REPORT OF INVESTIGATIONS NO. 51

HERBICIDES IN SHALLOW GROUND WATER AT TWO AGRICULTURAL SITES IN DELAWARE

by

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1993
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ABSTRACT

Several common herbicides used on corn and soybeans were detected in ground water at two agricultural sites in Delaware as part of a study of the distribution of herbicides in shallow ground water and the environmental factors affecting their occurrence. Most herbicide concentrations were at or near the 0.1-microgram per liter (μg/L) laboratory-reporting limit. With the exception of one detection of alachlor, most detections were substantially below the U.S. Environmental Protection Agency’s maximum contaminant or health advisory levels.

The frequent occurrence of shallow ground water with low concentrations of herbicides commonly used on corn and soybeans at the Vandyke and Fairmount sites is comparable to that in other areas with similar land use and soil characteristics. The U.S. Geological Survey’s National Water-Quality Assessment (NAWQA) project on the Delmarva Peninsula found similar concentrations of herbicides in shallow ground water regionwide in areas of corn and soybean production.

Well networks were established at the Vandyke site, located within a 35-acre (0.055 square miles) field in southern New Castle County, and the Fairmount site, a 6.5-square-mile area in eastern Sussex County. Land use and soil characteristics for both sites are representative of larger areas of Delaware. Water samples were collected from selected wells in each network several times between August 1988 and January 1990 for laboratory analysis of herbicides (primarily triazines), major inorganic ions, and nutrients. Field water-quality properties were measured and an immunoassay screening was conducted for triazines at each site.

Triazine herbicides were detected at least once in water from about half of the wells at each site. Atrazine was detected in more water samples and commonly at higher concentrations than cyanazine and simazine. In addition, metolachlor, a chloroacetamide herbicide, was detected in shallow ground water at the Fairmount site but not at the Vandyke site. Alachlor was detected in one water sample from each site.

The highest herbicide concentrations were in water samples from wells screened near the water table that are located in, or adjacent to, fields used for corn production. Seasonal trends were not observed in herbicide concentrations, and nitrate concentration, commonly used as an indicator of the effects of agriculture on ground water, did not reliably indicate the presence of herbicides.

Median concentrations of atrazine in ground water were 0.4 μg/L at the Fairmount site and less than 0.1 μg/L at the Vandyke site. Although soil at both sites is primarily sandy loam with low organic-matter content, characteristics that favor herbicide mobility, the soil has a somewhat greater content of organic matter, silt, clay, and amorphous iron and aluminum hydroxides at the Vandyke site than at the Fairmount site. A greater potential to retard herbicide mobility through adsorption would be expected at the Vandyke site because of these characteristics.

INTRODUCTION

Agricultural practices in Delaware have received increasing attention from state and local officials as well as from the general public, mainly because of the effect of fertilizers and herbicides in runoff to surface-water bodies and nitrate contamination of ground water. Previous studies have shown that ground water in the unconfined aquifer in Delaware has been contaminated by nitrate from applied agricultural fertilizers and manure applications (Robertson, 1977; Ritter and Chirnside, 1982; Denver, 1986; and Andres, 1991). The potential for ground-water contamination by herbicides, which are chemicals that are used to control weeds in crops, is of concern for the same general reasons: (1) the subsurface materials consist mainly of permeable sand and gravel, which have little capacity to hinder chemical migration; and (2) the water table is shallow, which favors short transit times of chemicals from the land surface to the ground-water system. Research has established that certain herbicides (atrazine, simazine, metolachlor, cyanazine, dicamba) leach through the soil zone into the ground-water system in Delaware (Ritter et al., 1987). After mobile herbicides migrate to zones of reduced microbial activity in the aquifer, mechanisms for their removal from the ground-water system are greatly reduced.

Most domestic wells and many municipal-supply wells in the Coastal Plain of Delaware obtain water from the area's extensive unconfined aquifer. Because agriculture is the major use of land in this area, this aquifer is susceptible to contamination by agricultural chemicals. The presence of certain herbicides in drinking water could pose risks to human health (USEPA, 1989). For this reason, from January 1988 through September 1990, the U. S. Geological Survey (USGS), in cooperation with the Delaware Geological Survey (DGS), conducted an investigation of herbicides in ground water at two agricultural areas in Delaware. This study was closely coordinated with the USGS National Water Quality Assessment (NAWQA) project on the Delmarva Peninsula.

Purpose and Scope

This report (1) presents information on the extent of herbicides in shallow ground water at two agricultural sites in Delaware and (2) describes specific environmental factors affecting herbicide concentrations in these areas. Emphasis is placed on the occurrence and distribution of herbicides commonly used in the production of corn and soybeans.

The distribution of herbicides in ground water is described in relation to herbicide use in the study areas, the
physical and chemical characteristics of soils, and the hydrogeologic systems. Processes that limit the mobility of herbicides are identified in relation to these factors. The occurrence of herbicides in other areas on the Delmarva Peninsula are compared with results from the study sites.

Location and Regional Setting of Study Sites

Two areas with mixed agricultural and forested land uses were studied, the Vandyke site in southwestern New Castle County and the Fairmount site in eastern Sussex County (Fig. 1). Corn and soybeans are the major crops at both sites. These sites were selected because they are representative of other areas in the Coastal Plain of Delaware. These larger areas, identified as hydrogeomorphic regions, contain characteristic combinations of topography, land use, geology, geomorphology, and soils (Koterba et al., 1991). Because of differences between the hydrogeomorphic regions, ground-water-flow systems differ at the two study sites.

The Vandyke site is in the poorly drained upland hydrogeomorphic region, which encompasses approximately 21 percent of the Delmarva Peninsula (Fig. 2). This region is classified as poorly drained because the water table is generally within 7 ft of the land surface (Hamilton et al., 1993) and because there is a relatively small degree of stream incision, conditions that produce ground-water-flow gradients too low for the region to be efficiently drained (Koterba et al., 1991). Poorly drained soil, which dominates the region, is found in flats and depressions. Well-drained soil is found in uplands interspersed among the poorly

Figure 1. Location of the Vandyke and Fairmount study areas.

Figure 2. Hydrogeomorphic regions of the Delmarva Peninsula (modified from Koterba et al., 1991).
drained areas. Agricultural fields generally occupy the well-drained uplands, and wooded areas occupy poorly drained flats and depressions.

The part of this region surrounding the Vandyke site is characterized by short (<1,000 ft) ground-water-flow paths and local flow systems. This pattern is a response to the area’s undulating topography, which is marked by depressions that contain seasonal (ephemeral) ponds in most years, overlying a thin (20 to 40-ft-thick) unconfined aquifer.

The Fairmount site is in the well-drained upland hydrogeomorphic region and is adjacent to the poorly drained upland. The well-drained upland region covers approximately 33 percent of the Delmarva Peninsula (Fig. 2). The median depth to the water table is about 9 ft in this region (Hamilton et al., 1993). Most of the soil is well drained. Poorly drained soil is restricted to narrow zones in stream valleys. In the well-drained upland surrounding the Fairmount site, well-drained soil is found in forested as well as in agricultural areas, a situation unlike many areas of the Peninsula where poorly drained soil not suitable for agriculture is found in forested areas. In the area around the Fairmount site, soil in the wooded areas is commonly too well drained for successful agricultural production. Irrigation is required to maintain optimum crop production.

The part of the region surrounding the Fairmount site is characterized by a regional flow system several miles long. This type of system developed in response to flat topography underlain by an unconfined aquifer that is generally more than 80 ft thick. At this site, the flow path studied is more than 3 mi long. In contrast, the flow system studied at the Vandyke site is primarily contained within a 35-acre field.

**Herbicide Use**

Corn and soybeans have been the primary crops in Delaware since the mid-1950s when rapid expansion of the local poultry industry created a large demand for feed. Before that time, corn was grown to feed livestock. Soybeans were not a common crop. Both crops are grown with conventional till and no-till practices. Although acreage under no-till production has been increasing since the mid-1970s, most farms use a combination of conventional till and no-till practices. Herbicide use and application rates are similar statewide for each type of crop and cropping practice (F. J. Webb, University of Delaware Cooperative Extension Service, oral commun., 1990). Application rates of herbicides are generally less than 4 lb/acre, which are considerably less than the average 150 to 200 lb/acre of nitrogen fertilizer applied to corn.

