

# PESTICIDES AND METABOLITES IN THE SHALLOW GROUNDWATER OF AN EASTERN COASTAL PLAIN WATERSHED

J. M. Novak, D. W. Watts, K. C. Stone, M. H. Johnson, P. G. Hunt

**ABSTRACT.** *The occurrence of pesticides in drinking water sources is a public concern because of potential adverse health effects. We report the results of a three-year study to assess the occurrence of pesticides and metabolites in shallow groundwater in a USDA Water Quality Demonstration Project (WQDP). The Herrings Marsh Run (HMR) watershed is located in the eastern Coastal Plain region of North Carolina and has similar characteristics of other regional agricultural-intensive watersheds. Ninety-two shallow groundwater wells were installed on farms around the watershed in late 1992 and early 1993. Water samples were collected monthly from March 1993 to March 1995 and collected quarterly for the remainder of 1995 and early 1996. The samples (n = 2598) were initially screened for 11 pesticides (8 triazines, 2 chloroacetamides, 1 methylester) using immunoassay techniques. The positive detections (n = 266) were further analyzed by gas chromatographic (GC) and GC/MS (mass spectrometric) procedures. During the study period, we found that the majority (91%) of the wells had no detections for 11 compounds commonly used in the watershed. Pesticides were consistently detected in four wells, but the concentrations were usually below the health advisory limit (HAL). Overall, alachlor was the most frequently detected pesticide. The lack of 11 commonly used pesticides in a high number of wells suggests that these pesticides have had a minimal impact on the quality of HMR shallow groundwater.*

**Keywords.** *Pesticides, Metabolites, Groundwater, Coastal Plain, Wells.*

Pesticide detections in ground and surface waters of the USA have created a concern about the water quality status of drinking water supplies. Due to this concern, the USDA established several Water Quality Demonstration Projects (WQDP) around the USA to evaluate the occurrence of pesticides and nutrients and to evaluate best management practices (BMPs) that affect water quality. In the early 1990s, the Herrings Marsh Run watershed in Duplin County, North Carolina, was selected as a WQDP because, like many other Coastal Plain watersheds, it is under intensive agricultural and animal production (Stone et al., 1995). The watershed is located in the Coastal Plain region of North Carolina which is regarded as having a high potential for groundwater contamination by pesticides (Kellog, 1993). Intrinsic factors such as high rainfall, shallow water tables, sandy soils with a low organic matter content, and high pesticide

usage may contribute to the high contamination potential. Determination of pesticides in the shallow groundwater of the HMR watershed is important because of the heavy reliance of shallow groundwater as a drinking water source and the high frequency of shallow drinking water well depths (Stone et al., 1995).

Pesticide detection in residential and observation wells across the eastern Coastal Plain region of the USA has been reported (Florida Pesticide Review Council, 1993; Koterba et al., 1993; Bruggemann et al., 1995; Maas et al., 1995). In these reports, a limited number of pesticides were monitored in water samples that were collected infrequently during a short time period (<2 yrs). Long-term studies with more frequent samplings may be necessary to better evaluate pesticide movement to water sources, especially if shifting agricultural markets prompt changes in crop production and pesticide usage.

Our pesticide investigation considered the experimental approach of several other Coastal Plain pesticide studies (Koterba et al., 1993; Bruggemann et al., 1995; Maas et al., 1995). We collected more frequent shallow groundwater samples over a three-year period, and we monitored for more pesticides and two triazine metabolites than the previous pesticide investigations. The triazine metabolites were investigated because of the high frequency of detection in ground and surface waters of the USA (Thurman et al., 1992). Our objective was to assess pesticide and metabolite occurrence in shallow groundwater wells in the HMR watershed and relate occurrences to agricultural management practices and well characteristics.

