Arkansas Water Resources Center

COMPLETION REPORT: ARKANSAS STATE PESTICIDES IN GROUND WATER MONITORING PROJECT

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1993

Publication No. MSC-136

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MONITORING PROJECT

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Miscellaneous Report No. 136

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AWRC

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Completion Report: Arkansas State Pesticides in Ground Water Monitoring Project.

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I. Executive Summary. The Arkansas State Plant Board (ASPB) has completed a monitoring project in Ashley County, Arkansas. Twenty-nine samples from 23 wells were analyzed for 10 pesticides commonly used in Ashley County. The only detection was Metolachlor, at 0.71 ug/L, in one well. When the well was subsequently resampled no pesticides were detected. Fifteen of the wells were also tested for nitrate. In one of the wells nitrate was measured at 10.3 mg/L. The other wells were all below 0.05 mg/L. Extensive quality assurance (QA) data collected during the project indicate that 94% of the pesticide data meet all EPA requirements for useable data. Though technically suspect, the remaining 6%--due to redundant quality control measures--are considered acceptable.

II. Background. In 1990 EPA released the Phase I report on its National Pesticide Survey. This was the first large scale documentation of the extent of ground water contamination by pesticides. After this survey it was clear that pesticide contamination did exist in almost every state. Spurred by these findings EPA has moved to better protect the nation's ground waters from pesticides. To do this the "Pesticides And Ground-Water Strategy" was developed including the State Management Plan (SMP) concept (EPA, 1991).

Under this strategy certain pesticides would be designated by EPA to be used only in states which had developed state management plans for that chemical. Based on the idea that states could better determine which of its ground-water aquifers were vulnerable to contamination, SMPs taking into account the special characteristics of the state were to be developed by each state with guidance and support from EPA.

Arkansas completed its generic SMP--The Arkansas Agricultural Chemical Ground-Water Management Plan--in the spring of 1992. As one aspect of the plan, the Arkansas State Plant Board began a monitoring program directed at the most vulnerable areas of the state. The first year of the monitoring is now complete. This report contains the results of that program and a discussion of those results.

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III. Vulnerability Assessment. As spelled out in the SMP, monitoring for pesticides in ground water was to be directed initially to the area or areas of the state most likely to be contaminated. Thus prior to implementing a monitoring program, it was first necessary to rank areas of the state on the basis of vulnerability to pesticide contamination. Two components of vulnerability were considered. The first, called sensitivity, was a measure of the likelihood that a waterborne contaminant could reach the aquifer. Using the computer model DRASTIC, sensitivities for all areas of the state were determined. The second component is the actual use of pesticides in the area being examined. For this the Plant Board used estimates of pesticide use for each county developed by the Cooperative Extension Service. Counties high on the sensitivity scale and high on the pesticide use scale were designated as highly vulnerable. Several counties stood out as being relatively high in both categories. Of these Ashley County, in southeast Arkansas, received the highest combined score.

IV. Ashley County. Ashley County lies on the southern border of Arkansas between latitudes 33°0′ and 33°24′ and longitude 91°27′ and 92°9′. One county, Chicot, lies between it and the Mississippi River. The county is roughly rectangular in shape and has an area of 933 square miles. The land surface is flat to gently undulating and ranges in altitude from 60 to 220 feet above sea level. Near its eastern boundary it is traversed from north to south by Bayou Bartholomew. The Saline and Quachita rivers form the western boundary. The central part, about two-thirds of the county area, is a broad terrace. It is bounded on its eastern and western sides by low bluffs. These are closely parallel to the main streams, bordering the flood plain of Bayou Bartholomew on the east and the flood plains of the Saline and Ouachita rivers on the west.

Roughly, the eastern quarter of the county is farm land. This corresponds to everything east of and including the Bayou Bartholomew flood plain. Actually it is that part of the Mississippi River flood plain which extends into Ashley County. Going east toward the Mississippi River and into Chicot County one can notice little change in land use or elevation. Figure 1 shows a map of Ashley County with the main agricultural area delineated.

Three crops constitute most of the agricultural production in Ashley County. On the basis of the amount of land used, cotton with 50,300 acres harvested in 1990 is the largest crop. Of these acres 45,000 were irrigated. Soybeans with 41,000 acres in 1990 is the second largest followed by rice with 20,400 acres. Wheat and oats are also grown but the acreage is small by comparison (Arkansas Agricultural Statistics Survey, 1990). Water for these fields and for a growing number of catfish farms comes from shallow, alluvial aquifers. Drinking water, in the past, was also drawn from shallow wells. Now, however, deeper wells are being drilled for both public and private systems and the availability of "city water"

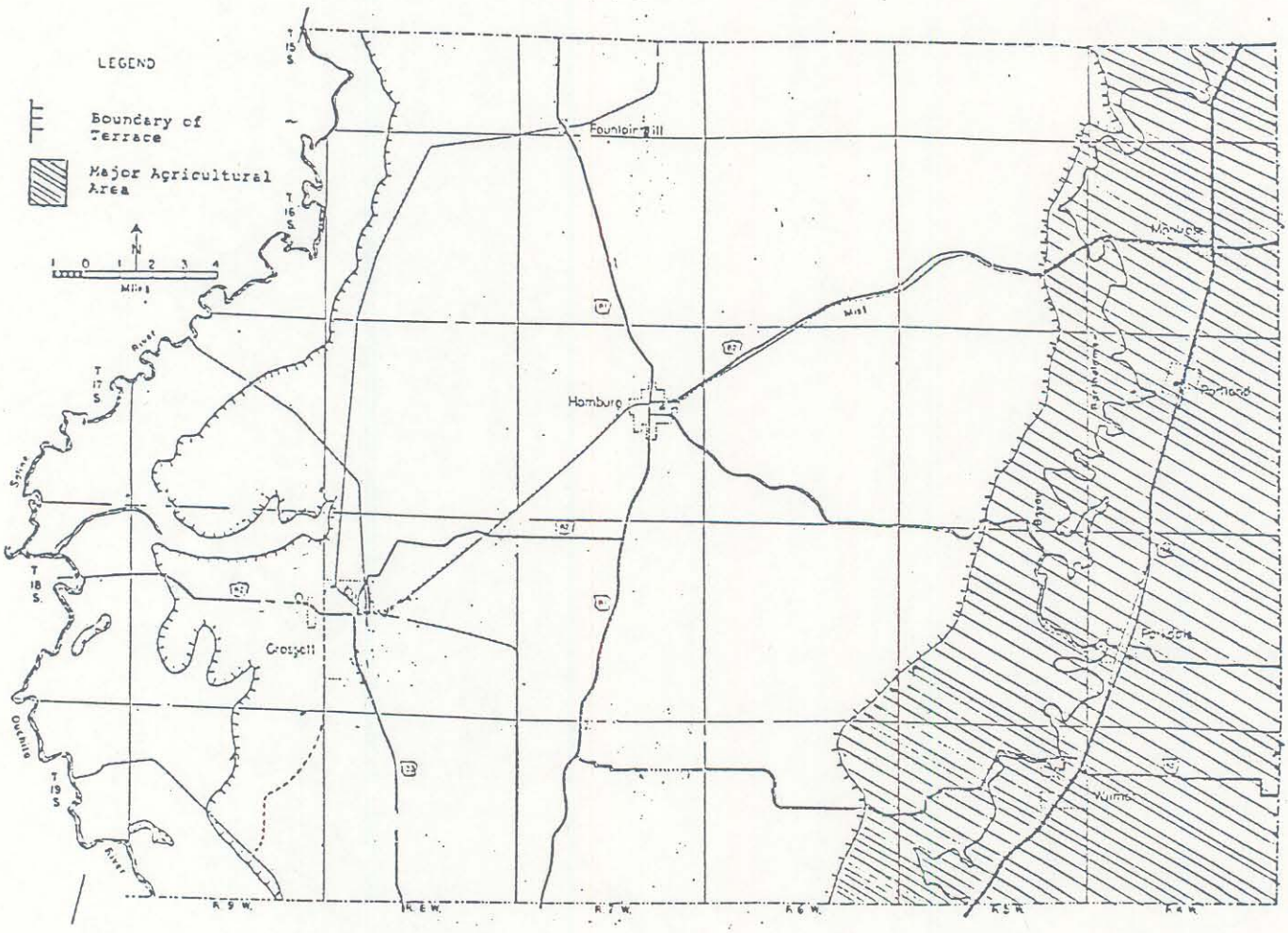

Figure 1. Ashley County. The Major Agricultural Area is Indicated by Hatch Marks (modified from Hewitt, Baker and Billingsley, c. 1950).

is increasing across this area as the small town water systems are extended further and further into the neighboring agricultural fields.

V. Sampling Plan. As specified in the project plan, a total of 20 samples were to be collected in Ashley County. This was to include up to five commercial pesticide mixing\loading sites which were to be sampled twice--before and after purging. The remaining sites were to be spaced evenly across the agricultural area. When sampling began in September, 1992, it was discovered that there were only 3 commercial mixing\loading sites which had their own wells. The remainder are

now on "city water." Of the three, two had been in use just prior to sampling so no "before purging" sample was taken. Later, the well at a large, private mixing\loading site was sampled both before and after purging, making two wells where this before\after approach was used. Including the six samples from these 4 mixing\loading sites, a total of twenty-nine samples were drawn from 23 wells.

