Alachlor, metolachlor and propanil were analyzed by GLC, while acifluorfen, atrazine, cyanazine, diuron, fluometruon and linuron were analyzed by HPLC. Samples were prepared for analysis by the following procedure. 500 ml aliquots of each sample were taken. 50 gm (10%) of NaCl was added and dissolved. Samples for HPLC analysis also received 5 ml (1%) of glacial acetic acid. Samples were extracted by sorbent trapping onto prepackaged Baker-10-SPE 3 ml C_{18} disposable columns. The columns were conditioned by passing through two column lengths of acetone, followed by two column lengths of deionized H_2O. The samples were then passed through the column at a flow rate of 1-2 drops/second. The analytes were then eluted with 4 ml of acetone. Samples for GLC analysis were then reduced under N_2 to a final volume of 2 ml. Analysis was performed on a Perkin Elmer Sigma I Gas Chromatograph using an electron capture detector and cyanopropyl phenyl column. Operating temperature was 190^{o} C. Samples for HPLC analysis were evaporated to dryness under N_2. The residues were then redissolved in 3 ml of 30% CH_3CN/H_2O. Samples were examined under two different solvent conditions. Samples to be analyzed for atrazine, cyanazine, diuron, fluometuron and linuron were examined using 30% CH_3CN/H_2O as the mobile phase, while samples to be analyzed for acifluorfen used 40% CH_3CN/H_2O with 1% glacial acetic acid as the mobile phase. Flow rate was 3 ml/minute.

PRINCIPLE FINDINGS AND SIGNIFICANCE

Sampling of the selected 28 irrigation wells and agricultural

water sources has been completed. Eleven wells at both the Altheimer and Dumas locations were sampled during May - June and once again during August. Six wells were sampled at both times at the Kelso location. Every effort was made to sample the same wells at both sampling dates. This, however, was not possible for two wells, one made inoperable by lightning and the other by vandalism. In both cases, a replacement well in the same general vicinity was sampled.

To-date, in excess of 520 analytical determinations have been completed by either gas or liquid chromatography. In addition, both laboratory-prepared and field-prepared fortified samples were interspersed among, and analyzed with, the actual samples. The per cent recovery ranged from 72 to 118% for the laboratory fortified samples (Table 2) and from 74 to 106% for the field fortified samples (Table 3).

A limit of detection was then determined for each pesticide using the per cent recovery data. The mean per cent recovery and the standard deviation of the mean was determined for each pesticide at the lowest fortification level (see Table 2). If the mean was greater than three times the standard deviation, then we felt confident we could detect at least that amount of pesticide. Table 4 lists the limit of detection for each pesticide. However, based on the signal to noise ratio obtained from the chromatograms of fortified samples, we believe it will be possible to detect lower levels of each pesticide than reported here. By analyzing additional fortified samples at lower levels we will determine if it is possible to lower current limits.

Table 2. Recovery Data for Laboratory-Prepared Fortified Samples

Pesticide		Level of fortification (in ppb) 1	5	10	25
Acifluorfen	$\bar{X}$	——	4.50	9.67	23.65
	Std. dev.		0.57	2.00	3.21
	% recovery		90.0%	96.7%	94.4%
Alachlor	$\bar{X}$	1.06	5.91	11.59	——
	Std. dev.	0.25	0.96	1.35	
	% recovery	106.1%	118.2%	115.9%	
Atrazine	$\bar{X}$	0	4.62	8.13	——
	Std. dev.	——	1.22	1.33	
	% recovery	0%	92.4%	81.3%	
Cyanazine	$\bar{X}$	——	5.38	10.81	26.67
	Std. dev.		1.60	3.21	2.96
	% recovery		107.6%	108.1%	106.7%
Diuron	$\bar{X}$	0	4.51	9.28	21.81
	Std. dev.	——	1.16	1.51	2.72
	% recovery	0	90.2%	92.8%	87.2%
Fluometuron	$\bar{X}$	1.15	3.95	8.76	21.67
	Std. dev.	0.68	1.12	2.94	1.93
	% recovery	115.0%	79%	87.6%	86.7%
Linuron	$\bar{X}$	1.47	4.15	7.99	21.25
	Std. dev.	0.85	1.05	1.19	1.88
	% recovery	147.0%	83.0%	79.9%	85.0%
Metolachlor	$\bar{X}$	0.72	3.99		——
	Std. dev.	0.13	0.72		
	% recovery	72.3%	80%		
Propanil	$\bar{X}$	0.83	4.28	8.36	——
	Std. dev.	0.11	0.39	1.11	
	% recovery	82.7%	85.6%	83.6%	

Table 3. Recovery Data for Field-Prepared Fortified Samples.

	Level of Fortification (in ppb)					
	10 ppb			20 ppb		
Pesticide	$\bar{X}$	Standard Deviation	% Recovery	$\bar{X}$	Standard Deviation	% Recovery
Acifluorfen	—	—	—	21.55	4.85	102.4%
Alachlor	10.66	1.95	106.6%			
Atrazine	7.42	2.01	74.2%	15.22	2.54	76.1%
Diuron	9.17	2.82	91.7%	15.98	2.12	79.9%
Fluometuron	—	—	—	15.04	3.38	75.02
Linuron	10.18	4.38	101.8%	17.97	3.11	89.9%
Metolachlor	10.51	1.81	105.1%			
Propanil	8.72	1.44	87.2%			

Table 4. Limit of Detection for each Pesticide

Pesticide	Limit of Detection (ppb)*
Acifluorfen	5
Alachlor	1
Atrazine	5
Cyanazine	5
Diuron	5
Fluometuron	5
Linuron	5
Metolachlor	1
Propanil	1

*Possibilities exist for lower detection limits by working with additional analytical determinations at lower concentration levels.