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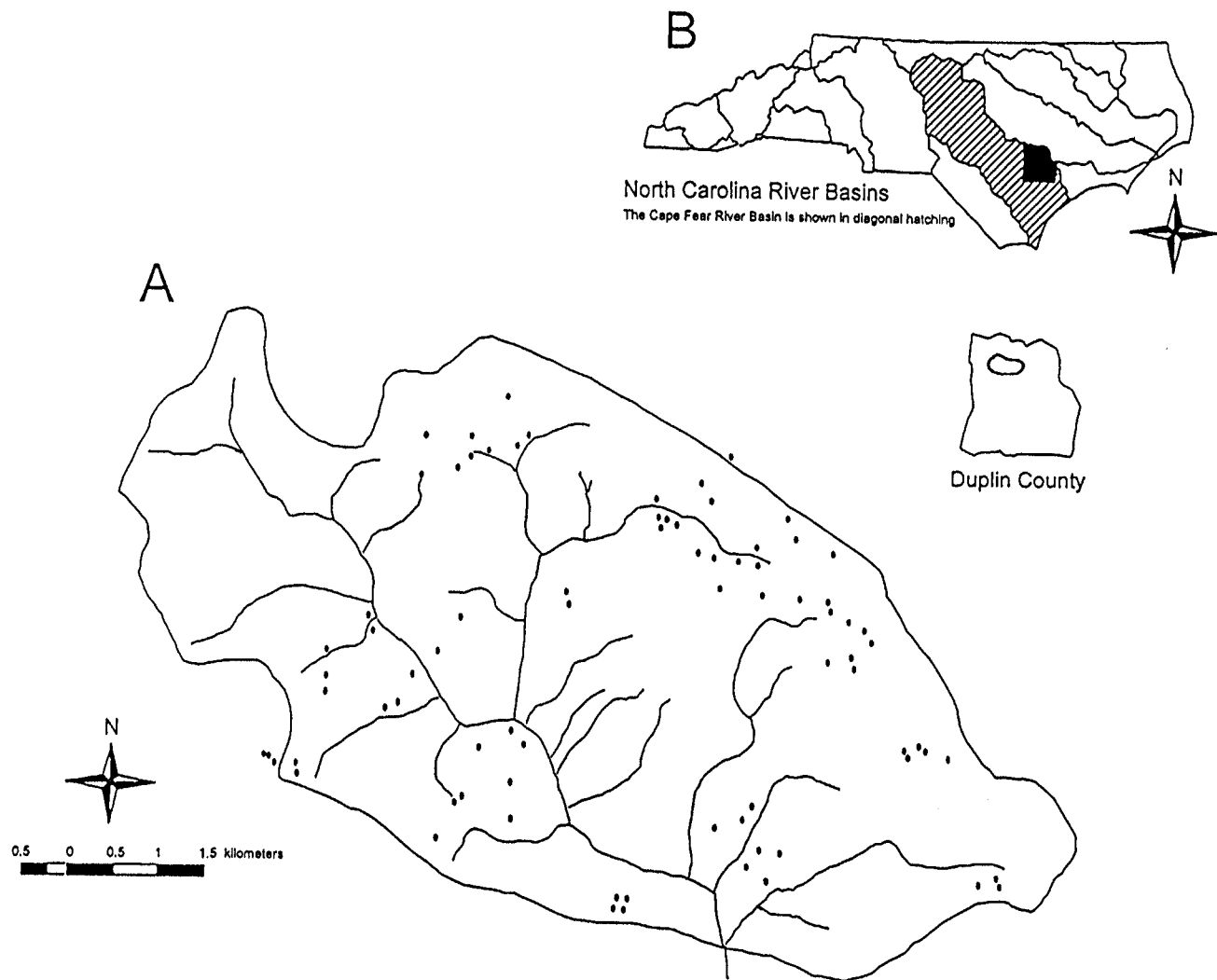


Figure 1—Location of monitoring wells (dots) and stream drainage network (A) in the Herrings Marsh Run watershed located in the Cape Fear River Basin (B) of eastern North Carolina.

## METHODS

### SITE, WELL DESCRIPTION, AND PESTICIDE APPLICATION

The HMR watershed is located in the Cape Fear River Basin of Duplin County, North Carolina (fig. 1), and is part of the Middle Coastal Plain physiographic region. The landscape of the watershed is flat to rolling, with gentle valley slopes truncated by drainage ways and local streams (Daniels et al., 1966). Two principal aquifers, a surficial and a Cretaceous, have been described within the watershed (Coble et al., 1984). Soil parent material in the watershed is marine and fluvial sediments (Daniels et al., 1984) with two dominant soil series—Autryville (loamy, siliceous, thermic *Arenic Paleudult*) and Norfolk (fine-loamy, siliceous, thermic *Typic Paleudult*). Daniels et al. (1984) reported that soils in the Middle Coastal Plain region of North Carolina are frequently underlain (2-5 m deep) by a finer-textured material that is less permeable and can perch groundwater within 1 to 2 m of the surface. Mean annual rainfall recorded at the Warsaw, North Carolina, weather station (approximately 6 km away) for 1993, 1994, and 1995 was 117, 136, and 127 cm, respectively. Approximately 54% of the 2040-ha watershed was farmed with row and truck crops. The Duplin County

Cooperative Extension Service determined that on a watershed basis more than 35 different pesticides were used yearly (C. Fountain, formerly with Duplin County Extension, 1995, personal communication). In addition, pesticide application records were available for approximately 60% of the farmland surrounding the 92 wells. Our selection of pesticides and metabolites to investigate was narrowed to 11 (table 1) by considering actual pesticide usage within the watershed (table 2), in fields around the wells, and by selecting compounds that have been frequently detected in other pesticide investigations in the Coastal Plain region. The application of pesticides within the watershed usually occurred between early March to mid-June.

Ninety-two wells were installed on 21 farm sites in and around the watershed in late 1992 and early 1993 as outlined by Stone et al. (1994). The wells were located on agricultural field borders, near fence rows, or near poultry/swine houses. The well depths in our study ranged from 2.5 to 15.4 m, with a mean depth of 7.11 m (n = 92). All wells were sealed with concrete and were protected with a lockable steel cover.