Figures 2 and 3 are maps showing the area sampled and the locations of the wells within that area. Sixteen of the wells were in Ashley County while 6 wells from Chicot County and one from Drew County--all near the Ashley County line--were also included. Samples were collected outside of Ashley County because the growing number of households served by rural water systems made it difficult to find shallow wells currently in use. Also the land use patterns and geology are very similar.

As both time and funding were limited, it was necessary to choose a restricted list of pesticides for analysis. Table 1 lists the fifteen most used pesticides in Ashley County which were considered to be potential leachers. Those with an asterisk are the ones analyzed under this project.

Table 1. The Fifteen Most Used Pesticides in Ashley County, AR (USDA Soil Conservation Service and University of Arkansas Cooperative Extension Service).

PESTICIDE	HALF-LIFE (DAYS)	LEACHING POTENTIAL	USE# (LBS)
NORFLURAZON*	45	MEDIUM	57382
FLUOMETURON*	14	M	40689
METOLACHLOR*	20	M	26737
MOLINATE*	21	M	17724
CYANAZINE*	20	M	13496
ALACHLOR*	60	M	11480
ALDICARB	30	LARGE	10422
2,4-D	10	M	9603
BENTAZON	10	M	6116
ATRAZINE*	60	L	5265
METRIBUZIN*	30	L	3328
ACIFLUROFEN	30	M	3090
PROPICONAZOLE	20	M	2968
DIURON*	60	M	2836
OXAMYL	7	L	2550

Estimates based on 1990 crop data.
* Analyzed in this project.

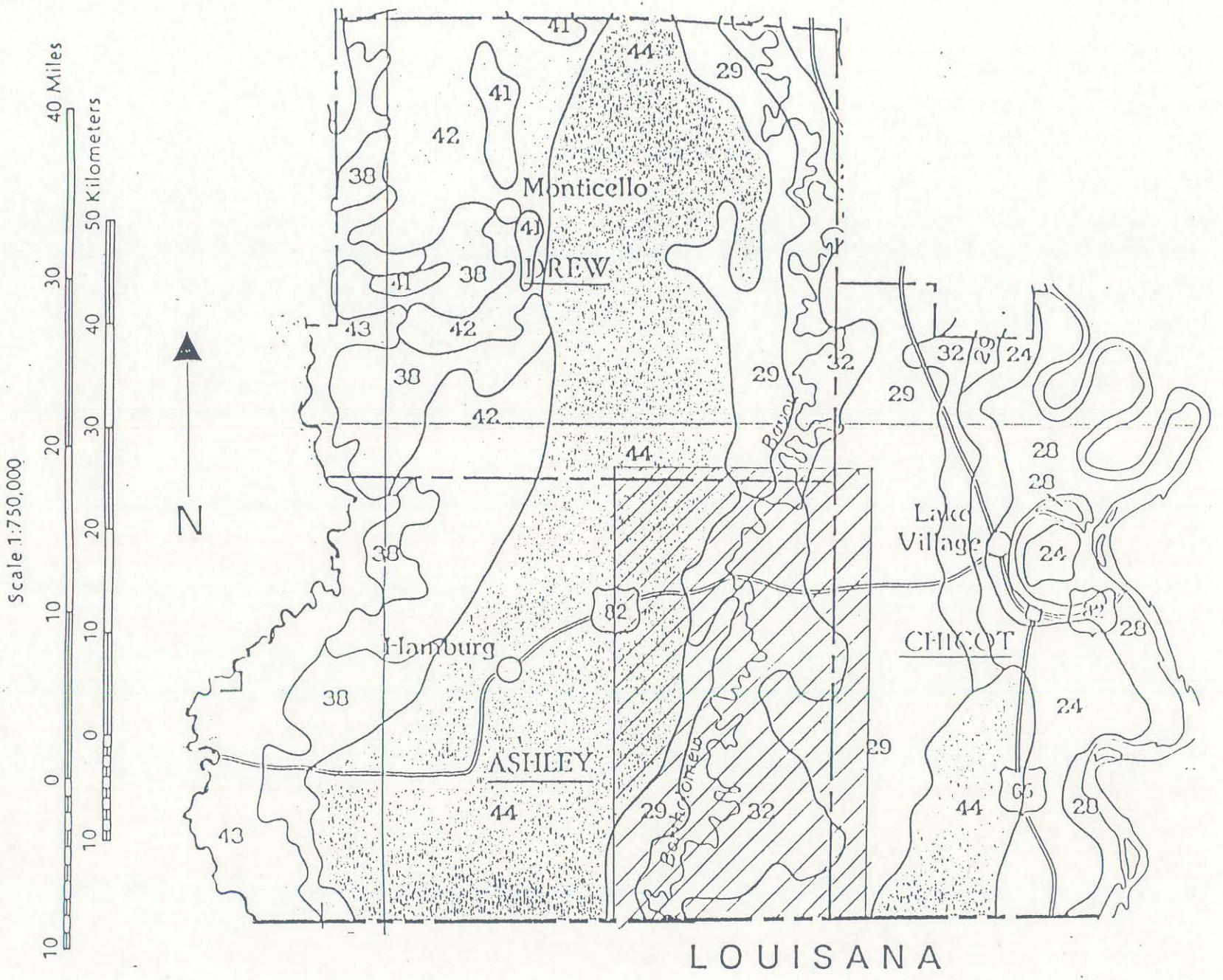

Figure 2. Ashley, Drew, and Chicot Counties. Monitoring Area Indicated by Hatch Marks

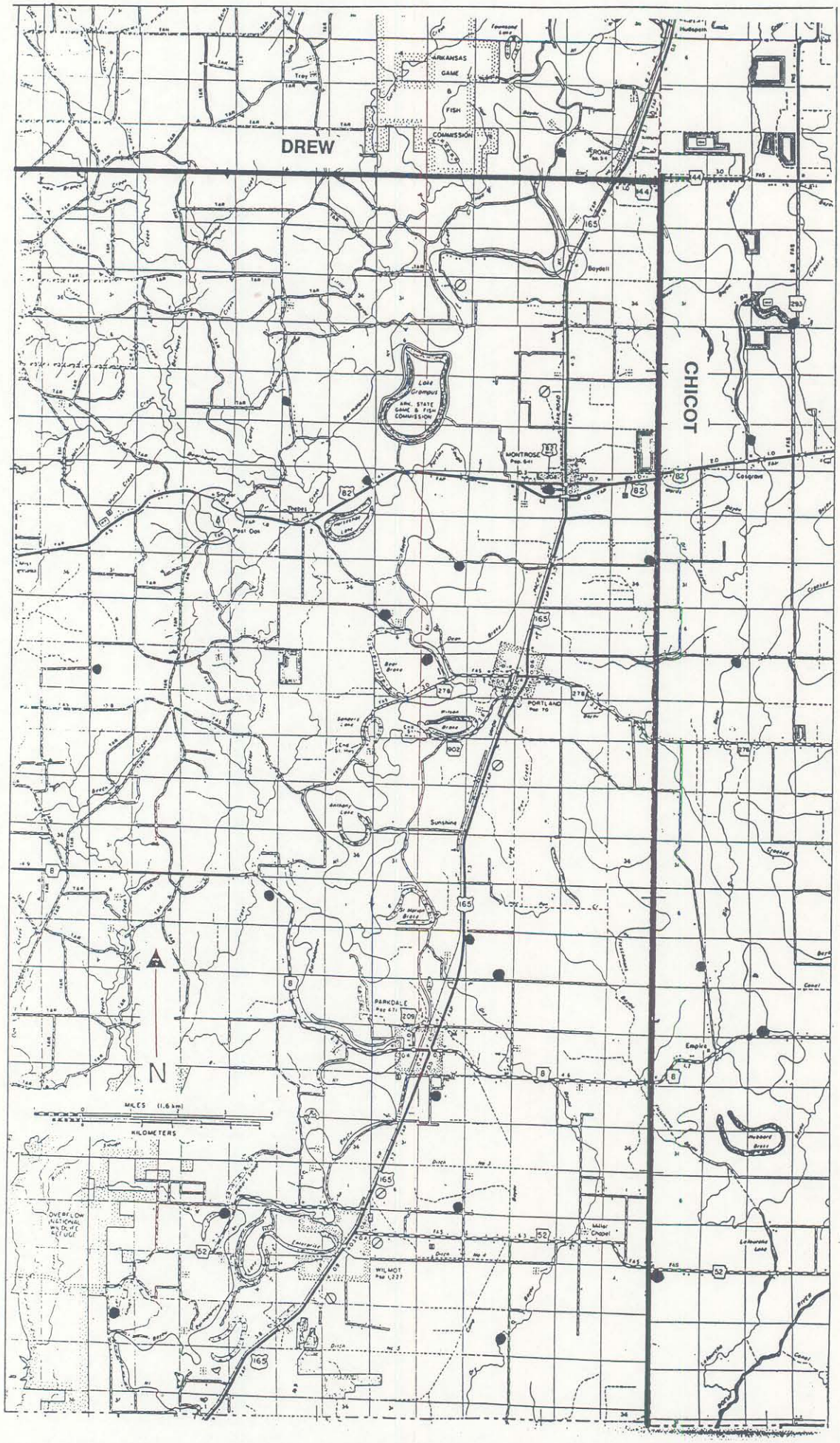

Figure 3. Enlargement of Monitoring Area. Dots Indicate the Locations of the Wells

VI. Methods of Analysis. Two EPA derived analytical methods were used to analyze for the ten pesticides marked in Table 1. These are EPA Method 507 and National Pesticide Survey Method 4. Both were perfected during the National Pesticide Survey. These methods are dealt with at length in the QA Report (see Appendix A). Both use liquid/liquid extraction with methylene chloride. The resulting extract is analyzed by gas chromatograph in EPA 507 and by high performance liquid chromatograph in NPS 4.

