# Pesticide Occurrence in Ground and Surface Waters in a Coastal Plain Watershed

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## Introduction

There is public concern that pesticide migration from soil into shallow ground- and surface-water may contaminate drinking water supplies and damage sensitive surface-water ecosystems of the Coastal Plain region. This concern is supported by the finding of pesticides in ground-water wells on Long Island (Holden, 1986), in California (McKay and Smith, 1990), and in the eastern Coastal Plain region of the Delmarva Peninsula (Koterba et al., 1993) and in surface runoff from a Maryland Coastal Plain watershed (Wu et al., 1983). Pesticide detection in ground and surface water in the eastern Coastal Plain region confirms Kellog's (1993) contention that a high pesticide leaching probability exists for this region because of the high rainfall and sandy soil textures.

In 1990, investigation of pesticides was part of a USDA Water Quality Demonstration Project. This project involved landowners and federal, state, and local agencies and was located on the 2044-ha Herrings Marsh Run (HMR) watershed in Duplin Co., North Carolina. This watershed has many of the characteristics of other intensive agricultural watersheds and contains soils typical of the Coastal Plain region (Stone et al., 1995). Major agricultural crops in the watershed include corn, soybeans, cotton, vegetables, tobacco, and wheat. A survey for pesticide usage for 1995 indicated that 668 kg (a.i.) of alachlor, 298 for ametryn, 370 for atrazine, 70 for cyanazine, 24 for metalaxyl, and 655 for metolachlor were applied in the watershed (C. D. Fountain, 1995, personal communication). Nearly 100% of the producers in the watershed are utilizing at least one type of pesticide best management practices (BMPs) for handling, storage, and application of pesticides (C.D. Fountain, 1995, personal communication). Although the majority of producers are using some type of pesticide BMP, there remains room for fine-tuning of additional BMP adoption. Our objective was to evaluate the effects of these pesticide BMPs on maintaining high quality surface- and ground-water supplies by conducting monitoring studies for pesticides in shallow ground- and surface-water sources within the HMR watershed.

## Methods

Shallow ground-water monitoring wells were established in the HMR watershed from August 1991 to March 1993 on 21 farms that exemplify typical agricultural practices. The wells were installed to a depth from 3 to 8 m and were sealed with bentonite clay; and a lockable, steel casing inserted in concrete was placed around the PVC well head. Well samples were collected monthly from March 1993 to March 1995 and thereafter collected quarterly.

Immunoassay techniques to detect alachlor, atrazine, and metolachlor in water samples have been reported to correlate well with gas chromatographic/mass spectrometric (GC/MS) results (Thurman et al., 1990; Lawruk et al., 1993; Gruessner et al., 1995). An immunoassay procedure was used to screen the well samples for the pesticides alachlor, atrazine, and metolachlor using Ohmicron (Ohmicron Corp, Newtown, Pennsylvania[1]) kits. The minimum detection limit for the kits was 0.1 µg/L. Immunoassay is a good screening tool, but confirmation by another analytical method is necessary to insure the presence of the parent pesticide. Subsamples that had

[1] Mention of a trade-mark, proprietary product, or vendor is for information only and does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

a positive immunoassay detection were analyzed by GC/MS techniques for confirmation using methods outlined in Pfeiffer and Steinheimer (1992).

Thirteen surface-water sampling locations around the watershed were established from January to November 1994. Grab samples were collected, weekly to monthly, from January 1994 to January 1996 and were extracted for 11 pesticides, which include the parent compounds (alachlor, ametryn, atrazine, cyanazine, metalaxyl, metolachlor, metribuzin, prometon, and prometryn) and two triazine metabolites (deethylatrazine, and deisopropylatrazine). The stream samples were passed through a Waters (Waters, Corp., Milford, Massachusetts) $C_{18}$ solid-phase extraction cartridge to extract the compounds as described by Novak and Watts (1996). Determination and quantification were achieved using a Varian (Varian Instr., Sugar Land, Texas) 3600 CX GC equipped with a thermionic specific detector. Extraction efficiencies for the parent compounds ranged from 85% to 99% and 19% to 60% for the two triazine metabolites. The minimum detectable limits using GC procedures for each compound, in the unextracted sample, ranged from 0.1 to 0.35 µg/L. Selected samples were confirmed for these pesticides using GC/MS procedures as outlined above.

## Results and Discussion

### Ground-water

A low percentage of positive immunoassay detections occurred in the ground-water samples (Table 1). Alachlor was the most frequently (14%) detected pesticide in the ground-water samples. Additionally, GC/MS confirmation on these samples showed that in many instances the parent compound was not present.

Although estimated usage of alachlor, atrazine, and metolachlor in the watershed is very high, only two wells out of 100 had confirmed detections for alachlor. In addition, we found that only one well had confirmed atrazine and no wells had confirmed metolachlor. These data indicate that pesticide BMPs used by local farmers are successful at maintaining high quality ground water.