Atrazine, the first triazine herbicide, was introduced in the late 1950s for weed control in corn fields. Alachlor, a chloroacetamide herbicide introduced in the early 1960s, was used in conjunction with atrazine on corn until the mid-1970s when no-till practices became widespread. Use of metolachlor, another chloroacetamide herbicide, replaced much of the alachlor use. The triazine herbicides simazine (developed in the early 1960s) and cyanazine (developed in the early 1970s) have been widely used on corn with the increase in no-till farming. A variety of other herbicides are also used on corn, although they are not used as consistently or as widely as atrazine, metolachlor, simazine, and cyanazine.

Herbicides commonly used in Delaware and their reported use at the study sites are listed in Table 1. Detailed information on application rates and the effects of specific herbicides is presented by the Cooperative Extension Services, University of Maryland and University of Delaware (1990).

When corn is grown using conventional tillage methods, herbicides are applied after planting but before the crop emerges (called pre-emergence). Most commonly, a combination of atrazine and metolachlor, or atrazine and alachlor, is sprayed on the soil or incorporated into the soil. Subsequently, tillage is used to control post-emergent weeds.

Herbicide use and variety are greater when corn is planted using no-till methods. Standard no-till cropping practices include application of simazine and 2,4-D about 15 to 30 days before planting to kill small weeds. Before crop emergence, atrazine is applied in combination with metolachlor, alachlor, or cyanazine. An additional pre-emergent herbicide, either glyphosate or paraquat, is usually applied to kill small weeds.

Although tillage practices for soybeans are similar to those for corn, triazine herbicides, which are toxic to soybeans, are not applied; broadleaf herbicides are used instead. These include linuron, imazaquin, and chlorimuron. In addition, metolachlor or alachlor are generally applied as pre-emergent herbicides. Soybeans can be grown as a full-season crop or double cropped with small grains (mostly wheat and barley). When small grains are grown, 2,4-D and dicamba are applied.

**Acknowledgments**

This study was conducted under a Joint-Funded Program between the DGS and USGS.

The author is grateful to the staff of the DGS, under the supervision of Robert R. Jordan, State Geologist, who provided drilling services and well logging and installation services at the two study sites. Additional thanks are given to A. Scott Andres, Richard N. Benson, and John H. Talley for reviewing the manuscript.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Trade name</th>
<th>Use reported in study area</th>
<th>Laboratory analysis, this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>Lasso</td>
<td>N</td>
<td>Y*</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Aatrex, Bipe</td>
<td>V, F</td>
<td>Y*</td>
</tr>
<tr>
<td>Chlorimuron</td>
<td>Gemini</td>
<td>V</td>
<td>N</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>Bladex</td>
<td>V, F</td>
<td>Y*</td>
</tr>
<tr>
<td>Dicamba</td>
<td>Barvel</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Fluazifop-p-butyl</td>
<td>Fusilade</td>
<td>F</td>
<td>N</td>
</tr>
<tr>
<td>Glyfosate</td>
<td>Roundup</td>
<td>F</td>
<td>N</td>
</tr>
<tr>
<td>Imazaquin</td>
<td>Scepter</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Imazethapyr</td>
<td>Pursuit</td>
<td>F</td>
<td>N</td>
</tr>
<tr>
<td>Linuron</td>
<td>Loxon, Gemini</td>
<td>V</td>
<td>N</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>Dual, Bipe</td>
<td>V, F</td>
<td>Y*</td>
</tr>
<tr>
<td>Paraquat</td>
<td>Gramoxone</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Pcloram</td>
<td>Tordon</td>
<td>N</td>
<td>Y*</td>
</tr>
<tr>
<td>Simazine</td>
<td>Princep</td>
<td>V, F</td>
<td>Y*</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>Treflan</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>2,4-D</td>
<td>—</td>
<td>N</td>
<td>Y</td>
</tr>
</tbody>
</table>

V, Vandyke site; F, Fairmount site; Y, yes; *, detected; N, no
Townsend’s, Inc., and the Shaffner family are thanked for allowing well installation and instrumentation on their properties. Soil sampling and analysis were contracted to J. Thomas Sims of the University of Delaware Department of Plant and Soil Sciences, who provided additional cooperation and support during data interpretation. Richard L. Hall, Charles D. Parker, and James D. Luzader of the U. S. Department of Agriculture, Soil Conservation Service, also helped with collection and analysis of soil samples.

Supplemental funding for chemical analysis for this study was provided by the USGS NAWQA study on the Delmarva Peninsula, whose staff provided extensive cooperation and assistance throughout this study. The author also acknowledges the valuable reviews provided by Daniel J. Hippe, of the USGS in Harrisburg, Pennsylvania, and Shannon E. Smith, of the USGS in St. Paul, Minnesota.

METHODS OF STUDY

Well Networks

Sixteen wells were installed at the Vandyke site; water from 14 of these wells was sampled. Most wells in this network are less than 20 ft deep. Three of the network wells, each located adjacent to a shallower well, were screened near the base of the aquifer, at depths of 25 to 30 ft below land surface.

The well network at the Fairmount site includes 42 wells. It includes ten clusters of two to five wells, each with different screened intervals (ranging from about 10 ft to 88 ft below land surface) along with several single shallow wells. Water from 33 of the 42 wells was sampled for this study.

All wells were assigned numbers according to the DGS numbering system (Talley and Windish, 1984, p. 4). Appendices 2 and 3 at the end of this report include basic information about the network wells.

Water Levels

Water-level data were collected once a month in all wells from May 1988 to November 1989. Additional wells were added to the water-level networks as the study progressed. At the Vandyke site, continuous water-level records were collected at three wells (Gb41-16, Gb41-17, and Gb41-20) from December 28, 1988, through July 18, 1991. Continuous records were also collected at a fourth well, Gb41-18, from December 28, 1988, to March 8, 1989. At the Fairmount site, continuous water-level records were collected at five wells (Ph13-03, Ph13-06, Ph13-33, Ph22-16, and Ph23-08) from January 13, 1989, to August 2, 1990. The elevations of all wells were surveyed to sea-level datum (NGVD, 1929). Water-level records are on file at the USGS office in Dover, Delaware.

Water-Sample Collection and Analysis

Samples of ground water were collected during five periods from August 1988 through January 1990. The most comprehensive sample collection was conducted in June 1989, when water samples from ten wells and a seasonal pond located in a wooded depression were collected at the Vandyke site, and water samples from 28 wells were collected at the Fairmount site. Field measurements of specific conductance, dissolved oxygen, pH, alkalinity, and temperature were made each time a water sample was collected. Most samples received laboratory analyses of major inorganic ions and nutrients; about half of the water samples were analyzed in the laboratory for selected herbicides - in particular, the triazines and the chloroacetamides alachlor and metolachlor. Laboratory analyses of water samples that were collected in conjunction with the Delmarva NAWQA project also included analysis for trace metals, dissolved organic carbon, organochlorine herbicides, and carbamate insecticides. Analytical results for these additional compounds are not included in this report; however, they are presented in annual water-data reports (U. S. Geological Survey 1989, 1990, and 1991).

Of 125 water samples collected for laboratory analysis, 114 received an additional field screening for triazine herbicides using the immunoassay technique. This test does not differentiate between the various triazines, and the results are based on a cumulative concentration of all triazine herbicides detected. The detection limits for triazine compounds to which the test is sensitive are presented in Table 2. Thurman et al. (1990) found the immunoassay tests were generally a good screening method for detecting the presence or absence of triazine herbicides in ground water. According to their test results, the tests are most sensitive to atrazine, simazine, and propazine; the test response was lower (and, therefore, less useful) for cyanazine and several breakdown products of atrazine.