Water for nitrate analysis also was collected from fifteen of the wells . While nitrate was not formally included in the project, the results are reported here. The analysis was done on an ion chromatograph.

VII. AWRC Water Quality Laboratory Analytical Results. The detailed results for each well are to be found in the QA Report (Appendix A). One pesticide, metolachlor, 0.71 ug/L, was found in one well. This detection was verified on the gas chromatograph\mass spectrometer at the Arkansas State Plant Board. The well (Drew 1) was resampled one month later at which time no pesticides were detected. Analytical results were all negative for all the other wells.

The analytical results from the pesticide monitoring are supported by the quality assurance data presented in the QA report. For every well and for both analytical methods, fortified samples were made up in the field. Processed through all the analytical steps, each fortified sample was checked for analyte recovery to assure that if pesticides were in a water sample they would be detected. In addition laboratory fortified reagent water and reagent blanks were analyzed along with each batch of samples. For each batch and each method duplicate water was drawn from at least one well to test for consistency of the analysis process. Also for each batch and each method one sample was injected twice to assure consistency of the instrument. Assessment of the QA data showed that 94% of the data points met all the stringent EPA requirements for valid data. Following EPA guidelines, the remaining 6% were reported as suspect, however, the authors believe there is no reason to think that there were any pesticides in these samples which went undetected.

Nitrate results are also reported in the QA Report. All of these were quite low, 0.5 mg/L or less, except for one large reading of 10.3 mg/L.

All analytical results were reported back to the well owners. While the pesticide detection was not considered to have health implications (Health Advisory Level = 100 ug/L), the nitrate result which was over the maximum contaminant level (MCL = 10 mg/L) does. The owner of that well was informed that the nitrate level was over the MCL. Further, it was suggested that he contact his county agent for possible retesting of the well for nitrate. Appendix B contains an example of the form used to report data to owners.

Currently, the analytical results are being put into the appropriate format for entry into the USEPA STORET data storage system. STORET follows the 80-column, punch-card format. Each well sampled is a new station for STORET, and a new station must be created for each well before the data can be entered. Codes and detailed instructions for doing this have been obtained from EPA.

VIII. Discussion of Results. The results present two major questions. What importance does the single metolachlor detection have? and, What are the implications of finding no pesticides (or almost none) in the county which our model indicated should be the one most vulnerable to ground water contamination by pesticides? The discussion is centered on these two questions.

A. Metolachlor Detection. Dual, manufactured by Ciba-Geigy, is the trade name for metolachlor. It is an acetamide compound used as a selective pre-emergence herbicide on soybeans, corn, peanuts and sorghum. It has a relatively short half-life of 20 days. It may be applied by air and sometimes is applied in combination with other pesticides--with atrazine,for example.

The possibility exists that the metolachlor detection was due to a problem in the laboratory which caused the sample to become contaminated. It was not, however, just a case of a false positive as the detection was confirmed on a different machine in a different laboratory using a different EPA method. As regards contamination in the laboratory, three reagent water blanks were extracted along with the samples. Two followed directly after field fortified samples and one followed an unfortified sample. None of the three showed any sign of contamination. On the basis of this information it must be concluded that the sample was not contaminated in the laboratory--that the detection is genuine.

While cotton is the main crop grown by the farmer where the detection occurred, soybeans are also grown occasionally. A son (an adult) of the farm owner reported that Dual had been mixed and applied the year before. This indicates that the potential for the well being contaminated with metolachlor does/did exist, even though the half-life in soil is only 20 days. Research has shown (Cavalier et. al., 1991) that in 15 °C water only 26 to 67% of the metolachlor originally present will have degraded after 18 months. However, the negative result from the retest indicates that the aquifer itself is not, or is no longer, contaminated. As regards aquifer contamination, one can only argue that the first sample may have been taken while a transitory plume of contamination was moving through, and that the plume was gone a month later when resampling took place.

It is more reasonable, perhaps, to think that there was no aquifer contamination; rather, one could postulate an incident--such as backsiphoning--which resulted in contamination at the wellhead. The farmer's son did not report

awareness of any incident, but if such an incident had occurred it might have gone unnoticed. One piece of evidence does exist. During the time between samples, the pressure tank on the well was replaced. At the time of the second sample, it was noted that the pressure tank looked brand new and the owner's son reported that it was newly installed. It is certainly plausible, then, that a backsiphoning incident could have caused the pressure tank or the piping to the hose bib to be contaminated; and, replacement of the pressure tank and adjoining plumbing led to the negative result when the well was resampled. While this is a likely scenario, there is no way to be completely sure.

B. Ground water not contaminated by pesticides. On the basis of the pesticide DRASTIC model and pesticide use estimates, Ashley County was chosen as the first county in Arkansas to be monitored under the SMP. Now that the monitoring is done and only one transient pesticide detection has occurred, one must ask what the implications are concerning the adequacy of our predictive model.

This question has been raised before, particularly in regard to the DRASTIC model. In its Phase II report on the National Pesticide Survey, EPA revealed that the DRASTIC model did not predict contaminated areas very well. EPA concluded "that DRASTIC, as it was used by the Survey, generally had not identified drinking water wells with a greater likelihood of detections. Localized or site-specific assessments appear to be necessary to obtain adequate evaluation of the sensitivity of drinking water wells to contamination (EPA, 1992)." The U.S. General Accounting Office (GAO) has also argued that DRASTIC is not an effective tool for predicting contamination. The point made by GAO is that the data needed to make DRASTIC an effective tool is non-existent. To be effective, they argue, DRASTIC needs input data that reflect small local differences. The data available to most states is aggregated at the state or county level, but what is needed is data aggregated at some sub-county level (GAO, 1992).

Ashley County may be a good example of the points made by GAO. In Arkansas, when the pesticide use estimates were combined with the sensitivity map in the GIS environment, the different levels of sensitivity in the counties were aggregated to get a single score for each county. This score reflected the average degree of sensitivity in each county. Looking at Ashley County on the original sensitivity map, however, shows that the county did not have consistent sensitivity all across the county. As illustrated in figure 4, the central terrace of the county has higher sensitivity to ground water contamination than the land to either the east or west of it. Out of the maximum of 260 possible points, the central terrace received a DRASTIC score of over 173 while the lands on either side were between 150 and 170. While the central terrace has highest sensitivity scores, the major portion of the farm land is mainly to the east of the terrace where sensitivity scores are lower. Because of the method used to combine pesticide use and sensitivity, the vulnerability of ground water in Ashley may have been exaggerated.

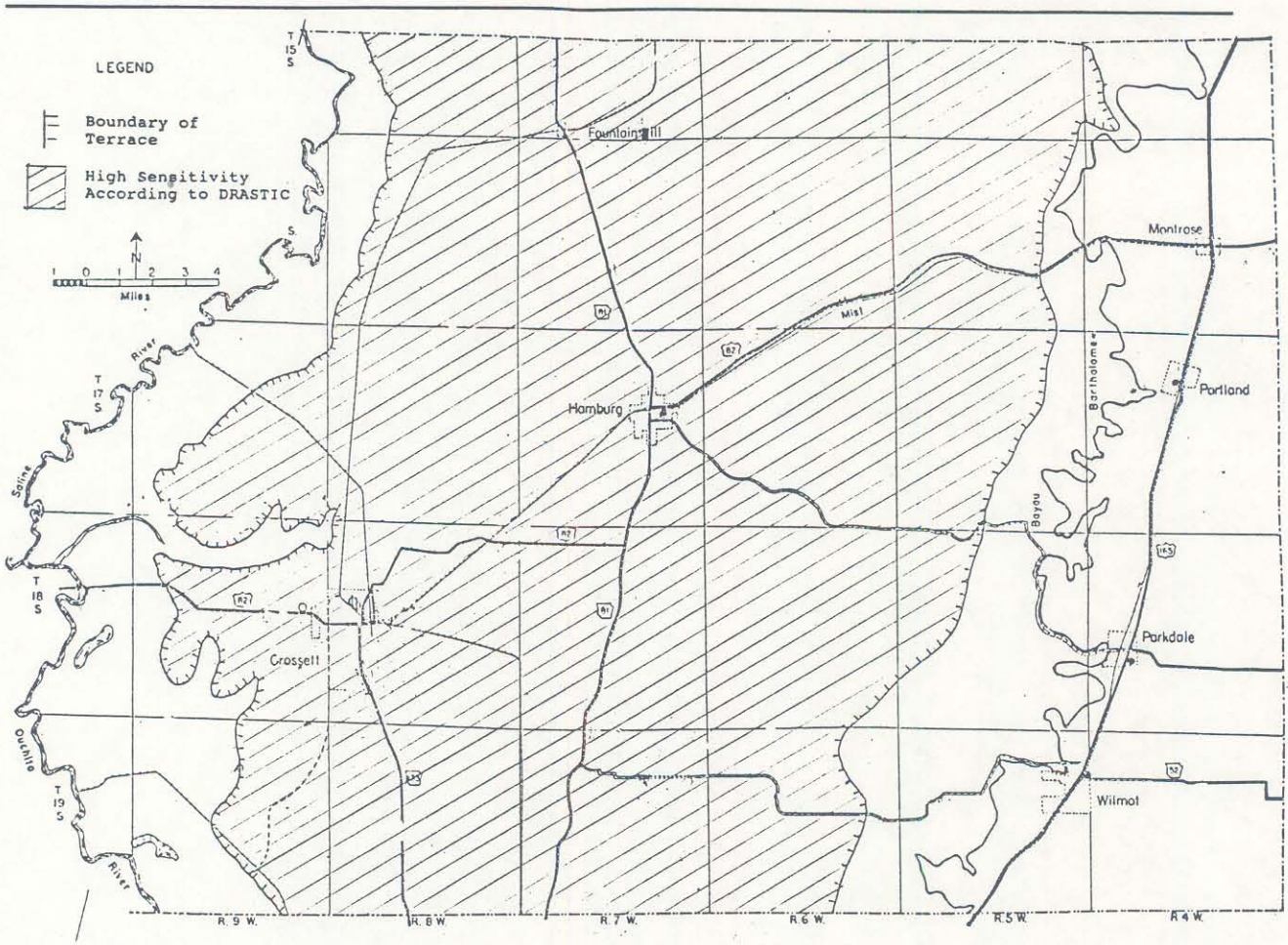

Figure 4. Ashley County with the Area of Highest Sensitivity Highlighted (modified from Hewitt, Baker, and Billingsley, 1949).

