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ABSTRACT

DETERMINING PESTICIDE AND NITRATE LEVELS IN SPRING WATER IN NORTHWEST ARKANSAS

Occurrences of pesticides in our nations ground water are on the rise. As states become aware of this problem and begin monitoring programs, incidence of contamination will probably increase. Since the problem of pesticides in groundwater is relatively new, little research has centered on the fate of pesticides after they reach the groundwater environment. In Northwest Arkansas efforts to monitor groundwater for pesticides have been small. Twenty-five springs in Northwest Arkansas were sampled in the fall of 1988, and spring of 1989. Analysis for atrazine, alachlor, metolachlor, diuron, and simazine in spring water was preformed using gas liquid chromatography and high performance liquid chromatography. No detectable residues of any of the selected pesticides were found. Northwest Arkansas is a leader in poultry production. Much of the manure from poultry houses is spread on the sourounding pastures. As this litter decomposes nitrates and phosphates are released. Nitrate and phosphate concentrations were also determined on water from the spring samples. No spring exceeded the EPA's limit of 45 mg/L for nitrate in drinking water. The highest concentration for phosphate in any spring was 1.05 mg/L.

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Keywords: Groundwater/Pesticide/Water Quality/Nitrate/Phosphate

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INTRODUCTION

Agriculture is dependent upon pesticides and fertilizers to increase productivity and efficiency. Concern over recent occurrences of these chemicals in ground water has prompted many to question the safety of using them. Some areas in which pesticides are used in Northwest Arkansas include pastures, right-of-ways, fence rows, and horticultural crops and lawns. Northwest Arkansas is also a leader in poultry production and much chicken manure is spread on pastures surrounding chicken houses as a means of disposal. Since only limited groundwater monitoring efforts for pesticides have been completed, and since no pesticide monitoring has occurred on water from springs in Northwest Arkansas this study was timely and important.

It has been suggested that worldwide a large proportion of human energy is spent weeding of crops (Personal Communication, R.E. Talbert, Univ. of Arkansas, Fayetteville., 1988). Spraying of herbicides to control weeds makes the farmer more efficient, enabling him to produce food at a much lower cost. Insecticides save crops from insect damage which can drastically reduce yields or completely obliterate a crop, costing the farmer thousands of dollars per year.

In general, when used properly, these chemicals are safe and effective. They can be hazardous to humans when ingested or when left in contact with the skin. Little is known about the results of long-term human exposure to low concentrations of farm chemicals; such exposure can take place from drinking water contaminated with pesticides. Half of this nation's residents are dependent upon ground water for drinking water. Rural residents depend upon ground water for 80% of their drinking and livestock water (LeVeen, 1985). Pesticide pollution of ground water could pose a serious health problem to the American public.

A. Purpose and Objectives

The Northwest corner of Arkansas has many springs where groundwater flows to the soil surface. Many of these springs are easily accessible to sampling and are used for drinking water by the rural residents. Since little pesticide monitoring has taken place in Northwest Arkansas to date, it was deemed important that we gathered data on the amount of pesticide, nitrate and phosphate contamination in these springs. This information will allow a baseline to be established to evaluate further monitoring.

Following are the objectives of this study:

1. Sample selected springs in Northwest Arkansas and analyze the sample for selected pesticides, nitrates and phosphates.
2. Re-sample any springs found to be contaminated with pesticides, and gather information about pesticide use and land management.

B. Related Research and Activities

Pollution of groundwater is wide-spread, and the U.S. EPA indicates that presently 17 agricultural chemicals have been detected in 23 states (Hallberg, 1986). As more states instigate monitoring, these totals are expected to rise. Other states have experienced problems with pesticide contamination; among them is Wisconsin. The Central Sands region of this state is an area of porous sandy soils and shallow water tables (McWilliams, 1984). Alachlor and atrazine have been found in the groundwater of the Sand Hills Region of Nebraska, an area also having sandy soils and a shallow water table (Spalding et al. 1980; Brejda et al. 1988). Soils in Northwest Arkansas have relatively small amounts of clay and organic matter, and most studies of pesticide leaching show that as these two soil constituents decrease leaching will increase.