Results of the immunoassay test are either positive, indicating the presence of one or more triazine compounds, or negative, indicating that triazines are absent or that the cumulative concentration of triazine compounds is less than the detection limits for all compounds. Agreement was generally good between immunoassay-test results and laboratory results where triazine herbicides were detected. Test results were positive in 33 of 36 (92 percent) of water samples in which triazine herbicides were detected. Test results were positive in 33 of 36 (92 percent) of water samples in which triazine herbicides were detected by laboratory analysis, and negative in all water samples in which no triazines were detected by laboratory analysis.

Quality Assurance and Quality Control

Augers, well casings, and well screens were steam-cleaned before drilling and well installation to remove grease, oil, or other contaminants that could influence pesti-

<table>
<thead>
<tr>
<th>Compounds detected</th>
<th>Detection limit (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>0.1</td>
</tr>
<tr>
<td>Prometryn</td>
<td>0.1</td>
</tr>
<tr>
<td>Propazine</td>
<td>0.1</td>
</tr>
<tr>
<td>Ametryn</td>
<td>0.1</td>
</tr>
<tr>
<td>Prometone</td>
<td>0.1</td>
</tr>
<tr>
<td>Simetryn</td>
<td>0.3</td>
</tr>
<tr>
<td>Simazine</td>
<td>1.0</td>
</tr>
<tr>
<td>Terbuthylazine</td>
<td>0.1</td>
</tr>
<tr>
<td>De-ethylated atrazine</td>
<td>0.4</td>
</tr>
<tr>
<td>Trietazine</td>
<td>1.0</td>
</tr>
<tr>
<td>G-hydroxy atrazine</td>
<td>1.0</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>1.0</td>
</tr>
</tbody>
</table>

1 Test kit manufactured by Immunosystems, Inc., Scarborough, Maine.
soil around the well sites before drilling and sealing the annulus of each well with bentonite, were taken to prevent potential contamination of the borehole with organic matter or pesticide residue.

Sampling procedures for this study closely followed the protocol used in the Delmarva NAWQA study and were patterned after those described by Hardy et al. (1988). Ten percent of the water samples collected for laboratory analysis of herbicides for this study were included in the quality-assurance and quality-control procedures of the NAWQA study. The sampling procedures were effective in minimizing external contamination of the pesticide samples (M. T. Koterba, U. S. Geological Survey, oral commun., 1991).

Soil Sampling and Analysis

Soil samples were collected in May 1988 at five locations at the Vandyke site and at 11 locations at the Fairmount site for classification of soil types and analysis of chemical and physical characteristics that could affect pesticide mobility. Samples were collected adjacent to existing monitor wells using a 3-in. diameter bucket auger inserted 5 ft deep, or to the water table if less than 5 ft below land surface. Soil horizons were identified on the bases of color and textural changes. A separate sample was obtained from each soil horizon. Analyses of the chemical and physical characteristics included particle-size distribution, pH, organic and humic matter content, effective cation-exchange capacity, anion-exchange capacity, percentages of crystalline and amorphous iron and aluminum oxides, and nutrient concentrations.

Soil samples were collected and analyzed under the direction of J. Thomas Sims of the University of Delaware Department of Plant and Soil Sciences. Complete results of the soil analyses and documentation of the analytical methods used to determine chemical and physical characteristics are available in the project report on file at the University of Delaware Department of Plant and Soil Sciences in Newark, and the USGS office in Dover.

GEOHYDROLOGY OF STUDY SITES

Vandyke Site

The Vandyke site (Fig. 3) is located in an agricultural field that contains a wooded depression and seasonal pond in southern New Castle County (Fig. 1). Saturated sediments of the Columbia Formation comprise the unconfined aquifer at the Vandyke site. The Columbia Formation is 30 to 40 ft thick at the site and unconformably overlies a 40-ft-thick clayey-silt unit of the Calvert Formation (Pickett and Benson, 1977). The Columbia Formation sediments consist predominately of fine- to medium-grained sand and silty sand to depths of about 10 ft; sediments in the lower part of the formation are predominantly medium- to coarse-grained sand. Sand grains are typically stained with limonite (hydrous ferric oxide). Limonite crusts are common, particularly at the base of the formation where a thin gravel layer occurs. One sample of this gravel brought to the surface during drilling was cemented by limonite. A boring at the edge of the depression penetrated 3 ft of dark gray, organic-rich sediment at the surface that graded progressively to limonite-stained sand with depth.

Figure 3. Land use, well network, and soil sampling sites at the Vandyke site.

The water table at the Vandyke site does not closely follow topography. Depth to water at the edge of the depression ranges from about 1 ft above land surface to 6 ft below land surface. In contrast, in well Gb41-16 (Fig. 3), beneath a topographic high, water levels range from 4 to 10 ft below land surface. The water table is usually higher near the depression than beneath the uplands (Fig. 4).

During dry periods, the water table is below the base of the depression and slopes gradually away from the drainage divide toward the headwaters of local streams (Fig. 5A). Differences between hydraulic heads of wells in different parts of the network were small during a dry period in January and February 1989 (Fig. 4).

During wet periods, the water table is highest beneath the depression because of slow infiltration through the underlying fine-grained sediments (Fig. 5B). From late March through June 1989, a ephemeral pond formed in the depression (Fig. 4). Infiltration of the ponded water is indicated during this period by the concave-downward part of the hydrograph of Gb41-20. The pond is fed by discharge of ground water from transient water-table mounds that form at the edges of the uplands adjacent to this type of pond during recharge events (Phillips and Shedlock, 1993) and by surface runoff. In general, water levels in the unconfined aquifer respond rapidly to rainfall amounts of 1 in. or more from a single storm.

Fairmount Site

The Fairmount site (Fig. 6) includes interspersed agricultural and forested land in eastern Sussex County, Delaware (Fig. 1). The primary surface-water feature at the Fairmount site is Phillips Branch, a perennial stream with headwaters in the western part of the site. This stream flows eastward to Hopkins Prong, a tributary to Rehoboth Bay (Fig. 6).

The unconfined aquifer at the Fairmount site ranges from 80 to more than 160 ft thick. It is comprised of the Bethany formation and the overlying Beaverdam Formation of the Columbia Group.
Figure 4. Ground-water levels and precipitation from January 1 to June 30, 1989, Vandyke site. (Precipitation data from National Oceanic and Atmospheric Administration, 1989.)

Figure 5. Configuration of the water table at the Vandyke site. A. low water table, October 27, 1988; B. high water table, June 14, 1989. Position of ground-water divide estimated from water levels and topography.
The Bethany formation consists of predominantly gray, blue-gray, or olive-gray, fine-to-very coarse-grained sand interbedded with gray, olive-gray, and blue-gray clay and silt (Andres, 1986, p. 14). At the site it is a complex section of lenticular sand and clay sediments.

The Beaverdam Formation consists mainly of white or buff to greenish-gray medium-grained quartz sand, with scattered beds of coarse-grained sand, gravelly sand, and silty clay (Groot et al., 1990). Two facies are recognized in the Beaverdam: a coarse sand with gravel in the lower part of the formation, and an upward-fining silty, medium- to coarse-grained sand in the upper part. Discontinuous clay beds are present primarily within the sand and gravel beds of the lower part.

Ground-water flow is predominantly from west to east across the Fairmount site (Fig. 7). The vertical head gradient is downward in the western part of the site, indicating a ground-water recharge area, and upward in the eastern part of the site, indicating a ground-water discharge area. For example, on July 19, 1989, the gradient was 0.7 ft downward in the western part of the site between wells Pg15-03 (15 ft deep) and Pg15-02 (70 ft deep); it was 0.20 ft upward between wells Ph13-03 (15 ft deep) and Ph13-02 (78 ft deep) in the eastern part of the site.