There is broad agreement that the DRASTIC model would do a better job of predicting ground water sensitivity if data for the seven factors become available at a finer level of resolution. The Arkansas Soil and Water Conservation Commission (ASWCC) is utilizing grant funds from Section 106 of the Clean Water Act to develop hydrogeologic and water-use data for eastern Arkansas. The U. S. Geological Survey (USGS), Arkansas District has contracted to provide data coverages including the potentiometric surface, recharge rates, areal extent of the aquifer, subcropping geological units, confining unit thickness, and water-use withdrawal points. Thus far these data have been incorporated into DRASTIC only for Woodruff County. The new DRASTIC map for Woodruff County based on this newly available data shows much greater detail and the areas indicated to be highly sensitive do correlate with pesticide detections resulting from previous USGS monitoring (AWSCC, 1992; H. D. Scott, 1992).

Previous comments not withstanding, Ashley County is one of the areas of the state most vulnerable to ground water contamination by pesticides and the lack of pesticide detections should be interpreted as good news. These data preclude widespread pesticide contamination. Our sample is large enough and sufficiently dispersed throughout the agricultural area to reach this conclusion. Isolated wells which we did not test may be contaminated, but there is no widespread pesticide contamination in Ashley County at this time. Whether because of the high soil temperatures causing rapid degradation of the pesticides, or the fine job being done by farmers and commercial applicators in avoiding excessive applications, or the thickness of the clay confining layer which was not considered in the original model; the absence of pesticides in the ground water should be reassuring to the residents of Ashley County.

IX. Acknowledgements. This monitoring program would not have been possible without input from various groups and individuals. This includes the members of the ASPB Liaison Committee and the AWRC Pesticide Committee who were active in the development of the state management plan of which this monitoring project is a part. Appreciation goes in particular to the Arkansas Cooperative Education Service, the USDA Soil Conservation Service, and the Arkansas Soil and Water Conservation Commission for help in the vulnerability assessment.

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APPENDIX A

QUALITY ASSURANCE REPORT:

ARKANSAS STATE

PESTICIDES IN GROUND WATER

MONITORING PROJECT

QUALITY ASSURANCE REPORT: ARKANSAS STATE PESTICIDES IN GROUND WATER MONITORING PROJECT

T. Nichols, P. Vendrell, K. Steele[1]

I. Introduction.

This monitoring program is being carried out by the Arkansas Water Resources Center (AWRC) for the Arkansas State Plant Board (ASPB). A Quality Assurance (QA) Project Plan was submitted to EPA and revised on the basis of comments received. Final approval for the plan was received in August, 1992. Ashley County was selected as the county in which to begin monitoring on the basis of sensitivity to aquifer contamination as measured by Pesticide DRASTIC and pesticide use estimates. Using data aggregated at a county level, Ashley was indicated to be the county most vulnerable to ground water contamination. Sampling began in September, 1993.

Initial investigation of farming patterns in the county revealed that roughly the eastern third of the county is farm land with the remainder being forested. The farming land was targeted for monitoring and it was decided that a few samples would be drawn from neighboring counties, one to the north (Drew) and one to the east (Chicot). It had been expected that wells at five commercial mixing\loading sites would be sampled, but investigation revealed that there were only three such sites utilizing on-site wells. In addition 20 domestic/farmstead wells were also sampled. Of these, 13 were in Ashley County, 1 was just across the county line in Drew County and 6 were close to the county line but actually in Chicot County. Six of the wells were sampled twice.

Table 1 shows the 10 pesticides for which the Ashley samples were analyzed. This includes eight of the 11 pesticides most used in Ashley County. Two methods, EPA Method 507 (Determination of Nitrogen- and Phosphorous-containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorous Detector) and National Pesticide Survey Method 4 (Determination of Pesticides in Ground Water by High Performance Liquid Chromatography with an Ultraviolet Detector), were used to analyze for these 10 chemicals. Laboratory QA information for both of these methods is contained in Appendix A along with the detailed monitoring results. The information from Appendix A is discussed later in this report. Initially the report considers field aspects of quality control.

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Table 1. Pesticide Analytes for Ashley County Monitoring.

Method 507	Method NPS4
Alachlor	Cyanazine
Atrazine	Diuron
Metolachlor	Fluometuron
Metribuzin	Linuron
Molinate	
Norflurazon	

II. Sampling Procedures and Chain of Custody.

A bound field notebook was used to enter pertinent information about the wells sampled. The following items were noted for all the wells (when the information was available):

1. Unique well number
2. Well owner's name and address
3. Date when sample was collected
4. Depth of well
5. Size of Casing
6. Presence or absence of a pad
7. Nearby land uses
8. Unique sample number for each sample collected
9. Analysis to be run on each sample
10. pH
11. temperature
12. conductivity

Other details of well construction, such as screen depth or depth to water surface, were generally not available. Lack of this information made it impossible to predetermine the needed amount of purging. Rather the well was purged until pH, temperature and conductivity stabilized. The samples were then collected from pre-existing taps into clean, dark-glass sampling containers to which 1 mL of preservative (mercuric chloride) had been added in the lab. None of the water collected had been chlorinated.

According to the original plan each sample container was to be tagged or labeled with several pieces of information. This was found to be impractical and each sample bottle was simply given a unique number. The sample bottle number and purpose of the sample were recorded in the field notebook.

At each well at least four samples (approximately 950 mL each) were taken--a sample and a fortified sample for each of the two methods. The water was collected from already-existing wells after purging, except for two mixing\loading-site wells (one commercial and one private) which were sampled both before and after purging. Wells at the other mixing\loading sites were in use just prior to sampling and it was decided not to take pre-purging samples. From 15 of the wells, samples for running nitrate were also taken. Five to eight wells were sampled on each sampling trip. Samples from each of the trips were treated as a batch for extraction and analysis. During each field trip one duplicate sample for each method was also collected.

Samples were immediately placed in ice chests which were kept full of ice. The samples were in the direct possession of the sampler or locked in the trunk of his car until the samples were delivered to the Water Quality Laboratory in Fayetteville. The samples were then placed in a walk-in cooler (4° C) until extracted. All extracts were also kept at 4° C until the analysis was performed. Chain-of-custody documents for all samples are on file at the laboratory.

The samples were collected and analyzed between September 1, 1992 and June 1, 1993. Initial problems in choosing the most vulnerable county and start-up problems with the two EPA methods account for not being able to finish the project by January 1, 1993.

III. Analytical Procedures and Data Reporting.

Analytical results and supporting quality control data are in Appendix A. Prior to analysis on a gas or liquid chromatograph, all the pesticide samples were extracted using liquid\liquid extraction techniques with methylene chloride. The nitrate samples were run on an ion chromatograph.

In brief, there was only one pesticide detection--metolachlor at 0.71 ug/L. The detection was confirmed by the State Plant Board Laboratory using gas chromatograph\mass spectrometer (GC\MS). However, when the well was resampled no detectable amount of metolachlor was found. Fifteen of the wells sampled were also tested for nitrate, with only one high result--10.33 ppm. No pesticides were found in this well.

Further discussion of the quality control aspects of the analyses are broken down by specific methods. EPA Method 507 is presented first followed by information on NPS 4.

A. EPA Method 507. Determination of Nitrogen- and Phosphorous-containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorous Detector.

In as much as infrequent detections were expected, the method was implemented using external standards at two concentrations. A low level standard, 2X, (approximately two times the EPA estimated detection limit) was included in each run to demonstrate ability to detect low concentrations of all analytes. Peak areas of at least 2000 area units were required for each of the analytes to ensure adequate sensitivity. Also included in each run was at least one standard at 10 times EPA's estimated detection level (10X)--the level of fortification used for both field and laboratory spikes. This standard was used to do a single point calibration to measure and compare analyte recoveries from the field and lab spikes. In the case of a detection, the method was recalibrated using the 2x standard to more accurately quantify the concentration of the detection.