None of the analytical determinations have yet to reveal the presence of any pesticide from any of the water source sampled. Table 5 lists the location, date sampled and the analytical results for the samples that have been analyzed at the present time. However, analysis of water samples for alachlor, cyanazine, metolachlor and propanil has not been completed. Results will not be reported until the additional purification and clean-up steps have been completed for these compounds and all the samples have been analyzed.

CONCLUSIONS

Of the 520 samples assayed to-date, no detectable levels of pesticides have been confirmed. Efforts are continuing to complete remaining alachlor, metolachlor, cyanazine and propanil samples.

Any subsequent water samples should be taken near areas where residents have shown concern with regard to the possibility of pesticides in their drinking water.

Table 5. Location, Sampling Date, and Analytical Results.

Location of Well	Date Sampled	Pesticide (conc. in ppb)				
		Acifluorfen	Atrazine	Diuron	Fluometuron	Linuron
Kelso AR						
Site 1	6-25-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd	nd	nd	nd
Site 2	6-25-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd	nd	nd	
Site 3	6-25-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd	nd	nd	nd
Site 4	6-25-85	nd	nd	nd	nd	nd
	8-13-85	nd		nd	nd	
Site 5	6-25-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd		nd	
Site 6	6-25-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd	nd	nd	nd
Altheimer AR						
Site 1	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd
Site 2	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd
Site 3	3-6-85	nd	nd	nd	nd	nd
	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd
Site 4	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd
Site 5	3-6-85	nd	nd	nd	nd	nd
	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd
Site 6	3-6-85	nd	nd	nd	nd	nd
Site 7	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd
Site 8	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd

Table 5. (continued)

Location of Well	Date Sampled	Pesticide (conc. in ppb)				
		Acifluorfen	Atrazine	Diuron	Fluometuron	Linuron
Altheimer AR						
Site 9	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd
Site 10	6-26-85	nd	nd	nd	nd	nd
	8-14-85	nd	nd	nd	nd	nd
Site 11	3-6-85	nd	nd	nd	nd	nd
	6-26-85	nd	nd	nd	nd	nd
Site 12	6-26-85	nd	nd	nd	nd	nd
	8-14-85		nd	nd	nd	nd
Pine Bluff AR Municipal Water	8-14-85	nd	nd	nd	nd	nd
Dumas AR Municipal Water	8-13-85	nd	nd	nd	nd	nd
Dumas AR						
Site 1	5-16-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd	nd	nd	nd
Site 2	5-16-85	nd	nd	nd	nd	nd
	8-13-85					
Site 3	5-16-85	nd	nd	nd	nd	nd
	8-13-85					
Site 4	5-16-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd	nd	nd	nd
Site 5	5-16-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd	nd	nd	nd
Site 6	5-16-85	nd	nd	nd	nd	nd
	8-13-85		nd	nd	nd	nd
Site 7	5-16-85	nd	nd	nd	nd	nd
	8-13-85		nd	nd	nd	nd

Table 5. (continued)

Location of Well	Date Sampled	Pesticide (conc. in ppb)				
		Acifluorfen	Atrazine	Diuron	Fluometuron	Linuron
Dumas AR						
Site 8	5-16-85	nd	nd	nd	nd	nd
	8-13-85		nd	nd	nd	nd
Site 9	5-16-85	nd				
	8-13-85	nd	nd	nd	nd	nd
Site 10	5-16-85	nd	nd	nd	nd	nd
	8-13-85	nd	nd	nd	nd	nd
Site 11	5-16-85	nd	nd	nd	nd	nd
	8-13-85					

nd = not detected (see Table 3 for limits of detection).


BENTON
CARROLL
BOONE
MARION
BAXTER
FULTON
RANDOLPH
CLAY
WASHINGTON
MADISON
NEWTON
SEARCY
IZARD
SHARP
LAWRENCE
GREENE
STONE
INDEPENDENCE
CRAIGHEAD
MISSISSIPPI
CRAWFORD
FRANKLIN
JOHNSON
POPE
VAN BUREN
CLEBURNE
JACKSON
POINSETT
CONWAY
FAULKNER
WHITE
CROSS
SEBASTIAN
LOGAN
WOODRUFF
CRITTENDEN
ST. FRANCIS
YELL
PERRY
SCOTT
PULASKI
LONOKE
PRAIRIE
LEE
SALINE
MONROE
GARLAND
POLK
MONTGOMERY
PHILLIPS
HOT SPRING
GRANT
JEFFERSON
ARKANSAS
HOWARD
PIKE
CLARK
SEVIER
DALLAS
CLEVELAND
LINCOLN
DESHA
LITTLE RIVER
HEMPSTEAD
NEVADA
OUACHITA
CALHOUN
BRADLEY
DREW
MILLER
COLUMBIA
UNION
ASHLEY
CHICOT
LAFAYETTE
▲ Indicates Sampling Sites

LITERATURE CITED

Cohen, S.Z., Creeger, S.M., Carsel, R.R. and Enfield, C.G. 1984. Potential for pesticide contamination of groundwater resulting from agricultural uses. Treatment and Disposal of Pesticide Wastes. Kreuger and Seiber, ed. Washington, D.C. pp. 297-325.