In Sullfolk County New York, aldicarb (2-methyl-2-(methylthio) propionaldehyde-O-(methycarbamoyl)) residues of 7 ppb or greater have been found in 1,121 (13.5 %) of 8,404 wells sampled. Fifty percent of the contaminated wells contained concentrations of aldicarb between 8 and 50 ug/L, 32% had between 31 and 75 ug/L and 16% had levels greater than 16 ug/L. The National Academy of Sciences recommends 7 ug/L as safe upper limit in drinking water (Zaik et al. 1982).

In the Central Sands region of Wisconsin aldicarb residues have been detected in 93 test or domestic wells near potato (Solanum tuberosum, (Urgens D.)) fields where it was used. The U.S. EPA states that these residues were the result of normal agricultural use and not cases of abuse (McWilliams, 1984).

Fourteen wells in the Central Platte region of Nebraska, known to contain high levels of nitrate were sampled in 1980. Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) levels were found in all 14 of the wells with concentrations ranging from 0.06 ug/L to 3.12 ug/L. Alachlor (2-chloro-2′,6′-diethyl-N-(methoxymethyl) acetanilide) levels ranged from 0.01 ug/L to 0.71 ug/L (Spalding et al. 1980).

In the United States 691.6 million hectares (ha) are sprayed with pesticides each year, and 543.4 million hectares are treated with fertilizer (LeVeen, 1985). Although other areas of Arkansas are more intensively farmed than Northwest Arkansas, pesticides are frequently used here.

Little monitoring of groundwater for pesticides has taken place in Northwest Arkansas.

Table 1 lists the pesticides frequently used in Northwest Arkansas for which the springs have been analyzed. Simazine (2-chloro-4,6-bis(ethlamino)-s-triazine) is used in Northwest Arkansas for control of annual grasses and broadleaves in established bermudagrass (*Cynodon dactylion* (L.Persoon)) pastures. Horticultural crops such as grapes (*Vitis labrisca* (L.)), and blackberries (*Rubus canadensis* (L.)) are grown in Northwest Arkansas and diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is popular for controlling grasses and broadleaf weeds in these crops (Berg, 1986). Atrazine and alachlor do not receive as much use in Northwest

Table 1

Chemicals Analyzed for In Spring Study

Common Name	Trade Name	Chemical Name
Atrazine	(Aatrex)	2-chloro-4-(ethylamino)-6-(isopro-pylamino)-s-triazine
Alachlor	(Lasso)	2-chloro-2',6'-diethyl-N-methoxymethyl) acetanilide 2-chloro-N-(2,6 diethyl-phenyl)-N-methoxymethylacetamide)
Diuron	(Karmex)	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Simazine	(Princep)	2-chloro-4,6-bis(ethylamino)-s-triazine
Metolachlor	(Dual)	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide

Arkansas as other compounds but have been found in ground water in other parts of the country (Hallberg, 1986; Cavalier, 1988).

Nitrate and phosphate contamination of ground water in Northwest Arkansas has not been a problem (1989; Brown and Willis, 1984; Steele and Adamski, 1987) however, Northwest Arkansas is a top producer of poultry, and applications of poultry litter are made to agricultural land here. As poultry litter decomposes, nitrates and phosphates can be released (Gilmour et al. 1987). Nitrates have the ability to leach because they are not adsorbed to soil colloids due to their negative charges. This ability to leach causes nitrates to be found in groundwater. Since phosphates as a general rule are adsorbed more readily to the soil they are more immobile and are found in lower concentrations in water.

METHODS AND PROCEDURES

A. Spring Site Descriptions

Spring locations (Figures 1 & 2) were selected with the help of Soil Conservation Service personnel and others familiar with Benton and Washington counties.