**Table 1. Pesticides and select metabolites monitored in ARS well samples**

Compound	Abbreviation	Chemical Name
Alachlor	ALA	2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide
Ametryn	AMET	N-ethyl-N'-(1-methylethyl)-6-methylthio-1,3,5-triazine-2,4-diamine
Atrazine	ATR	6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine
Cyanazine	CYAN	2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methyl propanenitrile
Deethylatrazine	DEA	2-chloro-4-amino-6-isopropylamino-1,3,5-triazine
Deisopropylatrazine	DIA	2-chloro-4-ethylamino-6-amino-1,3,5-triazine
Metolachlor	METOL	N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-alanine methyl ester
Metribuzin	METRI	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide
Prometon	PMT	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)on
Prometryn	PRYN	6-methoxy-N, N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine
Terbutylazine	TBA	N, N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
		6-chloro-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine

**Table 2. Estimated quantities of select pesticides applied in the HMR watershed from 1990 to 1995\***

Pesticide†	1990	1991	1992	1993‡	1994	1995
	(kg - a.i.)					
ALA	925	925	940	-	579	579
AMET	338	388	487	-	372	372
ATR	574	574	630	-	394	394
CYAN	104	104	33	-	70	70
METAL	62	62	52	-	46	46
METOL	817	817	835	-	669	669

\* Estimates provided by the North Carolina Cooperative Extension Service.

† Abbreviations defined in table 1.

‡ No data available.

#### ASSESSMENT OF BEST MANAGEMENT PRACTICES

Information from cooperators and pesticide management plans was gathered to determine the types of pesticide BMPs used within the HMR watershed. Identification of pesticide BMPs employed around each well was not possible due to an incomplete applicator survey. However, we were able to discern that at least one type of BMP is used by the pesticide applicators (C. Fountain, 1995, personal communication). These BMPs include both structural and non-structural practices. Examples of structural practices include creation of structures that reduce soil erosion and water runoff, sediment traps, concrete mixing pads, containment of rinsate by concrete dikes, and storage of rinsate in leak-proof containers. Examples of non-structural BMPs used by applicators include proper application rates, avoiding spills, proper rinsing and disposal of pesticide jugs, maintaining proper spray boundaries between fields and streams, minimizing drift, and tillage practices.

#### SAMPLE COLLECTION, PESTICIDE EXTRACTION, AND ANALYSES

Well samples were collected on a monthly basis from March 1993 to March 1995 and then quarterly until March 1996. Well sampling frequency in 1996 was reduced because of scarce pesticide detections in 1994 and 1995. Prior to sampling, the water table depth in each well was recorded using a water level meter (Testwell Instr., Georgetown, Ontario). One well volume was removed prior to sample collection in order to obtain a representative groundwater sample (Lee and Jones, 1983). Each well sample was collected in a 250-mL amber bottle, stored on ice, and transported back to the laboratory. Samples were refrigerated at 4°C for 24 to 48 h until immunoassay analyses commenced.

All samples (n = 2598) were initially screened for the 11 compounds of interest (table 1) using ALA, ATR, and METOL immunoassay test kits from Ohmicron (Newton, Pa.). These three test kits will detect the three parent compounds (ALA, ATR, and METOL) and will also cross-react with the other eight compounds of interest. Because the immunoassay test kits will react with the parent and cross-react with the eight other compounds, a positive immunoassay response ( $\geq 0.2 \mu\text{g L}^{-1}$ ) was interpreted to indicate the presence of the 8 triazines, 2 chloroacetamides, and 1 methylester (table 1). Only predicted immunoassay pesticide concentrations of  $\geq 0.2 \mu\text{g L}^{-1}$  were accepted because using very dilute spiked solutions, we determined the minimum detection limit (MDL) to be  $\geq 0.2 \mu\text{g L}^{-1}$ . Samples with a negative immunoassay detection were regarded as having pesticide concentrations below the detectable range for the 11 pesticides of interest and were discarded.

The samples (n = 266) with a positive immunoassay detection were extracted for 11 compounds of interest using solid-phase extraction (SPE) and GC techniques as outlined by Novak and Watts (1996). Approximately 50 g of water were extracted using a Waters tC<sub>18</sub> SEP-PAK (Waters Co., Milford, Mass.) SPE cartridge and were concentrated to approximately 1 mL. The extracts were GC analyzed for 11 compounds (table 1). A Varian 3600 CX GC (Walnut Creek, Calif.) fitted with a Varian nitrogen/phosphorus detector and a Restek (Bellefonte, Pa.) Rtx-35 column was used to chromatograph the compounds. Details of column conditions, gas flows, injection volumes, and MDLs are provided by Novak and Watts (1996). Method recovery efficiencies for the nine pesticides were found to range from 85 to 95%, while the DIA and DEA metabolites recovery was 19 and 60%, respectively. The concentration of DEA was corrected for 60% recovery when used to calculate the DAR [(DEA mol/L)/(ATR mol/L)]ratio since the values were compared to other corrected literature values. Since the remaining pesticide recoveries were usually > 85% on average, no correction for incomplete recovery was deemed necessary.

