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Nitrate and Selected Pesticides in Ground Water of the Mid-Atlantic Region

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Prepared in cooperation with the
U.S. ENVIRONMENTAL PROTECTION AGENCY

Water-Resources Investigations Report 97-4139

Mid Atlantic Integrated Assessment (MAIA) Region

ABSTRACT

Data from more than 850 sites were compiled and analyzed to document the occurrence of nitrate and pesticides in ground water of the Mid-Atlantic region as part of the Mid-Atlantic Integrated Assessment program of the U.S. Environmental Protection Agency. Only those data collected by the U.S. Geological Survey as part of regional networks between October 1985 and September 1996 (inclusive) were used in the analyses, and the data were examined to ensure analytical results are not biased toward sites at the same location or sites sampled multiple times during this period. Regional data are available for most of the Mid-Atlantic region but large spatial gaps in available data do exist.

Nitrate was detected in nearly three-quarters of the samples for which it was analyzed, commonly at levels that suggest anthropogenic sources. Ten percent of samples contained nitrate at concentrations exceeding the Federal Maximum Contaminant Level (MCL) of 10 milligrams per liter as nitrogen. Pesticide compounds (including atrazine, metolachlor, prometon, simazine, and desethylatrazine, an atrazine degradate) were detected in about half of the samples for which they were analyzed, but rarely at concentrations exceeding established MCL's. The most commonly detected pesticide compounds were desethylatrazine and atrazine.

The occurrence of nitrate and pesticides in ground water of the Mid-Atlantic region is related to land cover and rock type. Likely sources of nitrate and pesticides to ground water include agricultural and urban land-use practices; rock type affects the movement of these compounds into and through the ground-water system. Nitrate concentrations in the compiled data set are significantly higher in ground water in agricultural areas than in urban or forested areas, but concentrations in areas of row crops are statistically indistinguishable from those in areas of pastures. Detection frequencies of atrazine, desethylatrazine, and simazine are indistinguishable among urban areas, row crops, and pastures. Prometon was most commonly detected in ground water in urban areas. Ground-water samples from forested areas typically contained the lowest concentrations of nitrate and detection frequencies of pesticides. Concentrations of nitrate and detection frequencies of pesticides were significantly higher in samples from carbonate rocks than in those from any other rock type. Most areas of the Mid-Atlantic region that are underlain by carbonate rocks have been developed for agricultural or urban use and the solution channels that are typical of carbonate rocks allow for relatively rapid transport of surficial contaminants throughout the ground-water system. Nitrate concentrations in unconsolidated aquifers were among the lowest for all rock types, possibly because of denitrification in organic-rich subsoils and shallow sediments.

INTRODUCTION

Nitrogen is an essential nutrient for plants and animals and is used in various forms (such as fertilizer and manure) to enhance plant growth. When unused by plants, nitrogen may infiltrate into the ground water, commonly in the form of nitrate (NO_3^-). Pesticides are typically synthetic organic compounds used to control weeds, insects, and other organisms for a variety of agricultural and non-agricultural purposes. Many pesticides are water-soluble and may also become dissolved in ground water. Ground water containing elevated levels of nitrate or pesticides can be unfit for human consumption and can cause adverse environmental impacts when discharged to streams. Existing water-quality data from a large area of the Mid-Atlantic region were compiled and analyzed to document the occurrence of nitrate and selected pesticides in ground water of that area.

This report, prepared by the U.S. Geological Survey (USGS) in support of the U.S. Environmental Protection Agency's (USEPA) Mid-Atlantic Integrated Assessment (MAIA) program, describes the occurrence of nitrate and pesticides in ground water of the Mid-Atlantic region. Nitrate was selected for discussion because it is the most common contaminant in ground water (Freeze and Cherry, 1979). Of the more than 100 pesticides and pesticide degradates[1] for which data were compiled for this study, atrazine, desethylatrazine (an atrazine degradate), metolachlor, prometon, and simazine were selected for discussion because no other compound was detected in more than 10 percent of the samples for which it was analyzed. Major spatial gaps in ground-water nitrate and pesticide data recently collected by the USGS within the Mid-Atlantic region are identified, and limitations of currently available data for analyses of this type are discussed. The occurrence of nitrate and selected pesticides in ground water is compared to established Federal standards for drinking water and to possible explanatory variables such as land cover and rock type.