The water flowing from these springs finds many uses. Rural residents use spring water for drinking, washing , bathing, to water livestock, to irrigate crops and to supply fresh water to minnow farms and trout hatcheries. Water from some sites flows from caves which house the threatened Ozark cavefish (Amblopsis rasae) and the endangered gray bat (Myotis grisescens).

A description of each site and some of it's characteristics follows.

Benton County Sites (Figure 1).

1B- This site is located in Cave Springs AR. The flow of this spring is approximately 1892 liters (L) (500 gal) per minute. Water from the spring is used for a trout hatchery operation. The cave from which the water flows is home to the cavefish and gray bat.

4B- Site located near Siloam Springs, AR. The flow of here is approximately 378 L per minute. The main use of this water is to supply a pond of approximately 0.5 hectares (ha).

5B- Located near Centerton, AR. This spring flows approximately 946 L per minute, and feeds a small stream 1-2 meters wide.

6B- Located near Centerton, AR. Flow is greater than 3785 L per minute. This spring is the main source of water for the Centerton Fish Hatchery owned by the Arkansas Fish and Game Commission.

8B- Located near Centerton, AR. Flow is greater than 3785 L per minute. This site, known as the Civil War Cave, houses cavefish and gray bats.

12B- Located in Springtown, AR. Flow is greater tha 3785 L per minute. Many residents get their drinking water from this spring.

14B- Located near Avoca, AR. Flow is less than 378 L per minute. Site is located along county road and is used for drinking