During this study, the altitude of the water table ranged from 24 to 34 ft above sea level in well Pg15-02 located in the western part of the site, to about 6.5 to 9.5 ft above sea level in well Ph13-03 in the eastern part of the site (Fig. 6). The horizontal hydraulic gradient ranged from 0.0011 to 0.0015. Depth to ground water ranged from less than 1 ft to 19 ft below land surface. It is generally shallowest near downgradient discharge areas and deepest in upgradient recharge areas beneath sandy topographic highs. Seasonal fluctuations in water levels are 3 ft or less in downgradient discharge areas and as great as 10 ft in upgradient recharge areas. Figure 8 shows the differences between water-level hydrographs for well Ph13-33, which is in a downgradient area, and the remaining wells, which are in upgradient areas. As at the Vandyke site, about 1 in. or more of rainfall from a single storm is needed to recharge the aquifer and cause water levels to rise (Fig. 8).

Phillips Branch (Fig. 7) affects local ground-water flow, although where it flows north of the agricultural area of the Fairmount site it is not a discharge area for the regional flow system (Denver, 1989). Because of the predominance of ground-water flow from west to east, most water recharged in the agricultural fields at the Fairmount site discharges downgradient of the site.

The regional ground-water-flow system is locally affected by withdrawals for irrigation. The effects of withdrawals are apparent in the hydrograph for well Ph13-03 (Fig. 8) which is about 75 ft from an irrigation well (Fig. 6). Water levels decline about 2 ft when the irrigation well is pumped and recover rapidly when pumping ends. Well Ph13-03 is screened from 20 to 25 ft below land surface and the irrigation well is screened from 60 to 90 ft below land surface. Water levels in wells Ph23-08 and Ph13-06, located about 1,500 ft from the irrigation well, are slightly affected by pumping.
Figure 7. Configuration of the water table at the Fairmount site, July 19, 1989.

Figure 8. Ground-water levels and precipitation 1989, Fairmount site. (Precipitation data from National Oceanic Atmospheric Administration, 1989.)
HERBICIDES IN SHALLOW GROUND WATER AT THE STUDY SITES

Pesticides encompass a variety of organic chemicals with widely differing properties that affect their transport and fate in the environment. Herbicides are one of the types of pesticides, which also include insecticides, fungicides, and nematicides. Processes that affect transport and fate of pesticides through the soil zone and into ground water include water solubility, adsorption/desorption reactions, degradation, volatilization, runoff, and plant uptake (Helling and Gish, 1986). These processes are, in turn, affected by soil characteristics, depth to ground water, climate, and agricultural practices. The principal properties of pesticides that generally increase chances of transport through soil into ground water are high water solubility, low adsorption, long persistence, and high rate of soil incorporation during pesticide application. Soils that are sandy with low organic matter content, overlying shallow, unconfined aquifers, are least likely to inhibit pesticide mobility (Helling, 1986). The major factors that affect the transport and fate of pesticides in soil and ground water are summarized in Table 3.

<table>
<thead>
<tr>
<th>FACTOR</th>
<th>INFLUENCE ON PESTICIDE MOBILITY IN SUBSURFACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Adsorption of pesticides onto organic matter and clay is probably the most important factor affecting pesticide mobility in soils. Because adsorption is related to ionic properties of the molecules, pesticides have differing tendencies to be adsorbed or attracted to clay or organic matter. Most adsorption sites are negatively charged and constitute the cation-exchange capacity of the sediment. Adsorption is usually higher in more acid soils and lower in soils that are alkaline. More pesticides are adsorbed in dry soil than in soil with higher water content, because the polar water molecules compete with pesticide molecules for adsorption sites on the soil particles. The degree of adsorption also depends on the concentration of a pesticide in soil water and on the presence of other dissolved reactive compounds.</td>
</tr>
<tr>
<td>Solubility</td>
<td>Highly or moderately soluble pesticides (solubilities greater than 30 mg/L) are more readily leached through the soil zone to the water table than those that are less soluble. The affinity for clay or organic matter is also influenced by the pesticide's solubility; in general, there is an inverse relation between solubility and adsorption.</td>
</tr>
<tr>
<td>Microbial degradation</td>
<td>Decomposition of pesticide molecules by microorganisms is the principal means of pesticide degradation in soils. The rate of microbial degradation depends on the chemical structure of the pesticide, the presence or absence of oxygen, temperature, water content, pH, and earlier use of pesticides. This process is most active in warm, moist, well-aerated surface layers of the soil zone, where microorganisms use organic compounds as sources of nutrients and energy. The types and numbers of microorganisms decrease as soil depth increases and are positively correlated with the organic-matter content of the soil. Chemicals with relatively long half-lives (longer persistence) have the greatest chance to leach into ground water. Herbicides degrade with time into carbon dioxide, water, and other harmless compounds. Intermediate breakdown products, called metabolites, are produced that have similar leaching potential or greater leaching potential than the parent compound, depending on the chemical structure of the metabolites.</td>
</tr>
<tr>
<td>Chemical degradation</td>
<td>Chemical processes also affect pesticide degradation, but they are generally slower and less important than microbial degradation. The principal chemical processes are hydrolysis and oxidation.</td>
</tr>
<tr>
<td>Volatilization</td>
<td>Loss of pesticides through volatilization to the atmosphere is related to the vapor pressure, solubility, and adsorptive tendency of the molecule. There is little volatilization loss with cool, dry conditions in soil with high organic matter content. Warm, moist conditions result in greater desorption and volatilization loss.</td>
</tr>
<tr>
<td>Photodecomposition</td>
<td>Almost all pesticides undergo photodecomposition. Soil incorporation of the pesticides prevents excessive exposure to sunlight.</td>
</tr>
<tr>
<td>Uptake by plants</td>
<td>Factors leading to less adsorption, greater leaching, and increased microbial degradation result in increased availability of herbicides for uptake by plants.</td>
</tr>
<tr>
<td>Runoff and movement with eroded soil</td>
<td>Pesticides that can be desorbed or are in solution near the soil surface can be carried away in overland runoff. Wind or water erosion can transport pesticides adsorbed to soil surfaces.</td>
</tr>
<tr>
<td>Leaching with downward percolation of water</td>
<td>In general, pesticides are leached more rapidly through coarse-textured soils than fine-textured soils. Leaching of pesticides is greatest when intense rain falls on saturated coarse-textured soil.</td>
</tr>
<tr>
<td>Depth to the water table</td>
<td>The unsaturated zone is important for attenuation of pesticides through adsorption, microbial degradation, and volatilization. As residence time in this zone increases, the opportunity for pesticide attenuation also increases. An increase in depth to the water table could increase the residence time of pesticides in the unsaturated zone.</td>
</tr>
<tr>
<td>Movement in ground water</td>
<td>After pesticides reach the water table, their rate of movement depends on the hydraulic gradient, horizontal and vertical hydraulic conductivity, effective porosity, and attenuating capacity of the aquifer materials. The rate of pesticide movement is generally controlled by the velocity of the ground water. Mechanical dispersion and chemical diffusion can also influence pesticide transport. Pesticides are subject to sorption onto clay minerals and chemical and microbial degradation. Degradation rates are lower in the saturated zone than in the soil zone, because of decreased dissolved oxygen content, temperature, and microbial activity.</td>
</tr>
</tbody>
</table>

1 Council of Agricultural Science and Technology, 1985; Helling, 1986; Helling and Gish, 1986; Jackson et al., 1987; McEwen and Stephenson, 1979; McKenna et al., 1989; Perry et al., 1988; Thurman, 1986.
Herbicides were detected in ground water at concentrations at and above the laboratory-reporting level (0.1 μg/L) at the Fairmount and Vandyke sites (Appendices 2 and 3). The herbicides detected are among the most commonly used on corn crops - atrazine, cyanazine, and simazine. Metolachlor, commonly used on corn and soybean crops, was detected in ground water at the Fairmount site and only in pond water at the Vandyke site. Even though alachlor was not reported in the study area, it was detected in one water sample from one well, Ph23-12, at the Fairmount site, and one water sample from one well, Gb41-19, at the Vandyke site. Results of the chemical analyses are summarized in Table 4 as are crop use and selected chemical properties of the herbicides. None of the herbicide concentrations in ground-water samples exceeded the USEPA maximum contaminant or health advisory levels (U.S. Environmental Protection Agency, 1991 and 1989), with the exception of the alachlor detection at Fairmount (Table 4).