For every sample collected a fortified sample (spike) was made up in the field. For every batch of samples (results from one sampling trip) at least one laboratory fortified blank, one laboratory fortified matrix and one reagent water blank were passed through the extraction and analysis procedures along with the fortified and unfortified samples. Recoveries of the analytes were recorded for all fortified samples and surrogate recoveries were recorded for all samples. Also run with each batch, was a laboratory performance solution to measure sensitivity, peak tailing and resolution. Finally, in each batch one sample was injected twice to assess precision.

Initially the analysis was done as specified by EPA except a 2 uL injection was used instead of the recommended 1 uL. Of the QC data presented in Appendix A, those for the first trip (first batch) pertain to this configuration. For the second through the fourth trip a revised method was used, wherein the oven temperature was raised 20 degrees per minute as opposed to the initial specification of four degrees per minute and the injection was limited to 1 uL. This was done to decrease analysis time and improve reproducibility. As the QC statistics for the last three batches indicate, there was no problem resolving the peaks or measuring the areas, in fact recoveries increased under the new regime.

1. First Trip QC. Analyte recoveries from the field fortified samples were acceptable except for molinate where recoveries were in the 40 to 50 percent range. These spikes were run several times with molinate always being low. No reason for this was ever determined. Fortification is done by pipetting 1 mL of the same solution from which the calibration standards were made. If the sample had been fortified with a low concentration all of the analyte concentrations should have been low--not just molinate. If the fortifying solution were incorrectly mixed, both the standards and the spikes would have had low molinate.

This leads to the conclusion that the results for molinate are suspect. However, there was no question of quantifying a molinate detection and the area reported for the molinate (0.56 ug/L) peak in the 2X standard is large enough (during the analysis of the first batch the detector was turned up quite high, increasing sensitivity) to assure that levels of molinate at or above 0.1 ug/L would have been detected.

Consideration of the surrogate recoveries indicates that both times sample p1 was injected the surrogate recoveries were very low (EPA specifies a range from 70 to 130 percent). Other times this batch was run similar results were recorded. While the results for this sample must be reported as suspect, it is most likely that the wrong amount of surrogate was put into the sample during extraction. This water is from a mixing\loading site that was sampled before and after purging. Thus there are a total of four samples from this well--two samples and two fortified samples. The other three, p2, p7, and p9 showed acceptable surrogate recovery, indicating no matrix interference.

In addition to molinate, all the other analytes also had large peak areas for the 2X standard. This would indicate that we would have detected these analytes even at very low concentrations. Table 2 shows the analyte concentrations in the 2X spikes.

Table 2. Analyte Concentrations in the 2X Standard, EPA Method 507.

Analyte	Concentration (ug/L)
Alachlor	0.8
Atrazine	0.4
Metolachlor	2.0
Metribuzin	0.4
Molinate	0.56
Norflurazon	1.0

Several pieces of QC data are missing for this first batch. They are the results for a reagent blank and for laboratory fortified reagent water and sample matrix. While these should be present, and are in the later batches, their absence does not cast doubt on the non-detections.

One other QC problem that occurred with the first batch was a delay in analysis which caused the two week extract holding time to be exceeded. This delay was caused by an inablity to get reproducible results from the GC which in turn was the result of plumbing problems and operator inexperience. By the time

this was all resolved over a month separated extraction and analysis. However, the generally good spike and surrogate recoveries indicate that this was not a serious problem. For reassurance, nonetheless, the second batch of samples included repeat samples from three of the six wells sampled on the first trip and all three showed no detections.

2. Second Trip QC. Analyte recoveries for the second batch were all good except for one low concentration (64%) for norflurazon. Surrogate recoveries were all good with only one slightly below 70%. Both the fortified sample and the fortified reagent water show fine recoveries and the lab blank is all zeroes. Areas for all the analytes in the 2X standard are also acceptable. The percent relative standard deviation (%RSD) is good for both the field and laboratory duplicates. Results of the laboratory performance check are also good.

QC for the second trip is good. There is no reason to question any of the data. One point to note is the smaller areas for the analyte peaks in the 2X standard. This is due to two factors. First, the injection size was reduced from 2 uL to 1 uL between the first and second batches. This resulted in much improved reproducibility, as the larger injection was overloading the column. Also experience had shown that the detector need not be run at such a high energy level. Detector life is much longer when it is run at a lower level. For this reason the detector was turned down-- resulting in smaller peak areas.

3. Third Trip QC. All recoveries were acceptable for this batch except that one fortified reagent water showed a high (155%) surrogate recovery. The rather wide range of surrogate recoveries (74-155%) probably indicates poor consistency in making the 50 uL surrogate injection during the extraction. Analyte peak areas for the 2X standard are larger than they were for batch 2 as the result of a slightly higher setting on the detector.

4. Fourth Trip QC. All of these numbers are good. An effort was made to improve consistency of the surrogate injections and the range was reduced (88-118%). The %RSD for the field duplicate surrogate area comparison is still high--probably due to inconsistent surrogate injections. These very high quality QC data points indicate that the metolachlor detection in this batch is a valid detection, as supported by ASPB's confirmation on GC\MS.

5. Detection Limits for the Method. The EPA has published (EPA, Definition and Procedure for the Determination of the Method Detection Limit, 40 CFR, Ch. 1, Pt. 136, App. B, (7-1-91 Edition)) several alternative methods for computing a method detection limit (MDL) for a particular analytical method running in a particular lab. Briefly, the option used here was to fortify eight reagent water blanks, run them through the extraction and analysis process, and then see how close together the results were for each analyte. The closer together the results for a particular

analyte, the smaller the detection limit. Table 3 shows the detection limits for the six analytes.

Table 3. MDLs for EPA Method 507.

Analyte	MDL (ug/L)
Alachlor	0.034
Atrazine	0.032
Metolachlor	0.141
Metribuzin	0.09
Molinate	0.085
Norflurazon	0.122

The detection limits were determined in June, 1993 just prior to the writing of this report. They reflect the accuracy of our extraction process and analysis techniques after nine months of method development. These limits are all lower than those estimated by EPA (EDLs) when they published the method. The limit for metolachlor, 0.141 ug/L, is of particular interest as it clearly shows that the detection at 0.71 ug/L is well within our ability to quantify.

B. National Pesticide Survery Method 4. Determination of Pesticides in Ground Water by High Performance Liquid Chromatography with an Ultraviolet Detector.

General comments at the beginning of section A. also apply to this method with the exception that the minimum peak area for the 2X standard analytes was set at 500 area units for this method. Table 4 shows the concentrations for the 2X standard for this method. Extractions were done as specified in the method and the analysis procedure on the HPLC was modified only in that a 50 uL injection was used instead of 10 uL. There were no changes in procedure after the initial startup.

Table 4. Analyte Concentrations for the 2X Standard, NPS Method 4.

Analyte	Concentration (ug/L)
Cyanazine	1.2
Diuron	0.2
Fluometuron	0.2
Linuron	0.6

One QC task which was not carried out for this method was evaluation of a Laboratory Performance Check sample with each batch. This was due to the unavailability of the performance check solution which in turn was due to the unavailability of fenamifos sulfoxide one of the constituents. A source for the LPC solution (though uncertified) has now been found and it will be used in the future. However, the results up to now are not compromised by the lack of this check. We have been looking for minimum areas for our analyte peaks in the 2X standard. This insures that we have the needed sensitivity. None of the analyte peaks are so close together on the chromatogram so as to cause a problem resolving them from each other. Peak tailing, the third aspect checked by the LPC, is not a concern because we are using peak areas, not heights, to compute concentrations. In any event, no extreme peak tailing was observed on the sample chromatograms.

1. First Trip QC. Analyte recoveries from the field fortified samples were good with the exception of a low value for linuron in sample p23. The laboratory fortified sample, however, shows very low recoveries. In as much as recovery of the surrogate was high, 97%, and recoveries from all the other samples are good, it seems that the spike itself must have been inaccurate. As noted earlier some pipetting problems have occurred. These kinds of problems occurred frequently enough during the project that new pipetters have now been purchased. Appendix B contains two corrective action reports about pipetters.

The remainder of the QC data fall into the ranges specified by EPA except for the surrogate recovery from sample p23 which was just under 70%. The peak areas from the 2X standard far exceeded the minimum requirement and the %RSDs for the duplicates were very low.

2. Second Trip QC. All of the recoveries are good for this batch except for the anomalous 198% for diuron in the spiked sample, p45. Frequently the software will misdraw the baseline for a peak causing the area reported to be either too small or too large. In this case, however, the analyst physically examined the chromatograph and there seems to be no error. The peak is indeed almost twice as big as for the 10X standard. If this fortified sample had been spiked twice by mistake, all the analyte recoveries would be too big, but this is not the case. Also, a result like this would occur if the sample water contained 1 ppb diuron. Then the addition of the spiked amount to the amount already in the sample water would give about 200% recovery. However, this spike is associated with the non-spiked sample, p48, and examination of the chromatogram for p48 shows an absolutely flat line at the appropriate time for diuron. The anomaly is unexplained.

The problems with the second trip QC are problems of omission. During extraction the analyst forgot to add the surrogate to two samples so it was impossible to determine surrogate recovery for them. Also during analysis no

sample was designated to be injected twice so there is no laboratory duplicate to report.