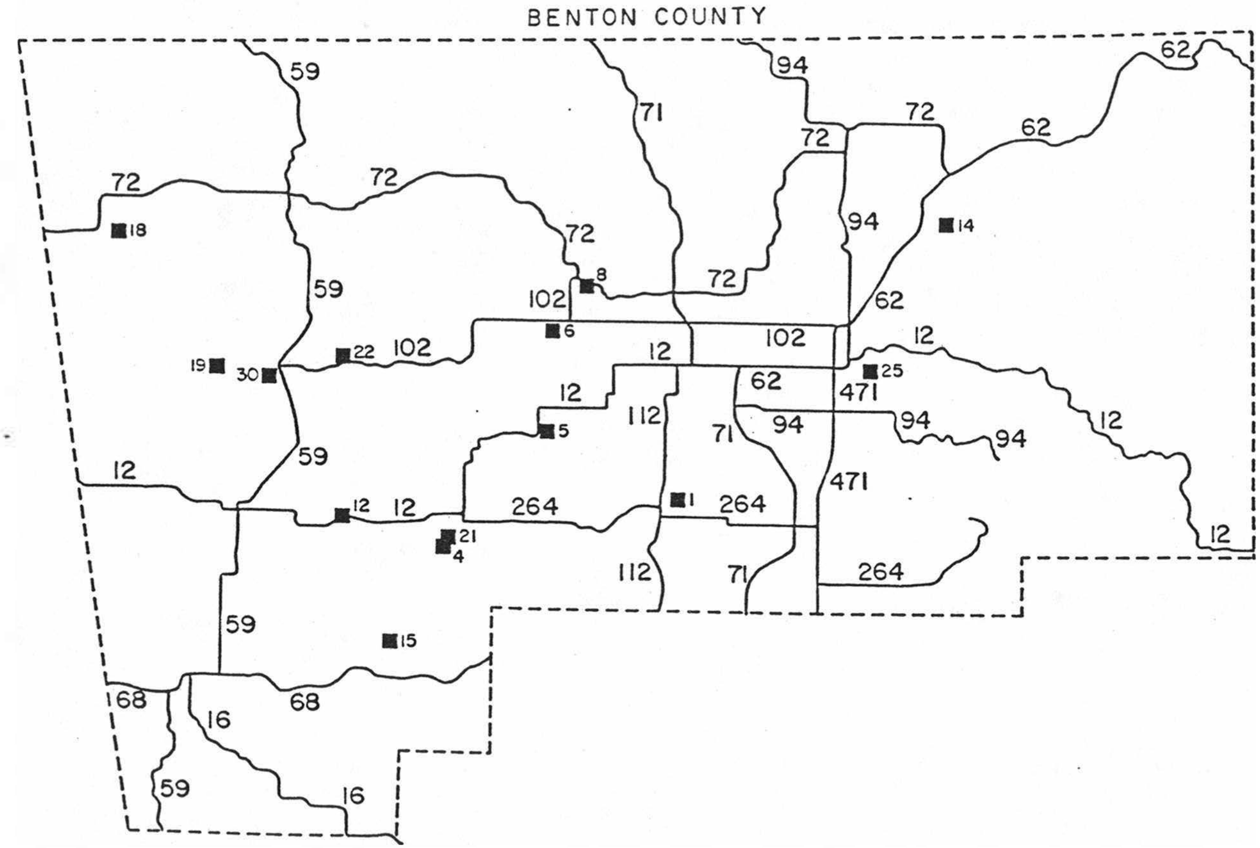

Figure 1

Location (■) of springs sampled in Benton County water.

15B- Located approximately 10 kilometers (km) east of Siloam Springs, AR. Flow is greater than 3785 L per minute. This site houses Ozark cavefish and gray bats.

18B- Located near Maysville, AR. Flow is approximately 3785 L per minute. Spring feeds a pond of approximately 1 ha in size. Owner also uses this water for drinking and to water livestock.

19B- Located near Decatur, AR. Flow is approximatley 37 L per minute.

21B- Located near Highfill, AR. Flow is less tha 37 L per minute.

22B- Located on highway 102 approximately 1 km east of Decatur, AR. Flow is approximately 378 L per minute. Water is used for drinking by local residents.

25B- Located at lake Atlanta near Rodgers, AR. Flow is greater than 7570 L per minute. Spring feeds lake Atlanta which is the main source of water for Rodgers residents.

30B- Located in Decatur, AR. Flow is approximately 1892 L per minute. Water is used for drinking.

Washington County Sites (Figure 2).

18W- Located approximately 4 km east of Fayetteville, AR on Highway 45. Flow is less than 37 L per minute. Water from this spring feeds a pond of approximately 0.5 ha. which is used for livestock water.