Pesticide confirmation using GC/MS techniques was performed on samples (n = 266 or 10% of total collected) with a positive immunoassay detection (limited to predicted concentrations of  $\geq 0.2 \mu\text{g L}^{-1}$ ) by the USDA-ARS National Soil Tilth Laboratory (Ames, Iowa) and by Dr. Richard McLaughlin at the North Carolina State University, Raleigh, N.C. The samples were sent to two collaborators because the GC/MS confirmation procedure of Pfeiffer (1992) only confirmed for the presence of ALA,

ATR, METOL, and METRIB. These four herbicides (ALA, ATR, METOL, and METRIB) were extracted using SPE, and conformational analyses was performed on the extracts using a Hewlett-Packard (HP) 5890 Series II GC (Palo Alto, Calif.) equipped with a HP 5970B mass selective detector (MSD) operating in the selective ion mode. The MDL of the four herbicides was  $0.2 \mu\text{g L}^{-1}$  on an unextracted basis. The GC/MS procedure of Dr. Rich McLaughlin routinely extracts for AMET, CYAN, DEA, DIA, METAL, PMT, and PRYN using a HP Model G1800A GC equipped with a HP-5 (cross-linked, 5% phenyl methyl silicon) capillary column and an Electron Ionization Detector (GCD). The GCD is a HP5890 Series II GC with an electronic pressure control coupled with an electron MSD. The MDL for the six pesticides confirmed by this procedure was  $0.2 \mu\text{g L}^{-1}$  on an unextracted basis.

#### FIELD AND LABORATORY QUALITY ASSURANCE/QUALITY CONTROL PROTOCOLS

All pesticide collection bottles were cleansed by washing with SP brand Micro cleaner (Baxter Corp., McGaw Park, Ill.), triple-rinsing with deionized water, and a final rinse with pesticide grade MeOH. During well evacuation, each bottle and cap was rinsed three times with groundwater effluent prior to final sample collection. Laboratory GC standards and MDL spikes were remade monthly, and solvents were tested monthly for pesticide contamination. During each batch extraction, SPE cartridges were tested for the presence of contaminants and for pesticide extraction efficiency using a  $100 \mu\text{g L}^{-1}$  GC spiking solution. Reproducibility of extraction efficiency was verified monthly by repeated ( $n = 3$ ) sample extractions, and the predicted concentrations of pesticides and metabolites generally agreed to within 10% (relative variation). The spike MDL ( $0$  to  $20 \mu\text{g L}^{-1}$ ) tests for all pesticides were also verified monthly.

#### STATISTICAL METHODS FOR PESTICIDE DETECTION

Our study revealed that continuous pesticide detection occurred in only a few monitoring wells; therefore, statistical analyses for pesticide detections trends were limited to these few wells. Linear regression analysis was used to identify pesticide concentration trends vs. time and the slopes of these regression lines were tested for significance at the 0.05 level of rejection using SigmaStat software (SigmaStat Corp., San Rafael, Calif.). Nonparametric (Kruskal-Wallis one-way analysis of variance on ranks) was used to determine if the DAR ratios for well B represent chance occurrence (null hypothesis,  $H_0$ ) or real differences (alternate hypothesis,  $H_a$ ) against period of sampling. If  $P < 0.05$ ,  $H_0$  is considered false which implies that the DAR ratios are not due to chance but are due to biogeochemical processes influencing ATR and DEA concentrations. A Pearson Product Moment Correlation was used to explore possible relationships between monthly well pesticide detections vs. monthly rainfall amounts and water table depths because it was speculated that migration of pesticides would be related to soil percolation of rainfall and hydrologic water flow. Correlation was also used to identify possible effects of well physical features (i.e., well depth, distance of well from field boundaries) with the overall mean pesticide concentration.

Seasonal patterns for monthly GC pesticide detection were analyzed using a Chi-square test of homogeneity of proportions (SAS, 1996). For this analyses, seasonal patterns for monthly pesticide detections versus non-detections were arbitrarily grouped into spring (March, April, May), summer (June, July, August), fall (September, October, November), and winter (December, January, February).

## RESULTS AND DISCUSSION

### INITIAL WELL SAMPLING, PESTICIDE DETECTION, AND CONFIRMATION

Immunoassay was chosen to sort the samples into groups with a positive/negative pesticide detection because the technique has been found to be a good initial screening tool (Thurman et al., 1990; 1996). This merit is due to the immunoassay test kits reacting with the parent pesticides ATR, ALA, and METOL as well as cross-reacting with the other eight structurally similar compounds of interest (Rubio et al., 1991; Aga et al., 1994; Watts and Novak, 1997). In addition, the immunoassay procedure is useful for initial sample pesticide screening because of the lack of false negative detections (Gruessner et al., 1995). Because of the cross-reactivity issue, a positive immunoassay response with one of the three test kits was interpreted to mean that the sample possibly contained either 8 triazines, 2 chloroacetamides, and 1 methylester.