3. Third Trip QC. Spike recoveries, peak areas of the 2X standard, and %RSDs are all good for this batch. No laboratory fortified sample matrix was analyzed. While it should have been done, the omission is not serious as a sample matrix was fortified in the field for every well that was monitored. The lab fortified matrix serves to determine if there is matrix interference, either in the extraction or the anlysis. This purpose is served by the field fortified samples if there is no degradation of the added chemicals. In this case, the recoveries from the field fortified samples were excellent

4. Fourth Trip QC. While most of the numbers for batch 4 look very good, the analyte recoveries for fortified sample 169 were all very low. This appears to indicate matrix interference or analyte degradation over time. However, the EPA 507 spike for this well had very good recoveries and there is no reason to believe that these analytes would degrade significantly faster than those for method 507 or that matrix interference would affect these analytes and not those for method 507. More likely, this is another pipetting problem. If so it should no longer be a problem as new pipetters have been purchased. Whatever the reason, the analytical results for this method for the Chicot-6 well must be reported as suspect.

5. Detection Limits for the Method. For NPS 4, seven reagent waters were fortified at the 2X level, extracted and analyzed. Table 5 shows the detection limits.

Table 5. Method Detection limits for NPS Method 4.

Analyte	MDL (ug/L)
Diuron	0.083
Fluometuron	0.056
Linuron	0.028

IV. QC Summary.

Though several QC problems have been identified, none of them is such that they would require any data to be discarded. There was only one detection in the data and there is no question about the validity of that data point. The most important QC data relating to the non-detections are the peak areas of the 2X

standards for each run of each method. These are all high enough to assure that small concentrations of pesticides (as low as the detection limits) would have shown up in the analyses. Further, analyte recoveries from the spikes were good enough that there is no reason to believe that pesticides might have degraded prior to extraction.

Table 6 lists those data points the results for which must be reported as suspect according to EPA guidelines. A total of 16 of 290 data points are suspect. This is less than 6%. Thus even if all these points are rejected the data is 94% complete. However, repeating for emphasis, the authors do not think these data points should be rejected. On the basis of the peak areas reported for the 2X standards, they believe the non-detections should be considered valid

Table 6. Data Points Considered Suspect in Light of QC Data.

Well Identification	Suspect Analytes
Ashley 1	Alachlor, Atrazine,Metolachlor, Metribuzin Molinate, Norflurazon
Ashley 1A	Molinate
Ashley 2	Molinate
Ashley 3	Linuron, Molinate
Ashley 4	Molinate
Ashley 5	Molinate
Chicot 6	Cyanazine, Diuron, Linuron, Fluometuron

APPENDIX A
(QA REPORT)

MONITORING RESULTS

AND

SUPPORTING QUALITY ASSURANCE DATA

RESULTS OF PESTICIDE MONITORING IN ASHLEY COUNTY-PAGE 1
(unk = unknown, NC = not collected, ND = not detected)

	1	2	3	4	5	6	7	8
WELL ID:	ASH-1	ASH-1A	ASH-2	ASH-3	ASH-4	ASH-5	ASH-4-2	ASH-6
DATE SAMPLED:	9/1/92	9/2/92	9/2/92	9/2/92	9/2/92	9/2/92	12/7/92	12/7/92
LATITUDE:	33° 14' 19"	33° 14' 19"	33° 06' 29"	33°08'34"	33°14'25"	33°15'55"	33°14'25"	33°15'6"
LONGITUDE:	91° 39' 51"	91° 39' 51"	91° 32' 30"	91°31'03"	91°32'21"	91°31'45"	91°32'21"	91°31'52"
DEPTH OF WELL, ft:	87	87	210	400+	32	90	32	80
pH, standard units:	7.3	7.1	7.5	7.4	7	6.9	6.2	6.8
CONDUCTIVITY (25° C), uS/cm:	531	700	1072	1029	848	480	804	262
TEMPERATURE, ° C :	20.5	20	21.2	22.5	24.5	20	17	18
NITRATE, mg/L:	NC	NC	NC	NC	NC	NC	10.33	0.01
ALACHLOR, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
ATRAZINE,ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
CYANAZINE, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
DIURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
FLUOMETURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
LINURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
METOLACHLOR, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
METRIBUZIN, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
MOLINATE, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
NORFLURAZON, ug/L	ND	ND	ND	ND	ND	ND	ND	ND

RESULTS OF PESTICIDE MONITORING IN ASHLEY COUNTY-PAGE 2
(unk = unknown, NC = not collected, ND = not detected)

	9	10	11	12	13	14	15	16
WELL ID:	ASH-5-2	CHIC-1	ASH-2-2	ASH-7	ASH-8	ASH-10	ASH-11	ASH-12
DATE SAMPLED:	12/7/92	12/8/92	12/8/92	12/8/92	2/7/93	2/7/93	2/7/93	2/7/93
LATITUDE:	33°15'55"	33°7'32"	33°06'29"	33°9"25"	33°2'19"	33°4'9"	33°10'14"	33°4'5"
LONGITUDE:	91°31'45"	91°24'19"	91°32'30"	91°24'16"	91°39'32"	91°36'50"	91°36'5"	91°31'56"
DEPTH OF WELL, ft:	90	hand dug	280	<50	70	80	70	ukn
pH, standard units:	6.3	6.7	7.4	7.1	6.5	7.2	6.9	7.5
CONDUCTIVITY (25° C), uS/cm:	200	3186	796	349	544	572	869	683
TEMPERATURE, ° C :	18	19	19	15	16.5	16	16.5	18
NITRATE, mg/L:	0	0.02	0.05	0	NC	0	0.13	NC
ALACHLOR, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
ATRAZINE,ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
CYANAZINE, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
DIURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
FLUOMETURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
LINURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
METOLACHLOR, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
METRIBUZIN, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
MOLINATE, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
NORFLURAZON, ug/L	ND	ND	ND	ND	ND	ND	ND	ND

RESULTS OF PESTICIDE MONITORING IN ASHLEY COUNTY-PAGE 3
(unk = unknown, NC = not collected, ND = not detected)

	17	18	19	20	21	22	23	24
WELL ID:	ASH-12A	ASH-13	CHIC-2	CHIC-3	CHIC-4	ASH-14	ASH-15	CHIC-5
DATE SAMPLED:	2/7/93	2/7/93	2/7/93	2/7/93	4/22/93	4/22/93	4/22/93	4/22/93
LATITUDE:	33°4'5"	33°1'50"	33°3'12"	33°6'16"	33°14'31"	33°16'20"	33°17'51"	33°20'37"
LONGITUDE:	91°31'56"	91°31'18"	91°27'35"	91°26'22"	91°25'40"	91°27'45"	91°29'54"	91°24'29"
DEPTH OF WELL, ft:	ukn	200+	ukn	45	145	ukn	80	50
pH, standard units:	7.5	7.6	7.3	7.4	8.3	7.8	7.7	7.4
CONDUCTIVITY (25° C), uS/cm:	653	215	388	170	1650	1140	1680	1530
TEMPERATURE, ° C :	18.5	17	18.5	16	16	18	17	17
NITRATE, mg/L:	0	0.02	0.47	0.12	0.41	0.18	0.48	NC
ALACHLOR, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
ATRAZINE,ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
CYANAZINE, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
DIURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
FLUOMETURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
LINURON, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
METOLACHLOR, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
METRIBUZIN, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
MOLINATE, ug/L:	ND	ND	ND	ND	ND	ND	ND	ND
NORFLURAZON, ug/L	ND	ND	ND	ND	ND	ND	ND	ND

RESULTS OF PESTICIDE MONITORING IN ASHLEY COUNTY-PAGE4
(unk = unknown, NC = not collected, ND = not detected)

	25	26	27	28	29
WELL ID:	DREW-1	ASH-16	CHIC-6	ASH-17	DREW-1-2
DATE SAMPLED:	4/22/93	4/22/93	4/22/93	4/23/93	5/20/93
LATITUDE:	33°23'49"	33°19'34"	33°18'41"	33°17'56"	33°23'49"
LONGITUDE:	91°29'44"	91°35'46"	91°25'29"	91°33'38"	91°29'44"
DEPTH OF WELL, ft:	ukn	<50	ukn	60-80	400
pH, standard units:	8.4	7.4	8.3	7.3	8.5
CONDUCTIVITY (25° C), uS/cm:	380	400	730	820	370
TEMPERATURE, ° C :	18	14	20	18	20
NITRATE, mg/L:	0.04	0.03	0.17	0.04	NC
ALACHLOR, ug/L:	ND	ND	ND	ND	ND
ATRAZINE,ug/L:	ND	ND	ND	ND	ND
CYANAZINE, ug/L:	ND	ND	ND	ND	ND
DIURON, ug/L:	ND	ND	ND	ND	ND
FLUOMETURON, ug/L:	ND	ND	ND	ND	ND
LINURON, ug/L:	ND	ND	ND	ND	ND
METOLACHLOR, ug/L:	0.7	ND	ND	ND	ND
METRIBUZIN, ug/L:	ND	ND	ND	ND	ND
MOLINATE, ug/L:	ND	ND	ND	ND	ND
NORFLURAZON, ug/L	ND	ND	ND	ND	ND

ASHLEY - 1ST TRIP

% RECOVERY OF SPIKES

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
(FIELD FORTIFIED SAMPLES)						
p2	43	77	81	72	74	76
p9	57	74	75	73	73	79
p14	53	72	71	67	68	84
p27	44	72	73	82	66	83
p32	42	79	87	78	74	91

% RECOVERY OF SURROGATE

SAMPLE ID	% RECOVERY	SAMPLE ID	% RECOVERY
p1	61	p16	82
p1dup	57	p22	78
p2ffm	88	p25eb	123
p3	87	p26	91
p7	106	p27ffm	116
p9ffm	98	p31	120
p13eb	94	p31dup	133
p14ffm	97	p32ffm	102

PEAK AREAS FOR A 2X* STANDARD

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
2X STAND.	85940	127557	38102	43694	134361	114216

FIELD DUPLICATE-SURROGATE AREA COMPARISON

p1	p3	%RSD
212963	301291	34.30

LBORATORY DUPLICATE-SURROGATE AREA COMPARISON

1ST RUN	2ND RUN	%RSD
212963	196970	7.80

LABORATORY PERFORMANCE CHECK

PGF	RESOLUTION	SIGNAL/NOISE
.7<PGF<1.3	R>.7	>>3

*APPROXIMATELY EDL TIMES 2.