The USGS currently maintains a large data base on ground-water quality in the Mid-Atlantic region. Most of these data were collected as part of the National Water-Quality Assessment (NAWQA) program or of monitoring programs conducted by the USGS in cooperation with other local, State, and Federal agencies. Nitrate and pesticide data for this report were compiled from the set of ground-water-quality data collected by or in cooperation with the USGS within the Mid-Atlantic region between October 1985 and September 1996, inclusive. Only those data collected as part of regional networks or studies were used; data from study areas approximately the size of a single county or smaller were excluded from the analyses to reduce spatial bias.

The Mid-Atlantic Integrated Assessment Program

The MAIA program is an integrated environmental assessment program being conducted by USEPA, Region 3, and USEPA's Office of Research and Development, in partnership with other Federal and State agencies. Objectives of the MAIA program are to build

[1]Pesticide degradates include breakdown products of pesticide-active ingredients resulting from biological processes (metabolites) and chemical processes such as hydrolysis, photolysis, or photooxidation (U.S. Environmental Protection Agency, 1990). Other terms synonymous with degradate include "transformation product," "breakdown product," and "daughter product."

partnerships and get all stakeholders involved in helping to (1) identify questions needed for assessing major ecological resource areas such as ground water, surface water, forests, estuaries, wetlands, and landscapes; (2) characterize the health of each resource area, based upon exposure and effect information; (3) identify possible associations with stressors, including landscape attributes, that may explain impaired conditions for both specific resources and the overall ecosystem; (4) target geographic areas and critical resources for protection and restoration; and (5) monitor environmental management progress. MAIA will use this multidisciplinary approach to provide complete data for making informed management decisions based on good science, and serve as a demonstration of the integrated assessment framework for the Committee on Environment and Natural Resources in the White House Office of Science and Technology.

The MAIA study area (fig. 1) includes Federal Region 3 (Delaware, Maryland, Pennsylvania, Virginia, West Virginia and the District of Columbia) as well as adjacent parts of major river basins in New Jersey, New York, and North Carolina. The region includes the entire watersheds of Albemarle Sound, Chesapeake Bay, Delaware Bay, and Pamlico Sound, as well as those of the Allegheny, Kanawha, and Monongahela Rivers. Land cover in the region for the period 1990 to 1994 was predominantly forested (69 percent), with smaller areas of row crops (16 percent), pasture or hay (9 percent), and urban development (3 percent; Vogelmann and others, 1997). Urban centers include Baltimore, Md., Philadelphia, Pa., Pittsburgh, Pa., Richmond, Va., and Washington, D.C.

The geology of the Mid-Atlantic region is very diverse (fig. 2). Unconsolidated sediments are confined mainly to the coastal areas in the southeastern part of the region and to isolated areas of relatively recent alluvial and glacial deposits. Northwest of the coastal sediments is a band of crystalline (igneous or metamorphic) rocks. Sedimentary rocks dominate the northern and western parts of the Mid-Atlantic region. These rocks are mainly siliciclastic (predominantly sandstones or shales), although areas of locally extensive carbonate rocks do exist (Cleaves and others, 1968; King and Beikman, 1974; Cardwell and others, 1986; Bennison, 1989, 1995; Virginia Division of Mineral Resources, 1993).