20W- Located approximately 2 km north of Fayetteville, AR, on

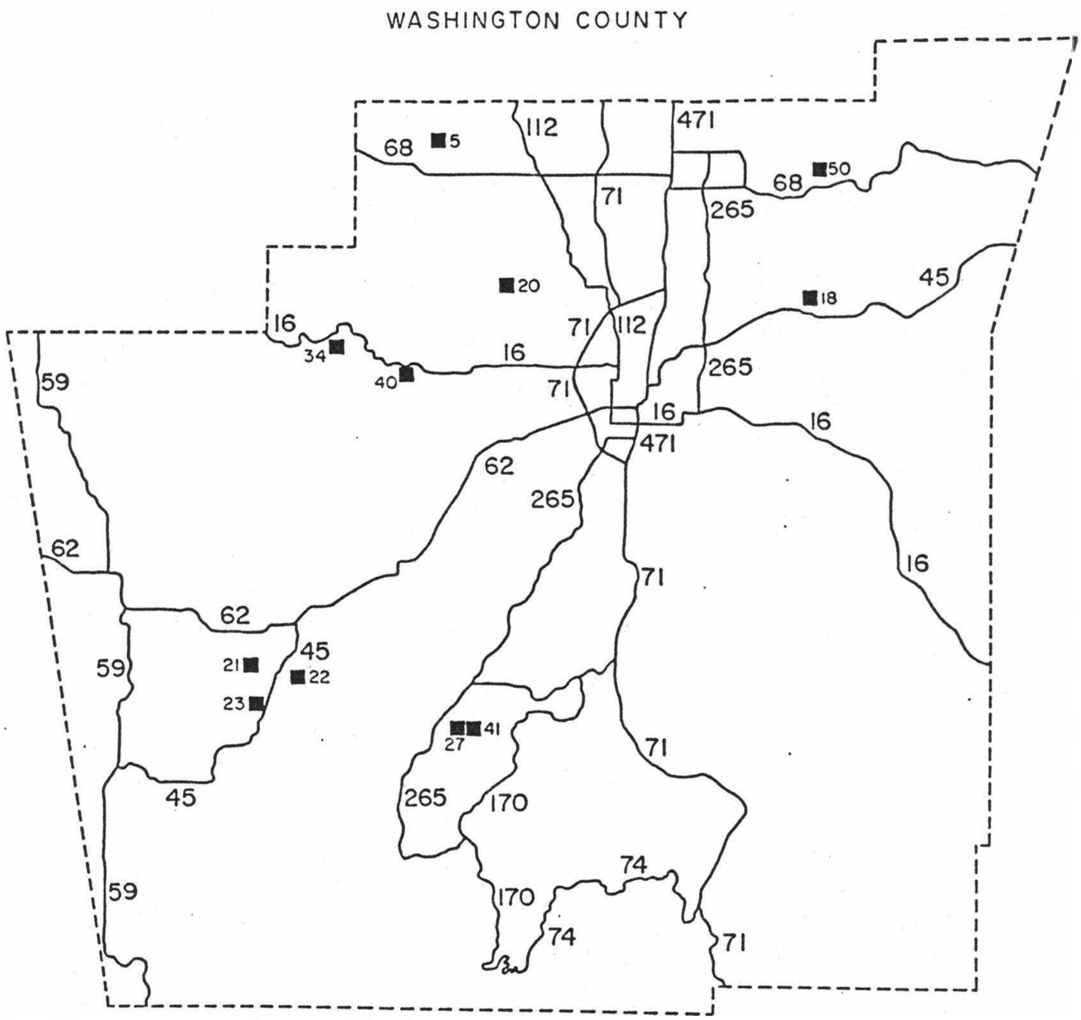

Figure 2

Location (■) of springs sampled in Washington County

Highway 112. Flow is 1892 L per minute. Water from this site is used for drinking by local residents.

21W- Located near Cane Hill, AR. Flow is greater than 3785 L. per minute. Water feeds a pond of approximately 0.25 ha and is also used for drinking and watering livestock.

22W- Located near Cane Hill, AR. Flow is approximately 378 L. per minute. Water from this site feeds a small stream.

23W- Located in Cane Hill, AR behind the Cane Hill College. Flow is approximately 378 L per minute. Water is used by the residents of Cane Hill for drinking.

27W- Located near Praire Grove, AR. Flow is greater tha 3785 L per minute. Water feeds a small creek.

34W- Located approximately 2 km west of Farmingtom, AR. Flow is less than 37.8 L per minute. Water feeds a small pond where livestock water.

40W- Located near Elkhorn, AR. Flow is 1892 L per minute. Water feeds a small pond approximately 0.5 ha.

41W- Located near Praire Grove, AR. Flow is approximately 378 L per minute. Water is used by local residents for drinking.

50W- Located approximately 3 km east of Springdale, AR on Highway 68. Flow is approximately 1892 L per minute. Water feeds two ponds of approximatley 0.5 ha apiece and is used for drinking by local residents. A landfill is located 1 km north and uphill of this site.

51W- Located south of Tontitown, AR approximatley 5 km. on Highway 84. Flow is approximatley 378 L per minute. Water is for drinking by local residents.

B. Sampling

Four one-liter brown glass jars were used to gather samples from each spring. Styrofoam cups were used to scoop up the springwater and pour it into the jar as opposed to submersing the jar into the spring. This method insured that any contamination on the outside of the jar would not get inside. A new cup was used for each site. The jars were labeled and immediately chilled on ice to prevent any degradation of contaminates while they were in transport to the laboratory. Once at the laboratory the samples were stored in a cold room at 1 C for approximately 10 months. At the time the samples were stored a one-liter sub-sample from each site was fortified to give a concentration of 5 ug/L of atrazine, alachlor, metolachlor, diuron, and simazine. Spring water was analyzed for the following water soluble herbicides: atrazine, alachlor, diuron, simazine and metolachlor (Table 1). Since analysis of the samples was time-consuming, there was a delay from the time the samples were collected to when they were analyzed. Use of the fortification procedure allowed us to account for degradation of any of the potential pollutants that might have occured prior to analysis. If degradation of the chemicals was occurring in the stored water, then an equivalent degradation would be shown from analysis of the fortified 5 ug/L sample.