Water samples collected from six of the 14 wells at the Vandyke site and 17 of the 33 wells at the Fairmount site tested positive for triazine herbicides at least once using the immunoassay technique. Results of these tests are included in Appendices 2 and 3. Agreement is generally good between immunoassay results and laboratory results where triazine herbicides were detected.

Atrazine was detected in more ground-water samples and was commonly at higher concentrations than cyanazine, metolachlor, and simazine (Table 4). This is partly attributed to the longer period of use of atrazine than of the other herbicides detected and its use with both conventional and no-till cropping practices. Cyanazine and simazine are generally applied to crops only when no-till techniques are used. Metolachlor is commonly used alternately with alachlor. Although recent alachlor use was not reported at either study site, alachlor was detected in one ground-water sample from each site.

Differences among chemical properties of the herbicides detected also affect their transport to ground water and the concentrations detected. Solubilities and half-lives indicate a greater combined potential for the transport of atrazine into ground water than for the transport of alachlor, cyanazine, metolachlor, and simazine (Table 4). Although cyanazine, metolachlor, and alachlor are soluble, their half-lives are short (14 - 20 days, 15 - 50 days, and 26 - 70 days, respectively), relative to the half-life of atrazine (67 to 365 days). Simazine, with a half-life comparable to that of atrazine, is essentially insoluble in water and would not be expected to migrate to ground water as readily as atrazine. These characteristics support the greater frequency of detection of atrazine in ground water than alachlor, cyanazine, metolachlor, and simazine.

Other herbicides were detected by laboratory analysis in some of the water samples from the Vandyke and Fairmount sites. Picloram was present at a concentration of 0.1 μg/L in one water sample from well Gb41-11 at the Vandyke site (Fig. 3). This chemical could have been used for weed control, as it is not usually used on corn and soybeans. Prometone was detected at a concentration of 0.2 μg/L in one water sample from well Ph13-25 at the Fairmount site (Fig. 6). Its presence could not be explained. Well Ph13-25 is 85 ft deep and prometone was not detected in water in any of the other wells at this site.

Several other chemicals that are occasionally used on corn and soybeans in Delaware were also included in the laboratory analyses - namely, the herbicides alachlor, dicamba, trifluralin, and 2,4-D (Table 1), and the insecticide carbofuran. With the exception of carbofuran, which had been used at the Fairmount site, no use of these chemicals was reported in either area and only alachlor was detected in ground water.

The types and concentrations of herbicides detected in water from wells at the Vandyke and Fairmount sites are similar to those detected in shallow ground water in other portions of the Delmarva Coastal Plain (Shedlock and others, 1991). Herbicides were detected in low concentrations in water samples from wells near the water table in most

### Table 4.

Summary of use, chemical properties, and concentrations of selected herbicides detected in water from wells at the Vandyke and Fairmount sites.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Crop use</th>
<th>Application rates (lb/acre)</th>
<th>Water solubility at 25°C</th>
<th>Koc</th>
<th>Half-Life (days)</th>
<th>MCL or HAL</th>
<th>Number of detections/number of wells sampled</th>
<th>Concentration (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, 4-D</td>
<td>Corn, grain</td>
<td>0.25-2</td>
<td>900</td>
<td>20</td>
<td>7-28</td>
<td>70</td>
<td>0/9/0/17</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Corn, grain</td>
<td>1.5-4</td>
<td>242</td>
<td>120</td>
<td>26-70</td>
<td>2</td>
<td>1/1/1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>Corn</td>
<td>2-4</td>
<td>70</td>
<td>150</td>
<td>67-365</td>
<td>3</td>
<td>4/11/17</td>
<td>0.1-0.17</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>Corn, soybeans</td>
<td>1-4</td>
<td>171</td>
<td>188</td>
<td>14-20</td>
<td>10</td>
<td>3/3/3</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>Simazine</td>
<td>Corn</td>
<td>0.25-3</td>
<td>181</td>
<td>181</td>
<td>14-20</td>
<td>4</td>
<td>0/3/0</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-4</td>
<td>4.98</td>
<td>140</td>
<td>14-20</td>
<td>4</td>
<td>3/3/3</td>
<td>0.1-0.5</td>
</tr>
</tbody>
</table>

1. McKenna et al. (1989).

1 Use of the terms "detected" or "not detected" in this report indicates that herbicide concentration is at or greater than the laboratory reporting level of 0.1 μg/L or not present or less than 0.1 μg/L, respectively.
agricultural and in some residential areas throughout the Delmarva Peninsula. The pre-emergent herbicides atrazine, alachlor, and cyanazine were the most commonly detected, followed by metolachlor, simazine, propazine, and dicamba. More than 95 percent of the herbicide detections in ground water sampled throughout the Delmarva Peninsula were at concentrations less than maximum contaminant and health advisory levels of the USEPA.

Occurrence and Distribution

**Vandyke Site**

Herbicides were detected at the Vandyke site in water from seven wells. Concentrations of most herbicide detections by laboratory analyses were at or near a concentration of 0.1 µg/L (Appendix 2). Herbicide detections in water samples from three of the wells were by immunoassay test only. Herbicides were found in water from some of the wells throughout the study period including a dry period from June 1988 through mid-February 1989 and during a wet period from March 1989 through June 1989.

Although water samples from several wells in the network were collected several times, no seasonal correlation was found between herbicide concentrations in ground water and herbicide application. Seasonal correlation was not expected because most of the wells have open intervals several feet below the water table and, therefore, water is not sampled from the top of the aquifer where seasonal changes in chemical inputs would be most apparent.

Comprehensive ground-water-quality sampling took place during June 14-21, 1989, which was shortly after application of pre-emergent herbicides in the last week of May and following a period of rainfall (June 4-8) that caused surface runoff from the field into the pond.2 Hydrographs indicate that ground water recharge occurred during June 5-8, before sampling took place (Fig. 4). Pond water contained much higher concentrations of atrazine (15 µg/L), cyanazine (12 µg/L), and simazine (3.8 µg/L) than did ground water (all herbicide concentrations in ground water were less than 1 µg/L). Metolachlor was not detected in ground-water samples but was detected in pond water (0.4 µg/L). Atrazine, cyanazine, and simazine had been applied to the field surrounding the pond before planting, and metolachlor was used on the field in 1988.

Herbicide in the pond water probably resulted from transport as dissolved and adsorbed phases during surface runoff events. Glotfelty et al. (1984) found that most herbicide transport in runoff occurs within two to six weeks after application and that most of the transport is within the first two weeks. A model of herbicide transport by Squillace and Thurman (1992) indicates that herbicides adsorbed onto sediments are carried from fields during overland transport and are rapidly desorbed from the sediment when they reach a surface-water body.

The areal distribution of triazine herbicides is shown in Figure 9. Triazine herbicides were detected in ground water with nitrate concentrations ranging from 0.7 to 9.4 mg/L (as nitrogen). Concentrations of nitrate were 5.0 mg/L or greater in water samples from all but one of these wells (Gb41-11). Concentrations of nitrate were 3.5 mg/L or less in water samples from wells less than 20 ft deep in which triazine herbicides were not detected. Triazine herbicides were not detected in wells greater than 20 ft deep (Gb41-22, Gb41-23, and Gb42-03) even though concentrations of nitrate ranged from 3.4 to 8.2 mg/L in these wells.

Nitrate is the major anion found in most water samples from the unconfined aquifer that are affected by agriculture (Denver, 1986); however, water chemistry at the Vandyke site is complicated by anaerobic conditions in parts of the aquifer. For example, the water from well Gb41-21, located adjacent to the depression at the interface between poorly drained and well-drained soils contained low dissolved-oxygen concentrations (0.0 to 1.7 mg/L), high dissolved-iron concentrations (1.9 to 2.9 mg/L), and variable nitrate concentrations (<0.1 to 5.0 mg/L, as nitrogen). This chemistry indicates water that is affected by the high organic content of the sediments (which promotes anaerobic conditions and stability of dissolved iron) beneath the pond as well as by the adjacent sandy soil (which promotes aerobic conditions and stability of nitrate). Other wells with water affected by anaerobic conditions are Gb41-19 and Gb41-20 (also adjacent to the depression) and well Gb41-11 (located along Road 47) (Fig. 9).