ASHLEY -2ND TRIP

% RECOVERY OF SPIKES

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
(FIELD FORTIFIED SAMPLES)						
42ffm	69	88	91	87	101	67
44ffm	78	100	119	97	114	78
50ffm	74	97	122	90	108	64
60ffm	78	97	117	94	108	77
61ffm	73	87	100	81	97	69
67ffm	69	94	103	83	97	71
(LAB FORTIFIED SAMPLES)						
47lfm	81	103	113	94	114	78
(LAB FORTIFIED REAGENT WATER)						
75lfb	74	73	112	92	110	75

CONCENTRATIONS FOR LAB BLANKS

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
P75	0	0	0	0	0	0

% RECOVERY OF SURROGATE

SAMPLE ID	% RECOVERY
38s	70
39fdup	68
42ffm	93
44ffm	85
46s	86
47lfm	98
50ffm	78
52s	109
55s	105
60ffm	101
61ffm	93
63s	96
67ffm	95
69s	88
69dup	86
74lrb	89
75lfb	73

ASHLEY -2ND TRIP (CONTINUED)

PEAK AREAS FOR A 2X* STANDARD

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
2X STAND.	6190	6443	5055	2421	6434	9482

LABORATORY DUPLICATE-SURROGATE AREA COMPARISON

1ST RUN	2ND RUN	%RSD
64789	63463	2.1

FIELD DUPLICATE-SURROGATE AREA COMPARISON

P38	P39	%RSD
51518	50033	2.9

LABORATORY PERFORMANCE CHECK

PGF	RESOLUTION	SIGNAL/NOISE
0.84	1	>>3

*APPROXIMATELY EDL TIMES 2

EPA METHOD 507

ASHLEY - 3RD TRIP

% RECOVERY OF SPIKES

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
(FIELD FORTIFIED SAMPLES)						
80bffm	93	118	127	119	108	124
86bffm	90	115	123	114	103	119
92bffm	94	113	118	112	102	119
98bffm	95	119	132	118	106	130
103bffm	87	110	121	105	100	117
109bffm	92	109	118	107	97	119
114bffm	81	101	115	99	89	111
119bffm	83	106	123	104	93	116
(LAB FORTIFIED SAMPLES)						
107lfm	91	112	140	108	97	118
(LAB FORTIFIED REAGENT WATER)						
125lfb	90	107	122	105	94	117
131 lfb	87	109	117	106	96	121
133lfb	79	102	98	95	87	110
134lfb	80	105	100	97	90	114

CONCENTRATIONS FOR LAB BLANKS

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
132blrb	0	0	0	0	0	0
124blrb	0	0	0	0	0	0

% RECOVERY OF SURROGATE

SAMPLE ID	% RECOVERY	SAMPLE ID	% RECOVERY
80bffm	114	90bdup87	104
86bffm	76	93bs	106
92bffm	108	99bs	106
98bffm	112	104bs	94
103bffm	113	108beb	111
107lfm	132	110bs	114
109bffm	113	115bs	118
114bffm	104	115bsdup	119
119bffm	111	120bs	111
125lfb	127	132blrb	109
131 lfb	90	133lfb	74
81bs	137	134lfb	155
87bs	123	124blrb	91

ASHLEY-3RD TRIP-CONTINUED

PEAK AREAS FOR A 2X* STANDARD

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
2X STAND.	8213	6916	4165	4116	10425	9592

LABORATORY DUPLICATE-SURROGATE AREA COMPARISON

1ST RUN	2ND RUN	%RSD
78487	79220	0.93

FIELD DUPLICATE-SURROGATE AREA COMPARISON

p87	p90	%RSD
81731	69174	16.64

LABORATORY PERFORMANCE CHECK

PGF	RESOLUTION	SIGNAL/NOISE
0.92	0.92	>>3

* APPROXIMATELY EDL TIMES 2

ASHLEY - 4TH TRIP

% RECOVERY OF SPIKES

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
(FIELD FORTIFIED SAMPLES)						
p140ffm	90	109	105	110	110	112
p145ffm	77	96	96	103	95	105
p151ffm	80	98	94	105	98	111
p155ffm	85	102	95	108	99	113
p160ffm	79	94	94	102	102	106
p164ffm	77	98	101	105	95	113
p170ffm	85	98	93	105	95	109
p175ffm	81	99	97	108	96	110
(LAB FORTIFIED SAMPLES)						
p149lfm	79	97	93	102	94	105
(LAB FORTIFIED REAGENT WATER)						
p180lfb	85	104	109	109	102	119
p181lfb	88	106	105	113	103	119
p184lfb	76	94	102	100	91	108

CONCENTRATIONS FOR LAB BLANKS

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
p179lrb	0	0	0	0	0	0
p182lrb	0	0	0	0	0	0
p183lrb	0	0	0	0	0	0

% RECOVERY OF SURROGATE

SAMPLE ID	% RECOVERY
p140ffm	105
p142s	115
p144fdup142	88
p145ffm	94
p147s	91
p147s	90
p149lfm	97
p151ffm	91
p179lrb	105
p153s	94
p180lfb	105
p155ffm	97
p157s	102

SAMPLE ID	% RECOVERY
P160ffm	98
p162s	102
p181lfb	124
p164ffm	102
p166s	117
p182lrb	92
p170ffm	118
p172s	99
p175ffm	97
p177s	102
p183lrb	103
p184lfb	92

ASHLEY-4TH TRIP-CONTINUED

PEAK AREAS FOR A 2X* STANDARD

SAMPLE ID	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
2X STAND.	13105	17748	6974	7766	18378	15873

FIELD DUPLICATE-SURROGATE AREA COMPARISON

P142	P144	%RSD
60990	46822	26.28

LBORATORY DUPLICATE-SURROGATE AREA COMPARISON

1ST RUN	2ND RUN	%RSD
48334	48009	0.67

LABORATORY PERFORMANCE CHECK

PGF	RESOLUTION	SIGNAL/NOISE
0.81	0.82	>>3

* APPROXIMATELY EDL TIMES 2

SHEET FOR CALCULATING DETECTION LIMITS
EIGHT 2X EXTRACTED LFB
1-Jun-93

	MOLINATE	ATRAZINE	METRIBUZIN	ALACHLOR	METOLACHLOR	NORFLURAZON
1	0.544	0.433	0.335	0.916	1.878	1.239
2	0.510	0.420	0.299	0.931	1.822	1.153
3	0.555	0.423	0.341	0.920	1.880	1.230
4	0.520	0.424	0.330	0.922	1.899	1.144
5	0.552	0.444	0.385	0.952	1.962	1.195
6	0.587	0.432	0.383	0.977	1.947	1.169
7	0.592	0.413	0.376	1.011	1.952	1.180
8	0.549	0.413	0.345	0.975	1.902	1.123

n	8	8	8	8	8	8
mean	0.551	0.425	0.349	0.951	1.905	1.179
theoretical mean	0.560	0.400	0.400	0.800	2.000	1.000
standard deviation	0.029	0.011	0.030	0.034	0.047	0.041
met. det. lim.	0.085	0.032	0.090	0.103	0.141	0.122
EPA est. det. lim.	0.150	0.130	0.150	0.380	0.750	0.500

ASHLEY - 1ST TRIP

NPS METHOD 4

% RECOVERY OF SPIKES

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
(FIELD FORTIFIED SAMPLES)				
p6ffm	85	75	86	78
p11ffm	98	79	85	78
p19ffm	93	69	83	72
p23ffm	97	74	73	65
p23dup	100	74	76	67
p29ffm	110	89	98	91
p34ffm	85	81	79	70
(LAB FORTIFIED SAMPLES)				
p10lfm	44	50	52	48
(LAB FORTIFIED REAGENT WATER)				
lfb	119	98	99	99
p37lfb	132	84	91	84

CONCENTRATIONS FOR LAB BLANKS

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
p35RB	0	0	0	0
p36rb	0	0	0	0

% RECOVERY OF SURROGATE

SAMPLE ID	% RECOVERY
LFB	95
p4S	87
P4DUP	82
P6FFM	100
p10LFM	97
p11FFM	80
p12S	75
p35RB	65
p17s	78
p19ffm	71
p23ffm	67
p23dup	69
p24s	77
p28s	84
p29ffm	73
p30s	79
p33s	75
p34ffm	77
p36rb	84

ASHLEY-1ST TRIP-CONTINUED

PEAK AREAS FOR A 2X* STANDARD

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
2X STAND.	1471	1910	2807	8879