C. <u>Extraction</u>

Extractions were modified from the methods of Cavalier (1988). C-18 extraction was employed in this research for all compounds using a Baker 10 Extraction System with suction. Three milliliter (mL) C-18 cartridges were pre-conditioned by passing two column volumes of methanol (MeOH) through them to remove impurities deposited on them during their production. Following the MeOH, two column volumes of deionized water were passed through the column to remove any MeOH. The C-18 material was not allowed to dry out during these steps. Spring sample aliquots and lab fortified aliquots of 75 ml were then passed through the C-18 columns at a flow rate of one to two drops per second. After passage of the sample aliquots the C-18 material was vacuum dried for 10 minutes to remove any trace amounts of water. Three 0.5 mL aliquots of MeOH were passed through the columns to remove any pesticides that retained the C-18. MeOH was collected in 2 mL volumetric flasks and evaporated using a Nitrogen Evaporation system with a water temperature of 45° C. Samples analyzed by High Performance Liquid Chromatography (HPLC) (atrazine, diuron) were brought up to a total volume of 2 mL with 64% deionized water, 35% acetonitrile, 1% acetic acid, and 3 mM tert-butyl ammonium bromide. Two mL of hexane were added to samples analyized by Gas Chromatography, (alachlor, metolachlor, atrazine, and simazine), and flasks were shaken for one minute. Percent recoveries for the selected pesticides are listed in Table 2.

D. Analysis

Alachlor

Analysis for alachlor was preformed on a Perkin Elmer Sigma I Gas Chromatograph using a electron capture detector. Two columns were used 1) 15 M x 0.53 mm SPB-608 with flow rate of 5 mL per minute and column, inlet, and detector, temperatures of 210, 250, and 400° C, respectively and 2) 15 M x 0.53 mm SPB-5 with flow rate of 5 mL per minute and column, inlet, and detector temperatures of 170, 250 and 400° C, respectively.

Metolachlor

Analysis for metolachlor was also performed on a Perkin Elmer Sigma I Gas Chromatograph using a electron capture detector and two columns 1) 15 M x 0.53 mm SPB-608 with flow rate of 5 ml per minute and column, inlet, and detector, temperatures of 210, 250, and 400° C, respectively, and 2) 6′ x 2 mm id 3% SP-1000 on 100/200 Supelcoport, with column, inlet, and detector temperatures of 140, 250, and 350° C, respectively.

Atrazine and Simazine

Atrazine and simazine analysis was preformed using both gas and liquid chromatography techniques. A Perkin Elmer Sigma I Gas Chromatograph equipped with a nitrogen-phosphorus detector, a 15 M x 0.53 mm Sup-Herb column and a flow rate of 15 ml per minute was

Table 2

Recovery Data for Fortified Samples

Pesticide		Lab Fortified 10 ppb	Field Fortified 5 ppb
Alachlor	$\bar{X}$	8.4	4.0
	SD	1.69	.825
	% Rec	84.0	80.0
Metolachlor	$\bar{X}$	9.26	5.45
	SD	1.20	.735
	% Rec	92.6	109.0
Atrazine	$\bar{X}$	9.85	4.80
	SD	2.30	2.55
	% Rec	98.5	96.0
Simazine	$\bar{X}$	9.83	5.30
	SD	3.50	1.25
	% Rec	98.3	106.0
Diuron	$\bar{X}$	8.72	5.65
	SD	1.64	1.10
	% Rec	87.2	113.0

$\bar{X}$ - Average
SD - Standard Deviation
% Rec - % Recovery

used. Column, inlet and detector temperatures were 170, 250, and 400° C, respectively. A Waters Associates HPLC was used. The mobile phase was 64% deionized water, 35% acetonitrile, 1% acetic acid and 5 Mm tert-butyl ammonium bromide, flowing at 1.5 ml per minute. The column was a C-18 Whatman PartShpere and the detector was an ultra violet type with absorption at 254 nm.