### Surface-water

During 1994, 26% of surface-water samples contained one or more of the 11 compounds being investigated (Table 2). Most of these pesticides were detected in samples collected in a small subwatershed (SW-2) within the HMR watershed. All 11 compounds were detected at least once during the sampling year. Metolachlor was the most frequently detected pesticide, it was present in 11% of the collected samples at concentrations ranging from 0.30 to 1.20 µg/L. The frequent metolachlor detection was found to be due to a pesticide point of entry identified in a small headwater tributary in SW-2. Several pesticides (alachlor, atrazine, cyanazine, metribuzin, and metolachlor) were confirmed in this tributary. The concentrations decreased downstream as a result of dilution or by in-stream assimilation processes. Atrazine recorded the second highest occurrence rate (7%). Additionally, the two triazine metabolites (deisopropylatrazine and deethylatrazine) were detected in 6% of the samples. Our data showed that most of the 1994 stream samples at the HMR watershed outlet were free of pesticides at our detection limits.

Although alachlor was the most frequently detected pesticide in the wells (Table 2), it was found to occur less often in the stream grab samples. Ametryn and metalaxyl were only detected once in our samples, in spite of the known usage of these pesticides in the watershed.

Some temporal patterns of pesticide detections were noted predominately in SW-2 during our monitoring study. During July and August 1994, 41% and 55%, respectively, of the stream grab samples collected contained a measurable amount of a least one of the 11

**Table 1. Occurrence, range, and percentage confirmed for pesticides in shallow ground-water wells in the HMR watershed by year.**

| Pesticide | Year | No. samples collected | No. immuno. positive det. | % samples with †immuno. positive det. | % samples‡ confirmed | Range of confirmed samples |
|---|---|---|---|---|---|---|
| | | | | | | µg/L |
| alachlor | 1993 | 829 | 130 | 16 | 3 | 0.5-17.1 |
| | 1994 | 1078 | 134 | 12 | 2 | 0.6-10.6 |
| | 1995 | 518 | 88 | 10 | 3 | 0.3-8.2 |
| atrazine | 1993 | 917 | 72 | 8 | 1 | 0.2-0.7 |
| | 1994 | 1078 | 51 | 5 | 1 | 0.2-0.8 |
| | 1995 | 518 | 31 | 4 | 1 | 0.2-0.4 |
| metolachlor | 1993 | 917 | 66 | 7 | 0 | -- |
| | 1994 | 1078 | 29 | 3 | 0 | -- |
| | 1995 | 518 | 10 | 2 | 0 | -- |

† Calculated on a total number of samples collected per year.
‡ Confirmed by GC/MS and percentage calculated on a total yearly sample collection basis.

compounds of interest. These detections were presumably related to the spring (April and May) application of pesticides and their subsequent migration into the stream.

Temporal distributions of pesticide detections were markedly different between ground- and surface- water samples. No seasonal trend was noted in the GC/MS results from the ground-water samples. Usually, 2% to 3% (total sample basis) of samples contained some pesticides during each month of our monitoring study. However, considering the total amount of ground-water samples collected, the consistency of monthly confirmations suggests that, unlike the temporal trend noted in the stream samples, the ground water in our watershed exhibited no significant temporal pesticide detection trend.

**Table 2. Occurrence and range of select parent pesticides and metabolites in 1994 stream grab samples determined by GC analyses[†].**

| Compound | No. of detections | % of total | Range |
|---|---|---|---|
| | | | μg/L |
| alachlor | 13 | 4 | 0.35-13.1 |
| ametryn | 1 | <1 | 0.41 |
| atrazine | 26 | 7 | 0.15-1.07 |
| cyanazine | 19 | 5 | 0.10-6.04 |
| deethylatrazine | 6 | 2 | 0.17-0.40 |
| deisopropylatrazine | 16 | 5 | 0.16-1.36 |
| metalaxyl | 1 | <1 | 0.61 |
| metachlor | 40 | 11 | 0.30-1.20 |
| metribuzin | 5 | 1 | 0.60-1.0 |
| prometon | 3 | <1 | 0.20-0.78 |
| prometryn | 6 | 2 | 0.18-2.18 |

[†]Total number of 1994 stream grab samples analyzed was 358.

## Conclusions

Even though the HMR watershed has intensive agricultural production that utilizes high applications of pesticides and it is located in the sandy Coastal Plains, no major contamination of ground and surface water was found. Usually zero to very low amounts of pesticides were found in surface- and ground-water samples collected in the HMR watershed over the 3-yr monitoring period. The high frequency of ground-water samples with no pesticide confirmations indicates that implemented pesticide BMPs are successful in maintaining good water quality within the Water Quality Demonstration Project.

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