FIELD DUPLICATE-SURROGATE AREA COMPARISON

P28	P30	%RSD
83538	78015	6.84

LABORATORY DUPLICATE-SURROGATE AREA COMPARISON

1ST RUN	2ND RUN	%RSD
86184	81152	6.01

* APPROXIMATELY EDL TIMES 2

ASHLEY - 2ND TRIP

% RECOVERY OF SPIKES

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
(FIELD FORTIFIED SAMPLES)				
P43FFM	80	77	88	93
P45FFM	89	83	198	93
P51FFM	80	70	77	87
P59FFM	96	83	93	96
P62FFM	88	85	98	91
P68FFM	90	90	93	98
(LAB FORTIFIED SAMPLES)				
P66LFM	102	93	99	97
(LAB FORTIFIED REAGENT WATER)				
P76LFB	76	81	89	83

CONCENTRATIONS FOR LAB BLANKS

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
P73LRB	0	0	0	0

% RECOVERY OF SURROGATE

SAMPLE ID	% RECOVERY
P73LRB	83
51FFM	omitted
P53	omitted
P45FFM	93
P48	100
P57	96
P59FFM	96
P62FFM	84
P65	79
P66LFM	90
P68FFM	91
P71	93
P40	71
P41	81
P43FFM	76
P76LFB	74

ASHLEY-2ND TRIP-CONTINUED

PEAK AREAS FOR A 2X* STANDARD

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
2X STAND.	2555	799	2871	9058

FIELD DUPLICATE-SURROGATE AREA COMPARISON

p40	p41	%RSD
65866	75477	13.60

LABORATORY DUPLICATE-SURROGATE AREA COMPARISON

1ST RUN	2ND RUN	%RSD
NA	NA	NA

* APPROXIMATELY EDL TIMES 2

ASHLEY - 3RDTRIP

% RECOVERY OF SPIKES

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
(FIELD FORTIFIED SAMPLES)				
82,FFM	97	118	94	93
88,FFM	93	94	93	89
94,FFM	97	90	96	92
100,FFM	88	88	86	85
105,FFM	82	86	79	83
111,FFM	87	88	92	84
116,FFM	94	96	100	93
121,FFM	94	104	95	92
(LAB FORTIFIED SAMPLES)				
NA				
(LAB FORTIFIED REAGENT WATER)				
129,LFB	101	102	104	98
130,LFB	84	83	86	81

CONCENTRATIONS FOR LAB BLANKS

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
126LRB	0	0	0	0
128LRB	0	0	0	0

% RECOVERY OF SURROGATE

SAMPLE ID	% RECOVERY
P83,SAM	75
82,FFM	72
88,FFM	75
89,S	76
89,REP	75
126.LRB	76
95,S	76
94,FFM	73
96,DUP95	74
100,FFM	70
105,FFM	77
106,S	77
128,LRB	81
111,FFM	70
112,S	70
116,FFM	75
117,S	76
121,FFM	78
122,S	83
129,LFB	83
130,LFB	75

ASHLEY-3RD TRIP-CONTINUED

PEAK AREAS FOR A 2X* STANDARD

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
2X STAND.	2751	1318	2780	8711

FIELD DUPLICATE-SURROGATE AREA COMPARISON

P95	P96	%RSD
82952	80030	3.59

LABORATORY DUPLICATE-SURROGATE AREA COMPARISON

1ST RUN	2ND RUN	%RSD
82086	81688	0.49

* APPROXIMATELY EDL TIMES 2

NPS METHOD 4

ASHLEY - 4TH TRIP

% RECOVERY OF SPIKES

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
(FIELD FORTIFIED SAMPLES)				
141 ffm	93	89	104	91
150 ffm	95	63	99	90
156 ffm	70	67	66	63
159 ffm	96	95	93	91
165 ffm	93	115	100	88
169 ffm	34	30	23	32
174 ffm	95	85	97	89
(LAB FORTIFIED SAMPLES)				
146 lfm	87	72	97	76
(LAB FORTIFIED REAGENT WATER)				
185 lfb	83	84	105	80
188 lfb	90	86	97	84
189 lfb	108	95	90	81

CONCENTRATIONS FOR LAB BLANKS

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
186 lrb	0	0	0	0
187 lrb	0	0	0	0
190 lrb	0	0	0	0

% RECOVERY OF SURROGATE

SAMPLE ID	% RECOVERY
154 dup152	82
163 dup161	84
168 dup167	83
141 ffm	83
150 ffm	78
156 ffm	83
159 ffm	86
165 ffm	88
169 ffm	72
174 ffm	78
185 lfb	77
188 lfb	74
189 lfb	78
146 lfm	69
186 lrb	84
187 lrb	77
190 lrb	73
143 s	76
148 s	78
152 s	81
158 s	71
161 s	81
167 s	80
171 s	78
176 s	73

ASHLEY - 4TH TRIP-CONTINUED

PEAK AREAS FOR A 2X* STANDARD

SAMPLE ID	CYANAZINE	FLUOMETURON	DIURON	LINURON
2X STAND.	1690	1135	3236	9190

FIELD DUPLICATE-SURROGATE RECOVERY COMPARISON

SAMPLE		DUPLICATE		%RSD
152	81.00	154	82.30	1.59
161	80.50	163	84.30	4.61
167	80.20	168	82.60	2.95

LABORATORY (INS) DUPLICATE-SURROGATE RECOVERY COMPARISON

1ST RUN	2ND RUN	%RSD
107240	106229	0.95

* APPROXIMATELY EDL TIMES 2

NPS METHOD 4

SHEET FOR CALCULATING METHOD DETECTION LIMITS
ASHLEY NPS4 DETECTION LIMITS

SAMPLE ID		CYANAZINE	FLUOMETURON	DIURON	LINURON
110	1	0.870	0.163	0.144	0.442
111	2	0.944	0.136	0.140	0.456
112	3	0.906	0.147	0.150	0.436
113	4	0.811	0.102	0.129	0.388
114	5	1.024	0.138	0.116	0.406
115	6	0.957	0.131	0.144	0.440
116	7	0.810	0.144	0.204	0.385
	8				
n		7	7	7	7
mean		0.903	0.137	0.147	0.422
theoretical mean		1.2	0.2	0.2	0.6
standard deviation		0.079	0.019	0.028	0.028
method detection limit		0.236	0.056	0.083	0.085
EPA estimated det. lim.		0.15	0.13	0.15	0.38

APPENDIX B
(QA REPORT)

CORRECTIVE ACTION REPORTS

AWRC WATER QUALITY LABORATORY

MARCH 26, 1993

CORRECTIVE ACTION REPORT

On March 25, 1993 new standards were prepared for EPA method 507. Analysis of the standards showed that the 10X (10 times the EDL) standard was contaminated. The 10X was made again and was again found to be contaminated. Investigation showed that the 1 mL pipeter had gotten solvent inside causing the silicone grease to liquify and run down into the pipet tip during the pipetting process. The 1 mL pipeter was disassembled, cleaned and dried. After reassembly and calibration of the pipeter, a new 10X standard was made up and analyzed. No sign of contamination was found. It was concluded that the problem had been corrected.

Terry Nichols

Research Assistant

Paul Wendtland

AWRC WATER QUALITY LABORATORY

May 18, 1993

CORRECTIVE ACTION REPORT

All the pipetters used on this project are older models. They are fixed volume and seven different ones are necessary to do all the required spikes and standards. We have continued to have small problems with most of these pipeters. The main complaint has been lack of consistency in the volumes pipeted. For this reason it was decided today to purchase two new ajustable-volume pipetters to replace the seven older ones. This should improve consistency of spike and standard recoveries and will require keeping up with fewer pieces of equipment.

Terry Nichols

Terry Nichols

Research Assistant

APPENDIX B

EXAMPLE FORM FOR

REPORTING RESULTS TO LAND OWNERS

PESTICIDES IN GROUND WATER MONITORING RESULTS
ASHLEY COUNTY

NAME: Mr. Gussie Turner

ADDRESS: PO Box 370, Rt 1, Portland, AR

WELL ID: ASH-6

DATE: 12/7/92

LATITUDE: 33°15'6"

LONGITUDE: 91°31'52"

RESULTS:

pH:	6.8	pH units
CONDUCTVITY:	262	micromhos/cm
TEMPERATURE:	18	deg. C.
NITRATE:	0.01	NO3-N, mg/L

PESTICIDES:

ALACHLOR:	NOT DETECTED	mg/L
ATRAZINE:	NOT DETECTED	mg/L
CYANAZINE:	NOT DETECTED	mg/L
DIURON:	NOT DETECTED	mg/L
FLUOMETURON:	NOT DETECTED	mg/L
LINURON:	NOT DETECTED	mg/L
METOLACHLOR:	NOT DETECTED	mg/L
METRIBUZIN:	NOT DETECTED	mg/L
MOLINATE:	NOT DETECTED	mg/L
NORFLURAZON:	NOT DETECTED	mg/L

COMMENTS:

Nitrate Quality Assurance Data

Ashley 1st Trip:

None, nitrate samples were not collected.

Ashley 2nd Trip

Duplicate Analysis:	1st conc.	2nd conc.	%RSD
	10.33	10.41	0.8%

Spike Recovery:	Well ID	%Recovery
	ASH-6	122%

Ashley 3rd Trip

Duplicate Analysis:	1st conc.	2nd conc.	%RSD
	0.01	<0.01	Not Computed

Spike Recovery:	Well ID	%Recovery
	ASH-11	101%

Ashley 4th Trip

Duplicate Analysis:	1st conc.	2nd conc.	%RSD
	0.18	0.18	0%

Spike Recovery:	Well ID	%Recovery
	CHIC-4	87%