Diuron

Only HPLC methods were used for diuron and are the same as those for atrazine and simazine.

Nitrate and Phosphate Analyses

Nitrate analysis was preformed by the Cadnium Reduction Method. Nitra Vera 5 Nitrate Reagent Powder Pillow was added to a 25 mL aliquot and spring water and shaken vigorously for 1 minute (min). The sample was allowed to sit for 5 min. during which an amber color developed. If nitrate was present, nitrate concentration was then determined by absorbance on a Hach DR 2 spectraphotometer aL 500 nm.

Phosphate analysis was preformed by the Ascorbic Acid method. Phos Ver 3 Phosphate Reagent Powder Pillow was added to 25 mL of spring water and immediately mixed. If phosphate was present a blue color developed. Phosphate concentration was developed. Phosphate concentration was determined by absorbance or a Hach DR 2 spectraphotometer at 700 nm.

PRINCIPAL FINDINGS AND SIGNIFICANCE

A. <u>Pesticide Analyses</u>

Analyses showed no contamination by pesticides for either sampling period for any of the springs. Many factors can be attributed to this finding. Pesticide use in Northwest Arkansas is less intense than in other parts of the state. A majority of the pesticides sprayed on agricultural lands is used on agronomic crops such as soybeans, cotton, and rice, and on horticultural crops. Northwest Arkansas does have a small percentage of each, but cow pastures and woodlands cover a large part of the land here. Forage crops such as alfalfa and fescue are sprayed periodically with pesticides. Applications are usually post emergence and not pre-plant incorporated or pre-emergence. Therefore, less pesticide is applied directly to the soil in Nothwest Arkansas than in other parts of the state. These crops form a much denser canopy of vegetation over the soil at times of application, than do row crops, hence a larger percentage of the pesticide is retained on the plant where it is available for plant uptake, photodecomposition, and volatilization. This situation suggests that a smaller percentage of the sprayed pesticide reaches the soil surface. Pesticide that does reach the soil surface is likely to undergo chemical and microbial decomposition.

B. Nitrate and Phosphate Analysis

The United States Environmental Protection Agency has established a limit of 45 mg/L for nitrate in drinking water. In this study the highest concentration of nitrate in any spring sampled in either sampling period was 33 mg/L (Table 3). Land in Northwest Arkansas receives heavy applications of chicken manure, but nitrate levels in spring water in Northwest Arkansas are below EPA health advisory levels. No health advisory limit exists for phosphate in drinking water.

Plants such as tall fescue can accumulate nitrate levels that are toxic to cattle when heavy applications of nitrogen have been made to pastures and cloudy days are present. Anticipation of this event could prevent livestock producers from applying excessive amounts of chicken manure to their pastures and help explain the safe nitrate levels.

CONCLUSIONS

Agriculture is dependent upon pesticides to reduce human labor inputs and to lower costs of production. Contamination of ground water in the United States is occurring. Since many states have no pesticide monitoring programs, or only limited ones, the extent of this problem has not yet been determined. In areas where groundwater contamination has occurred, data are lacking that will give scientists an approximation of how long the pollutants will persist. In Arkansas, some pesticide monitoring has taken place in the Delta, a region that is intensively farmed. Pesticide monitoring of ground water in Northwest Arkansas has been minimal,so it is imperative that some monitoring is instigated to determine if any contamination has occurred and to establish a base line by which future studies

TABLE 3

Analysis for Nitrates, Phosphates, Calcium and pH.