The immunoassay screening revealed that only 266 samples with a positive detection out of 2,598 collected had a concentration ( $\geq 0.2 \mu\text{g L}^{-1}$ ) that was suitable for GC and GC/MS analyses. The GC and GC/MS analyses revealed the presence of ALA, ATR, DEA, METRIB, and PMT in only 131 samples. This means that of the 266 immunoassay positive detections, we were able to explain approximately 50% of the detections as due to reaction with the parent pesticide or to cross-reaction with one of the other compounds of interest. The lack of pesticide confirmation in many of the remaining samples was probably due to chromatographic analytical limitations or to the presence of unquantified cross-reactive metabolites. For instance, ALA false positive immunoassay detections have been attributed to cross-reaction with the metabolite ethane sulfonic acid (Aga et al., 1994; Richards et al., 1996).

### ADDITIONAL GC PESTICIDE ANALYSES

Over the three years of our study (1993-1996), 11 commonly used pesticides in the HMR watershed were not detected in 86 of the 92 wells. Only four of 92 wells (4%) consistently contained measurable concentrations of the compounds of interest. In these four wells, GC and GC/MS analyses showed that only ALA, ATR, PMT, and DEA were detected (table 3). In order of ranking, ALA was the most frequently detected pesticide, followed by ATR, PMT, and DEA. Two samples contained low concentrations ( $< 1 \mu\text{g L}^{-1}$ ) of ALA and METRIB in two different wells with no consistent seasonal detection trends. The detection of ATR and ALA is in agreement with Koterba et al. (1993) and Bruggeman et al. (1995) who reported ATR and ALA detections in Coastal Plain groundwater of the Delmarva Peninsula (Delaware, Maryland, and Virginia) and in some Coastal Plain wells in

**Table 3. Monthly pesticide detections in wells using combination of GC and GC/MS analyses\***

Sampling Period	No. Wells		Pesticide‡			
	Immunoassay Screened	No. Wells Extracted†	ALA	ATR	DEA	PMT
<b>1993</b>						
Mar	92	-	-	-	-	-
Apr	92	12	3	2	-	-
May	92	6	2	1	-	-
Jun	92	10	4	1	-	-
Jul	92	7	3	0	-	-
Aug	91	11	3	1	-	-
Sep	91	11	2	1	-	-
Oct	91	7	2	1	-	-
Nov	92	14	2	0	-	-
Dec	92	13	2	1	0	1
<b>1994</b>						
Jan	92	11	3	0	0	1
Feb	92	12	2	1	1	1
Mar	92	7	2	1	1	1
Apr	92	12	2	2	0	1
May	92	10	2	1	1	1
Jun	92	7	3	2	1	1
Jul	85	11	2	1	1	2
Aug	89	8	2	1	1	1
Sep	89	9	2	1	1	1
Oct	88	9	2	1	2	1
Nov	88	7	1	1	0	1
Dec	87	11	2	2	1	2
<b>1995</b>						
Jan	87	9	2	2	1	2
Feb	87	7	2	1	1	1
Mar	87	10	2	1	1	1
Jun	86	9	2	1	1	1
Sep	86	9	3	1	1	3
Dec	85	10	2	2	2	1
<b>1996</b>						
Mar	85	7	2	2	0	1
Total	2598	266	63	32	17	24
% of total wells extracted	-	-	24	12	6	9
No. > HAL	-	-	35	0	0	0

\* - indicates data not available.

† GC/MS data used for period 4/93 to 11/93, GC data used for remaining sampling periods.

‡ Abbreviations defined in table 1.

Virginia, respectively. We did not detect AMET, CYAN, DIA, METAL, METOL, or PRYN in any well samples. The lack of these particular pesticide detections could be explained simply by the low quantity applied and/or by decreasing pesticide application (table 2). Low pesticide detections may also be attributed to the rapid shift from corn/soybean (*Zea mays* L./*Glycine max* L. Merr.) to cotton (*Gossypium hirsutum* L.); the hectares of cotton increased from 153 ha to 662 ha in 1995 within the watershed due to lower production cost after the eradication of the boll weevil (*Anthonomus grandis* Boheman) (Bryant Spivey, 1996, Duplin County Cooperative Extension Service, personal communication). The widespread lack of METOL detection in our wells is important considering the high yearly usage (table 2) and suggests minimal vertical migration. Smith and Parrish (1993) also reported very little leaching of METOL below 0.3 m in the Coastal Plain region of Georgia.

The North Carolina Cooperative Extension Service conducted yearly pesticide application surveys to most

fields surrounding the wells. In order to explain the detects, these surveys were used to identify pesticide type and time of application to fields near the wells. Wells A and C had frequent detections for ALA, but pesticide application records indicate that no ALA has been applied to adjacent fields (within a 200 m radius) within the past five years. We cannot offer a satisfactory explanation for the nearly continuous detection of ALA in these wells. On the other hand, ATR detection in well B is probably the result of migration through the soil since yearly surveys show that it was applied to surrounding fields from 1990 to 1994. Well B also had some DEA detections, which is in agreement with Kolpin et al. (1996) who reported DEA detection in groundwater samples collected from several USA midwestern states. Prometon was continuously detected in well D, which is located approximately 1 m from a fence surrounding an animal barn. The application survey indicated that PMT was used several times per year for weed control in fence lines around this facility. It is likely that the PMT migrated through the soil into the shallow groundwater table (usually 1 to 2 m deep).