Well Gb41-21, located on the perimeter of the depression (Fig. 9), is the only well where herbicide concentrations in water samples were consistently above 0.1 µg/L. Rapid recharge through the thin unsaturated zone near the pond could explain these higher concentrations. However, concentrations of atrazine in water from wells Gb41-19 and Gb41-20, also located on the perimeter of the depression,
were at or below the detection level. Results from models of
ground-water-flow systems in hummocky terrain indicate
that recharge is commonly localized where thickness of the
unsaturated zone is small (Winter, 1988, p. 610). Localized
recharge of water with different concentrations of atrazine
and local-scale variations in sediment characteristics could
account for these differences. Water recharging the aquifer
through the base of the depression would not be expected to
contain measurable concentrations of herbicides because of
adsorption onto the fine-grained sediments and organic mat­
er. In addition, herbicides in water that remains in the pond
are likely to degrade. For example, atrazine and simazine
had half-lives of only about 30 days in the Wye River,
Maryland. (Glotfelty et al., 1984).

Another factor affecting herbicide distribution and
nitrate concentration in the aquifer at the Vandyke site is
that shallow wells (<15 ft deep) are commonly located in
grassy areas adjacent to roads. Shallow water chemistry is
likely to be affected by recharge through the grassy area and
by infiltration of runoff from the road in addition to the
adjacent agricultural area. As a result, nitrate concentrations
in water from the shallow wells along Road 47 are lower
than those in water from deeper wells located along Road
47, whereas deeper ground-water chemistry is affected pri­
marily by upgradient agricultural land use.

All but two of the water samples in which triazine her­
bicides were detected were from wells no deeper than 15 ft.
The immunoassay test for water from Gb41-12 (18 ft deep)
was positive in June 1989, but the laboratory analyses did
not detect triazines (Appendix 2). Concentrations of 0.1
µg/L atrazine, 0.2 µg/L cyanazine, and 0.1 µg/L simazine
were detected in water from well Gb42-03 (23 ft deep) in
June 1989. No herbicides were detected in four other water
samples collected at different times from this well
(Appendix 2). Because the concentrations of herbicides in
ground water are at or near the 0.1 µg/L laboratory detec­
tion limit, any attenuation of water containing herbicides in
the aquifer would cause concentrations to be less than the
detection limit. A combination of adsorption, degradation,
dispersion, and dilution is the likely cause of fewer detec­
tions of herbicides in the deeper ground water than shallow
ground water at the Vandyke site. A smaller number of
water samples collected from wells in the deep part of the
aquifer than in the shallow part is another possible cause.

The overall range in concentrations of major ions in
ground water at the Vandyke site in which herbicides were
detected is illustrated in Figure 10. Sodium and bicarbonate,
derived from atmospheric precipitation and weathering of sili­
cate minerals, usually comprise the largest percentage of ions
under natural conditions (Denver, 1986). In addition, under
natural conditions, chloride concentrations are generally less
than 6 mg/L, nitrate concentrations are less than 1 mg/L (as
nitrogen), and specific conductance is generally less than 100
µS/cm (Denver, 1986). At the Vandyke site, chemistry of
water from well Gb41-24 is the closest to natural conditions.
Most ground water at the Vandyke site, however, does not

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**EXPLANATION**

- Chemical analysis of water.
- Indicates triazine herbicides detected
  at or above 0.1 micrograms per liter.
- Gb41-24
- Well number for sample with nearly
  natural water quality.

Note: Some sulfate (SO₄) concentrations are
estimated from previous analyses and the
charge balance for the analysis shown.

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**Figure 10.** Relative proportions of major ions in water from the Vandyke site, June 1989 and January 1990.
have these characteristics (Fig. 10). The water generally has larger proportions of calcium, magnesium, chloride, and sulfate (from agricultural and anthropogenic sources, such as road salt and septic-system effluent), than proportions of sodium and bicarbonate (from natural sources).

**Fairmount Site**

Triazine herbicides are widespread in ground water in shallow wells at the Fairmount site (Fig. 11). In laboratory analyses, atrazine was detected more often and usually at higher levels than the other herbicides (Table 4). During June 1989, the median atrazine concentration was 0.4 μg/L in laboratory-analyzed water samples from 11 wells. The median concentrations of cyanazine, simazine, and metolachlor were less than 0.1 μg/L.

Atrazine concentrations were consistently highest in water from well Ph22-12 during four sampling periods (Appendix 3). Concentrations of metolachlor also were usually higher in water from this well than in water from other wells sampled for this study. Well Ph22-12 is located near the entrance to a field and was damaged by a vehicle shortly after it was installed. The damage could have broken the well seal and enabled chemicals applied on the land surface to leak downward along the well casing. Analytical results for water from this well were not included in the calculation of median herbicide concentrations because of the uncertainty associated with those data.

Triazine herbicides were present in water from 16 of 28 wells sampled in June 1989 (Fig. 12). The median depth for the 16 wells with positive immunoassay results was 27 ft; the median depth for all 28 wells sampled was 38 ft. Positive immunoassay results were found in water from wells that were 13 to 60 ft deep.

The distribution of concentrations of nitrate and atrazine in the ground-water system is shown on Figure 13. Higher concentrations of atrazine (greater than 0.1 μg/L) were typically measured in water samples from wells less than 30 ft deep in areas of agricultural land use than in deeper wells, although a concentration of 0.2 μg/L was measured in water from well Ph23-18, which is 56 ft deep. Additionally, a positive immunoassay result was observed in water from well Ph23-19 (86 ft deep), although laboratory analyses of triazines were less than 0.1 μg/L. Positive immunoassay test results for water samples from greater depths in the aquifer are commonly in, or immediately

![Figure 11](image) Areal distribution of triazine herbicides based on immunoassay test results in water from shallow wells at the Fairmount site, June 1989.

![Figure 12](image) Distribution of triazine herbicides in ground water at the Fairmount site by well depth.
downgradient of the intensive agricultural area. This deep zone also is affected by irrigation pumping, which induces rapid downward flow of water in the aquifer (Denver, 1989). Herbicide concentrations were less than or equal to 0.1 \( \mu \text{g/L} \) (as determined by laboratory or immunoassay analyses) in water from wells with recharge areas upgradient (Pg15-02, Pg15-03, Ph22-15, and Ph22-11) of the agricultural area, and in water from wells considerably downgradient (PhI3-25, PhI3-29, PhI3-30, and PhI3-31) of the agricultural area (Fig. 13).

The presence or absence of herbicides in water from a particular well was usually consistent during the study period at the Fairmount site (Appendix 3). Atrazine, in particular, was consistently detected at similar concentrations each time a specific well was sampled. The failure to detect herbicides by laboratory analyses and negative immunoassay results also were usually consistent for successive water samples. As with the Vandyke site, no seasonal correlation of herbicide concentrations in ground water to herbicide application was found. In addition, herbicide detection did not correlate to depth to the water table for shallow wells at the Fairmount site. Depth to water ranged from 3.3 to 15.3 ft for water samples in which herbicides were not detected, and from 4.7 to 17.1 ft for water samples in which herbicides were detected. Concentrations of atrazine (measured with laboratory analyses) compared to the depth to the water table when the sample was collected are illustrated in Figure 14.

The distribution of major ions in ground water from the Fairmount site is shown in Figure 15. Natural ground-water chemistry is represented by the analyses for wells Pg15-02 and Pg15-03, which are located on the upgradient end of the Fairmount network, and Ph13-14, which is located near
manure, and calcium and magnesium leached from lime, dominate water chemistry in parts of the aquifer affected by recharge through agricultural areas (Denver 1986, 1989). Consequently, concentrations of these ions are indicators of the degree of the effect of agricultural chemicals on ground water at the Fairmount site. Although Figure 15 does not include results of nitrate analyses, nitrate increases in proportion to calcium plus magnesium. Most detections of triazine herbicides are in water with the greatest concentrations of ions from agricultural sources, although all tested ground water with characteristics of agricultural origin did not contain detectable concentrations of herbicides (Fig. 15).