Spring Site	County	Sampling Period	pH	PO4 mg/L	Ca mg/L	NO3 mg/L
1	Benton	Fall	7.60	0.37	54.40	13.20
1	Benton	Spring	7.44	0.15	49.60	17.60
4	Benton	Fall	7.93	0.15	34.40	13.20
4	Benton	Spring	7.35	0.22	32.00	12.76
5	Benton	Fall	7.66	0.25	43.20	13.64
5	Benton	Spring	7.81	0.14	47.20	13.64
6	Benton	Fall	7.40	0.30	48.80	16.72
6	Benton	Spring	7.15	0.20	8.00	15.84
8	Benton	Fall	7.68	0.36	63.20	22.00
8	Benton	Spring	7.47	0.14	60.00	22.44
12	Benton	Fall	7.74	0.34	35.20	6.60
12	Benton	Spring	7.12	0.25	33.60	7.92
14	Benton	Fall	8.10	0.25	59.20	11.00
14	Benton	Spring	7.45	0.08	56.80	5.28
15	Benton	Fall	7.85	1.00	39.20	11.88
15	Benton	Spring	7.04	0.12	19.20	8.80
18	Benton	Fall	8.00	0.30	52.80	8.80
18	Benton	Spring	7.35	0.18	44.00	7.92
19	Benton	Fall	7.70	0.20	56.00	17.16
19	Benton	Spring	7.37	0.18	53.60	15.40
21	Benton	Fall	7.85	0.21	44.00	4.40
21	Benton	Spring	7.20	0.87	21.60	0.44
22	Benton	Fall	8.07	0.19	48.80	6.60
22	Benton	Spring	7.21	0.10	57.60	8.80
25	Benton	Fall	7.50	0.22	50.40	13.20
25	Benton	Spring	7.30	0.14	57.60	12.76
30	Benton	Fall	7.12	0.18	28.00	16.72
30	Benton	Spring	6.97	0.12	26.40	13.40
40	Benton	Spring	7.19	0.23	42.40	4.84
18	Washington	Fall	7.40	0.39	36.00	3.96
18	Washington	Spring	7.01	0.12	24.00	3.08
20	Washington	Fall	7.63	0.20	68.80	11.00
20	Washington	Spring	7.20	0.18	51.20	12.32
21	Washington	Fall	8.05	0.45	45.60	21.56
21	Washington	Spring	7.42	0.29	47.20	33.00
22	Washington	Fall	7.80	0.44	37.60	8.80
22	Washington	Spring	7.11	0.24	36.80	8.80
23	Washington	Fall	8.20	0.30	64.00	14.08
23	Washington	Spring	7.50	0.35	60.00	12.32

TABLE 3 (Con't)

Analysis for Nitrates, Phosphates, Calcium and pH.

Spring Site	County	Sampling Period	pH	PO4 mg/L	Ca mg/L	NO3 mg/L
27	Washington	Fall	7.58	0.17	16.80	3.08
27	Washington	Spring	6.89	0.13	20.80	2.20
34	Washington	Fall	7.90	0.14	43.20	5.72
34	Washington	Spring	7.20	0.20	25.60	8.36
40	Washington	Fall	7.36	0.28	49.60	4.40
41	Washington	Fall	7.95	0.30	35.20	2.64
41	Washington	Spring	7.12	0.09	28.80	1.76
50	Washington	Fall	7.45	0.29	66.40	8.36
50	Washington	Spring	6.89	0.07	64.80	7.92
51	Washington	Fall	7.76	0.17	47.20	17.16
51	Washington	Spring	7.11	0.17	51.20	17.16

can be judged.

Northwest Arkansas is a leader in poultry production and the litter from these operations is spread on the land. As poultry litter decomposes it can release nitrates and phosphates (Gilmour et al. 1987).

The pesticides that were analyzed in this study were selected on the basis of the relative amount used in Benton and Washington counties as assessed by county agricultural extension agents. Additional pesticide selections were based on their occurrences in ground water in other parts of the country.

None of the selected pesticides were found in the springs sampled in either the fall of 1988 or the spring of 1989. These observations suggest that pesticide use is not currently contributing to groundwater pollution in Benton and Washington counties, and that current land management and pesticide use practices in these two counties are sound.

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