The continuous detection of ALA, ATR, and PMT in the wells may be due to high persistence in the aquifer or to transport by recharging groundwater. Detection of ATR in well B for three years is greater than the reported ATR half-life of 101 to 147 d (Zacharias et al., 1991) but is consistent with reports of Klint et al. (1993) who found no ATR degradation in groundwater after 593 d of incubation in a laboratory batch experiment. Alachlor detection over three years also suggests that the half-life may be greater than the 337- to 553-d half-life reported under anaerobic conditions (Pothuluri et al., 1990). Others have reported prolonged persistence of ALA in subsoils (Gallagher et al., 1996; Lavy et al., 1996; Clay et al., 1997). With respect to PMT, the continuous detection in well D is the result of

**Table 4. Summary of GC compound detections by year for select monitoring wells**

ARS Well	Compound Detected	Year†	Pesticide Summary				
			N	$\bar{x}$	sd	min	max
A	ALA	1993*	9	8.4	3.8	4.4	17.1
		1994	11	7.0	1.7	4.5	10.8
		1995	6	4.7	1.6	3.2	6.9
		1996	1	7.0	-	-	-
B	ATR	1993	10	0.5	0.2	0.2	0.7
		1994	11	0.6	0.3	0.4	1.1
		1995	3	0.3	0.1	0.2	0.4
		1996	1	0.5	-	-	-
	DEA	1993	-	-	-	-	-
		1994	9	0.4	0.2	0.2	0.6
		1995	4	0.4	0.2	0.2	0.6
		1996	-	-	-	-	-
C	ALA	1993	8	2.9	0.7	2.0	4.0
		1994	12	2.5	0.5	1.9	3.5
		1995	6	1.9	0.5	1.3	2.7
		1996	1	1.6	-	-	-
D	PMT	1993	1	3.0	-	-	-
		1994	12	2.4	1.0	0.9	5.0
		1995	6	1.3	0.7	1.2	2.3
		1996	1	1.6	-	-	-

\* Data in 1993 supplemented with GC/MS results when possible.

† Abbreviations defined in table 1.