The distribution of triazine herbicides was compared to nitrate concentrations for all samples with laboratory or immunoassay results (Fig. 16). Although triazine herbicides were detected most frequently in water from wells with high nitrate concentrations (median concentration of 22 mg/L (as nitrogen)), nitrate concentration alone is not a reliable indicator of the presence of triazine herbicides, as illustrated by results of analysis of water samples from wells Ph23-14 and Ph13-31. Nitrate concentrations in water at these wells exceeded 20 mg/L (as nitrogen), but no herbicides were detected (Appendix 3). Well Ph23-14 (85 ft deep) is screened near the base of the unconfined aquifer. Well Ph13-31, although shallower than well Ph23-14 (39 ft deep), is located downgradient of the agricultural area (Fig. 13). In contrast, herbicides also were detected in water with

Phillips Branch (Fig. 6). These analyses characterize the water as a sodium bicarbonate chloride type; additionally, the water is aerobic. Specific conductances were less than 60 μS/cm and nitrate concentrations were less than 1 mg/L (as nitrogen) in water samples from these wells. Concentrations of nitrate, leached from fertilizer and

![Figure 14. Relation of depth to water below land surface to atrazine concentration in water from shallow wells at the Fairmount site.](image)

![Figure 15. Relative proportions of major ions in ground water at the Fairmount site, June 1989.](image)
Soil at both sites is stratified. Textural discontinuities probably have implications for water flow and pesticide retention because of the coexistence of organic matter, clay, and aluminum and iron oxides in fine-textured horizons. The effective cation exchange capacity (ECEC) of the soil, which is a measure of affinity of a soil for pesticides and nutrients, is generally high in clays and correlates positively with amorphous aluminum and iron oxides. The range of ECEC in the soil is similar at both study sites (Table 5).

The pH of soil varies widely at each site. Adsorption of herbicides in the surface horizons of soil correlates closely to organic-matter content and soil acidity, therefore, variations in pH could have significant effects on soil retention of atrazine and other ionizable herbicides (including cyanazine and simazine). In general, below the uppermost one foot of the land surface, pH is low and changes slowly; the most extreme changes in soil pH occur in the uppermost one foot of the soil where organic matter (and herbicide retention) is greatest. (J. T. Sims, University of Delaware, Department of Plant and Soil Sciences, oral commun., 1990). Because adsorption and desorption is pH dependent, the dissolution of lime (which causes pH to increase) and nitrification (which causes pH to decrease) could result in alteration of adsorption and desorption of ionizable herbicides. Consequently, concentrations of atrazine (the only herbicide whose concentrations are consistently above the detection limit) in ground water implies repeated cycles of application and leaching and subsequent adsorption and desorption in the soil zone. This pattern could contribute to the detection of atrazine in water from several wells at both sites each time water samples from the wells were collected (Appendices 2 and 3). Adsorption of ionizable pesticides by clay, amorphous aluminum, and iron oxides also is affected by pH and is enhanced by a decrease in pH with depth in the soil profile.

### Table 5.
Summary of chemical and physical properties of soil at the Vandyke and Fairmount Sites.

<table>
<thead>
<tr>
<th>Property</th>
<th>Vandyke site</th>
<th>Fairmount site</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.61 - 6.23</td>
<td>4.35 - 7.25</td>
</tr>
<tr>
<td>Effective cation exchange capacity (cmol/kg)</td>
<td>0.81 - 4.64</td>
<td>0.74 - 5.01</td>
</tr>
<tr>
<td>Acidity (cmol/kg)</td>
<td>0.06 - 2.34</td>
<td>0 - 3.06</td>
</tr>
<tr>
<td>Organic matter - surface, %</td>
<td>1.06 - 2.27 (1.64)</td>
<td>0.73 - 2.45 (1.37)</td>
</tr>
<tr>
<td>subsoil, %</td>
<td>0.06 - 0.46</td>
<td>0.02 - 0.40</td>
</tr>
<tr>
<td>Humic matter - surface, %</td>
<td>0.32 - 0.61 (0.49)</td>
<td>0.12 - 0.40 (0.26)</td>
</tr>
<tr>
<td>subsoil, %</td>
<td>0.03 - 0.83</td>
<td>0.02 - 0.69</td>
</tr>
<tr>
<td>Amorphous aluminum, %</td>
<td>0.04 - 0.30</td>
<td>0.02 - 0.19</td>
</tr>
<tr>
<td>Amorphous iron, %</td>
<td>0.05 - 0.61</td>
<td>0.01 - 0.29</td>
</tr>
<tr>
<td>Total aluminum, %</td>
<td>0.06 - 0.31</td>
<td>0.02 - 0.19</td>
</tr>
<tr>
<td>Total iron, %</td>
<td>0.09 - 1.75</td>
<td>0.01 - 0.29</td>
</tr>
<tr>
<td>Sand content, median, %</td>
<td>65</td>
<td>76.5</td>
</tr>
<tr>
<td>Silt content, median, %</td>
<td>18.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Clay content, median, %</td>
<td>15.5</td>
<td>13</td>
</tr>
</tbody>
</table>

cmol/kg, 100 times molecular weight per kilogram; [ ], mean value; %, percent

1 Excluding sample with 1.58% in 30 to 51 centimeter depth horizon near well GB-41-20.
Slightly higher concentrations of atrazine were measured in ground water from the Fairmount site than from the Vandyke site (Table 4), consistent with the results of the soil analyses. The potential for herbicide retention, however, is low at both sites, because of low organic-matter content and sandy texture of the soil. These results are supported by a study of the adsorption and mobility of atrazine and metolachlor in four soil types in samples collected at the Fairmount site (Johnson and Sims, 1991) in which retention of atrazine and metolachlor correlated to organic-matter content and exchangeable acidity.

The distribution of atrazine and two of its metabolites, desethylatrazine and deisopropylatrazine, were measured in ground water at the Fairmount site by Denver and Sandstrom (1991). Degradation of atrazine in the ground-water system at the Fairmount site was implied by changes in proportions of atrazine to the metabolite desethylatrazine. The ratio of desethylatrazine to total atrazine (atrazine, desethylatrazine, and deisopropylatrazine) increased from less than 0.1 to 0.8 to 1.0 along a ground-water-flow path originating in an agricultural area.

Denver and Sandstrom (1991) found that desethylatrazine was the predominant metabolite and was present in water samples from most wells; it also was present in higher concentrations than atrazine (although concentrations of desethylatrazine were less than 3 µg/L). Adams and Thurman (1991) also found that desethylatrazine was the primary metabolite in soil water and soil cores collected in Kansas and that concentrations of desethylatrazine were greater than those of atrazine. Their study implies that most atrazine breakdown occurs in the soil zone. The degradation half-lives of herbicides in ground water were found to be more than 10 times longer than those in the soil zone in a study in Kansas because conditions favoring herbicide degradation are greatly reduced in the ground-water system (Perry, 1990).

SUMMARY AND CONCLUSIONS

This report describes the occurrence and distribution of herbicides, primarily triazines, in ground water of the unconfined aquifer at two sites in Delaware. The areas studied, referred to as the Vandyke and Fairmount sites, have soil and land use practices that generally are representative of other areas in the Coastal Plain of Delaware. Land use at the Vandyke and Fairmount sites is primarily agricultural interspersed with forest. Corn and soybean production has been the major agricultural land use since the mid-1950s at both sites. The most commonly used pesticides include the pre-emergent herbicides atrazine, cyanazine, simazine, and metolachlor.

Herbicides were detected by laboratory analysis or immunoassay screening in water from about half of the wells sampled at each site. Concentrations of herbicides detected were low, less than the USEPA's maximum contaminant and health advisory levels (with the exception of one detection of alachlor at 2.91 µg/L at Fairmount). With few exceptions the presence or absence of detectable herbicide concentrations in water from wells sampled several times was consistent; no correlation between time of application and concentration in ground water was observed in either area. These results are probably indicative of herbicide contamination from crop applications to corn and soybeans that could be expected in ground water of similar areas throughout the region. This inference is supported by a recent regional USGS NAWQA study on the Delmarva Peninsula (Shedlock et al., 1991). Herbicides commonly used on corn and soybeans detected throughout the shallow unconfined aquifer in the NAWQA study and their concentrations are of the same order of magnitude as in this study.