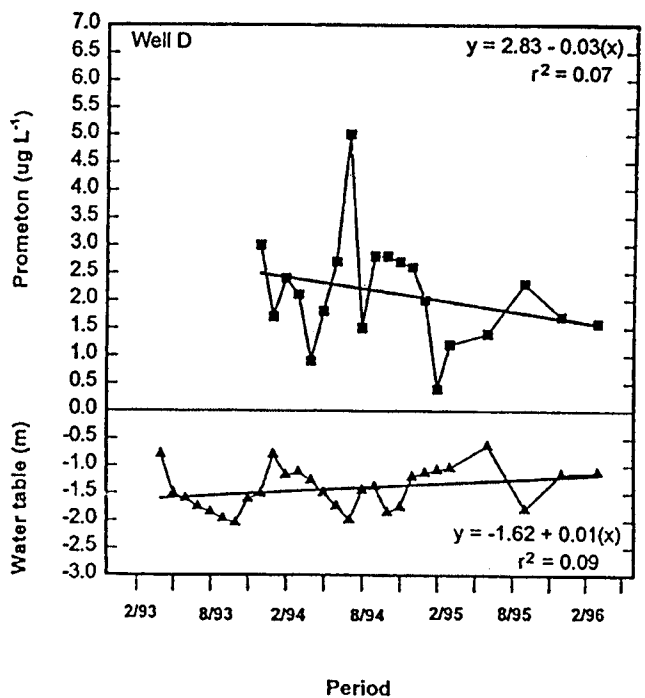
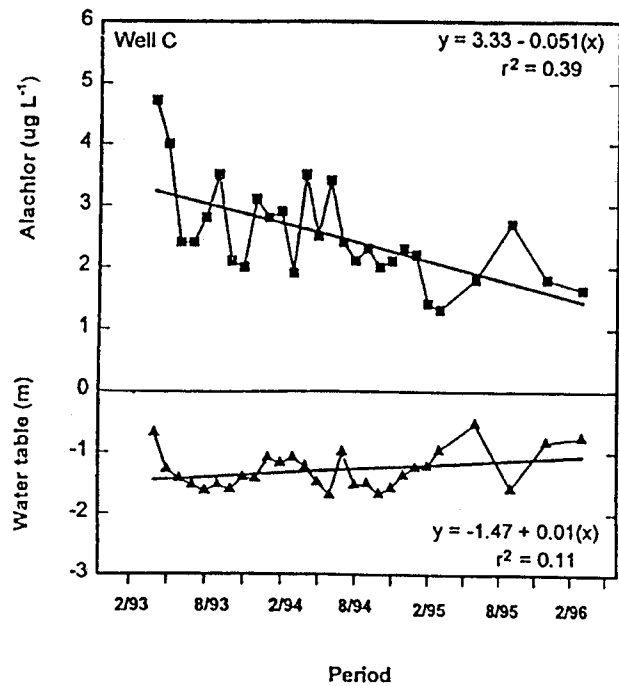
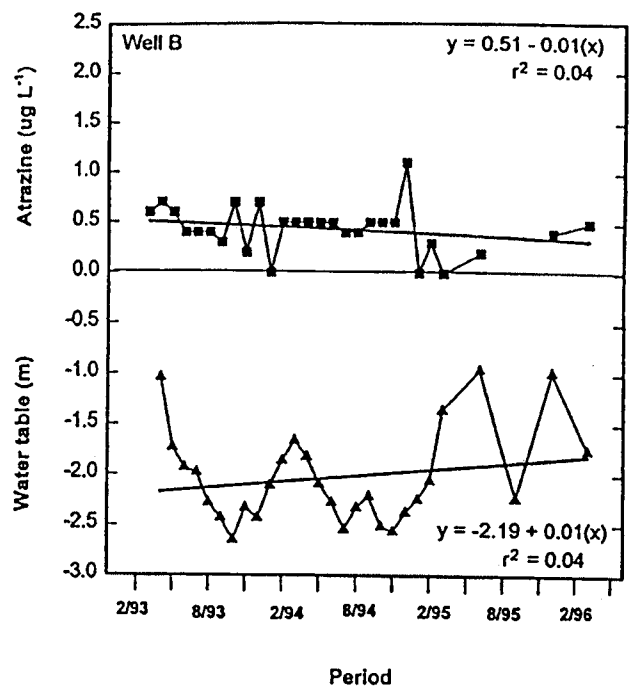
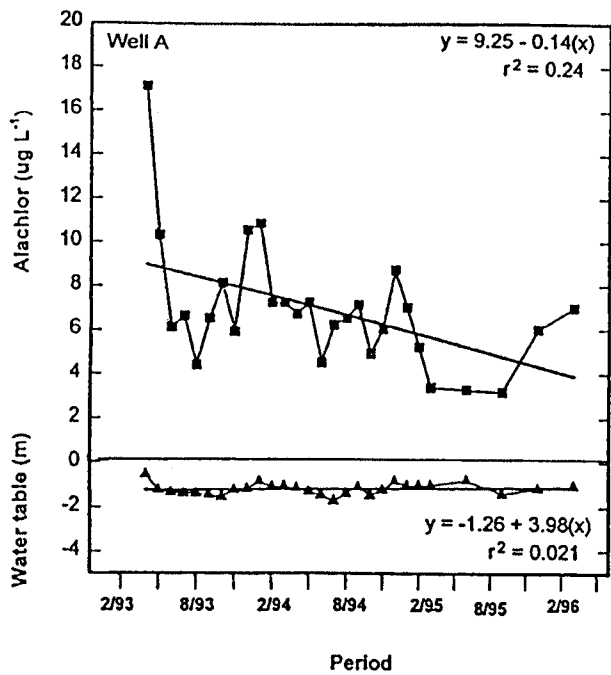


Figure 2—Relationship between the water table depth (relative to soil surface) vs. pesticide concentration in wells A, B, C, and D during the survey period. Linear regression equations represent relationship between period of sampling vs pesticide concentration and water table depth.

frequent application and migration. A BMP modification of less frequent PMT application or switching to another herbicide is probably necessary around well D.

There is a general decline in yearly mean pesticide concentrations only in wells A and C (table 4) which was supported by a significant ( $P < 0.05$ ) negative regression slope between pesticide concentration and period of sampling (fig. 2). The decline in monthly pesticide concentrations suggests that less pesticides were migrating to these wells or that some biodegradation may be occurring. The yearly mean pesticide concentration for wells B and D

were similar and the slopes of the regression equations were not significantly different than zero ( $P > 0.25$ ). This suggest that the parent pesticide concentrations are remaining unchanged, however, the formation of DEA in groundwater around well B indicates that some biodegradation of ATR has occurred.

#### DAR RATIO

The DAR [(DEA)/(ATR)] ratio has been used to distinguish point and nonpoint source contamination (Adams and Thurman, 1991), to distinguish seasonal differences in

ATR degradation rates (Schottler et al., 1994), and residence time in the soil during transport of ATR (Jayachandran et al., 1994). Since soil microorganisms can convert ATR to DEA, prolonged soil ATR residence time should result in large (> 1) DAR values (Jayachandran et al., 1994). Conversely, small DAR (< 1) values should occur when ATR rapidly leaches through soil via preferential flow processes (Jayachandran et al., 1994) or by mixing with ATR-contaminated groundwater from external point sources (Adams and Thurman, 1991).

The Kruskal-Wallis one way analysis of variance on ranks showed that the DAR ratios were statistically significant ( $P < 0.001$ ). The DAR values for well B during February to June 1994 and 1995 are  $\geq 1$ , indicating that ATR was being degraded (fig. 3). Schottler et al. (1994) reported that groundwater DAR values > 1 occur in early spring due to the previous year's ATR application and DEA formation not being flushed from the soil profile. This finding is consistent with the 1990-1994 ATR application to fields surrounding well B as indicated by the landowner. In four out of five cases, a DAR value < 1 was observed during July to December 1994, indicating the short soil residence time of ATR or the inflow and mixing with ATR-contaminated groundwater from external point sources. The seasonal variation in DAR values in groundwater around well B indicated that distinct periods of ATR accumulation/degradation and DEA formation occurred over the year.

#### PESTICIDE DETECTION AND WELL CHARACTERISTICS

Pesticide detections for wells A, B, C, and D were found to be poorly correlated ( $r = 0.24$  to  $-0.46$ ;  $P > 0.5$ ) with well depth, distance from field edge, and monthly rainfall. The lack of correlation may simply be due to differences in soils, well location, or to groundwater flow patterns. Correlating pesticide concentrations versus water table height showed no relationship for wells B and C ( $r = -0.09$  to  $-0.17$ ;  $P > 0.40$ ) and a weak but significant correlation

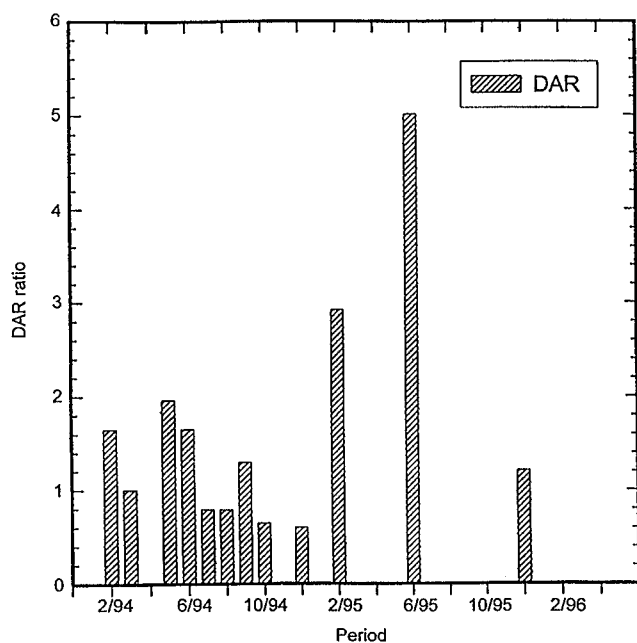


Figure 3—Relationship between deethylatrazine-to-atrazine (DAR) ratio vs survey period occurring in shallow groundwater around well B.

for wells A and D ( $r = 0.40$  to  $-0.67$ ;  $P < 0.03$ ). Differences in correlation trends between these wells could reflect differences in residue sorption, well depth, and hydrologic pesticide transport mechanisms.

#### TEMPORAL PESTICIDE DETECTION TRENDS

The GC pesticide detection vs. non-detection during each sampling period was arbitrarily segregated into seasonal periods to determine whether temporal detection trends were occurring. Chi-square tests of homogeneity of proportions were performed for detects versus non-detects sorted by season for individual and combined years, and they showed no significant temporal trends ( $X^2_3 = 1.3$ ,  $P > 0.38$ ). This finding is not surprising since the ratio of pesticide detect versus non-detect is very low (0.03 to 0.10).

#### CONCLUSIONS

Considering the high yearly pesticide usage within the HMR watershed, we found that most (91%) of the wells contained no measurable concentrations of several commonly used agricultural chemicals and that only five compounds were present in a limited number of wells. With respect to the 11 compounds investigated, our results indicate that, in general, these pesticides applied to sandy Coastal Plain soils in the HMR watershed have not caused widespread shallow groundwater contamination. The low amount of pesticide detections in the shallow groundwater may be due to several factors. Our applicator surveys showed that the quantity of certain pesticides applied in the watershed declined, and there was a shift from corn/soybeans to cotton production. The shift in agriculture crop production also caused a shift in pesticide usage patterns. The use of pesticide BMPs by applicators probably contributed also to the low number of pesticide detections. Although evaluation of specific mechanisms that regulate pesticide movement and dissipation were beyond the scope of our investigation, the literature contains ample research to support our postulations that minimal pesticide movement through the sandy soils may occur because of sorption to mineral surfaces (Wolfe et al., 1990; Weber et al., 1993), microbial degradation (Bollag and Liu, 1990), or by sorption with soil organic matter (Novak et al., 1996). Additionally, restricted downward pesticide movement by clay layers commonly present in North Carolina Middle Coastal Plain soils (Daniels et al., 1984) may contribute to the low number of pesticide detects. Our results indicate that the 11 commonly used pesticides in the HMR watershed have had a minimal impact on the quality of groundwater within the Coastal Plain watershed.

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