Triazine herbicides (atrazine, cyanazine, and simazine) were detected in ground water at both sites. Metolachlor, a chloroacetamide herbicide, also was detected in ground water at the Fairmount site and in a sample of pond water from the Vandyke site. Alachlor, another chloroacetamide herbicide, was detected in one ground-water sample from each site. Atrazine was detected most frequently, often at higher concentrations than the other herbicides. In Delaware, atrazine has been in use longer than simazine, cyanazine, metolachlor, or alachlor. Chemically, the combination of its solubility in water and half-life in soils indicates that atrazine has a greater persistence in the environment than for the other herbicides that were detected.

At the Vandyke site, most herbicide concentrations were at 0.1 µg/L, the laboratory reporting limit. Exceptions were in water samples from a shallow well (12 ft deep) at the edge of the depression and water from the pond, which consistently had the greatest concentrations of atrazine. Herbicides were detected at the Vandyke site in water samples containing a wide range of nitrate concentrations from below the detection limit of 0.1 to 9.4 mg/L (as nitrogen).

At the Fairmount site atrazine concentrations ranged from less than 0.1 to 2.2 µg/L. The median atrazine concentration in water from 11 wells sampled in June 1989 was 0.4 µg/L. The median concentrations of simazine, cyanazine, and metolachlor for the same water samples were less than 0.1 µg/L. Herbicide concentrations at and greater than 0.1 µg/L are common in water from wells at the Fairmount site that are located in or near agricultural fields and are screened up to 30 ft deep. Positive immunoassay results, however, indicate the presence of triazine herbicides to depths 87 ft below land surface in and downgradient of areas with intense agricultural land use. Irrigation pumping, which affects local ground-water flow, appears to promote downward movement of herbicides.

Although large nitrate concentrations are associated with herbicide detections at the Fairmount site, nitrate alone is not a reliable indicator of herbicides in deep, downgradient parts of the flow system. In these areas, nitrate concentrations are as high as 20 mg/L (as nitrogen), although herbicides are not detected. These results imply that herbicide mobility is retarded by adsorption on the aquifer sediments in the shallower parts of the aquifer and that herbicide concentrations are reduced by microbial degradation and (or) by dilution.

The presence of herbicides in ground water and soil characteristics at the study sites indicate that conditions favor their transport through the soil zone. Most soil at the Vandyke and Fairmount sites is classified as sandy loam and has a low (less than 2 percent) organic-matter content. These soil characteristics indicate that the potential to retard herbicides is low at both sites. Soil samples from the
REFERENCES CITED


Cooperative Extension Services, University of Maryland and University of Delaware, 1990, Pest management recommendations for field crops: University of Maryland Bulletin 237, 177 p.


Ritter, W. F., and Chirnside, A. E. M., 1982, Ground-water quality in selected areas of Kent and Sussex counties, Delaware: Newark, Delaware, University of Delaware Agricultural Engineering Department, 70 p.


Robertson, F. N., 1977, The quality and potential problems of the ground water in coastal Sussex County, Delaware: Newark, Delaware, University of Delaware Water Resources Center, 58 p.


APPENDIX 1.

Conversion factors, vertical datum, abbreviated water-quality units, and product disclaimer

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Sea Level: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 - a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentrations, water temperature, and specific conductance are given in metric units. Chemical concentration is expressed in milligrams per liter (mg/L), micrograms per liter (µg/L), or milliequivalents per liter (meq/L).

Water temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by using the following equation:

\[ °F = 1.8 \times °C + 32 \]

Specific conductance is expressed in microsiemens per centimeter at 25 degrees Celsius (µS/cm). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius (µmho/cm), formerly used by the U.S. Geological Survey.

Use of trade names in this report does not imply endorsement by the U.S. Geological Survey or the Delaware Geological Survey.


APPENDICES
APPENDIX 2.
Well records and chemical analyses of ground water and surface water at the Vandyke site.

[μS/cm, microsiemens per centimeter at 25°C; deg. C, degrees Celsius; <, less than; mg/L, milligrams per liter; μg/L, micrograms per liter; ft, feet; +, positive; -, negative; i, indeterminant; —, no analysis]

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## APPENDIX 2. (cont.)

Well records and chemical analyses of ground water and surface water at the Vandyke site

[$\mu S/cm$, microsiemens per centimeter at 25°C; deg. C, degrees Celsius; 
<, less than; mg/L, milligrams per liter; $\mu g/L$, micrograms per liter; 
ft, feet; +, positive; -, negative; i, indeterminant; —, no analysis]

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APPENDIX 2. (Cont.)
Well records and chemical analyses of ground water and surface water at the Vandyke site

\[ \mu \text{S/cm, microsiemens per centimeter at } 25^\circ \text{C; deg. C, degrees Celsius;}
<, \text{ less than; mg/L, milligrams per liter; } \mu \text{g/L, micrograms per liter;}
\text{ft, feet; +, positive; -, negative; i, indeterminant; —, no analysis} \]

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<th>Nitrogen, ammonia plus organic dissolved (mg/L as N)</th>
<th>Iron, dissolved (mg/L as Fe)</th>
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<th>Cynazine, total (ug/L)</th>
<th>Metachlor, water whole total recoverable (ug/L)</th>
<th>Simazine, total (ug/L)</th>
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22
APPENDIX 3.

Well records and chemical analyses of ground water at the Fairmount site.

[μS/cm, microsiemens per centimeter at 25°C; deg. C, degrees Celsius; <, less than; mg/L, milligrams per liter; μg/L, micrograms per liter; ft, feet; +, positive; -, negative; i, indeterminant; —, no analysis]

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<th>pH (standard units)</th>
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APPENDIX 3. (Cont.)
Well records and chemical analyses of ground water at the Fairmount site.

[μS/cm, microsiemens per centimeter at 25°C; deg. C, degrees Celsius;
<, less than; mg/L, milligrams per liter; μg/L, micrograms per liter;
ft, feet; +, positive; -, negative; i, indeterminant; --, no analysis]

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**APPENDIX 3. (Cont.)**

Well records and chemical analyses of ground water at the Fairmount site

[μS/cm, microsiemens per centimeter at 25°C; deg. C, degrees Celsius; <, less than; mg/L, milligrams per liter; μg/L, micrograms per liter; ft, feet; +, positive; -, negative; i, indeterminant; —, no analysis]

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<th>Nitrogen, ammonia dissolved (mg/L as N)</th>
<th>Nitrogen, ammonia plus organic dissolved (mg/L as N)</th>
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<th>Cynazine, total (μg/L)</th>
<th>Metachlor, water whole total recoverable (μg/L)</th>
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APPENDIX 3. (Cont.)

Well records and chemical analyses of ground water at the Fairmount site.

[μS/cm, microsiemens per centimeter at 25°C; deg. C, degrees Celsius; <, less than; mg/L, milligrams per liter; μg/L, micrograms per liter; ft, feet; +, positive; -, negative; i, indeterminant; —, no analysis]

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APPENDIX 3. (Cont.)
Well records and chemical analyses of ground water at the Fairmount site.

[µS/cm, microsiemens per centimeter at 25°C; deg. C, degrees Celsius; 
<, less than; mg/L, milligrams per liter; µg/L, micrograms per liter; 
ft, feet; +, positive; -, negative; i, indeterminant; —, no analysis]

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APPENDIX 3. (Cont.)

Well records and chemical analyses of ground water at the Fairmount site

[μS/cm, microsiemens per centimeter at 25°C; deg. C, degrees Celsius;
<, less than; mg/L, milligrams per liter; μg/L, micrograms per liter;
ft, feet; +, positive; -, negative; i, indeterminant; —, no analysis]

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