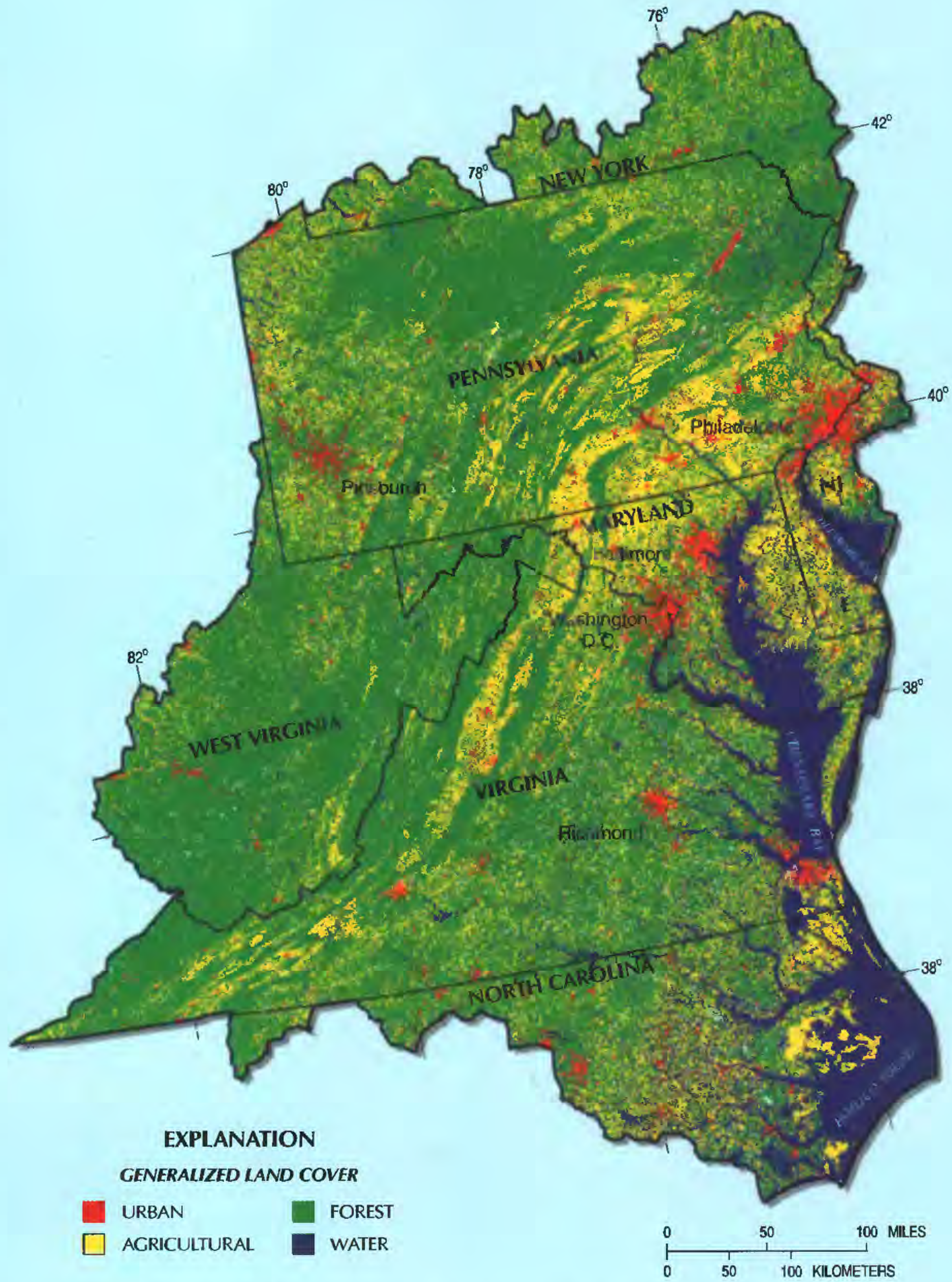

Figure 1. *Generalized land cover in the Mid-Atlantic region (Vogelmann and others, 1997).*

Nitrate

Nitrate is the most common form of dissolved nitrogen in ground water and is very soluble, moving freely with ground water under most environmental conditions (Freeze and Cherry, 1979). Natural sources of nitrate include minerals, animal wastes, microbial assimilation, and biodegradation (Hem, 1985). Elevated concentrations of nitrate are typically from anthropogenic (human-derived) sources, including atmospheric deposition from fossil-fuel combustion, animal manure and commercial fertilizers from agricultural areas, and septic systems. Nitrogen has been applied to agricultural lands in the United States in increasing amounts in recent decades (Mueller and others, 1995). Nitrogen inputs to the Mid-Atlantic region for the early 1990's are estimated to be 1.1 billion pounds per year from manure (Puckett, 1995; U.S. Department of Commerce, 1995) and 930 million pounds per year from fertilizers (Battaglin and Goolsby, 1994). Based on work by Sisterson (1990), annual atmospheric inputs of nitrogen to the Mid-Atlantic region from 1985 through 1987 have been estimated at 820 million pounds and are likely greatest near urban areas and at higher altitudes.

Ground water containing elevated nitrate levels may cause health problems when used for human consumption and adverse environmental effects when discharged to streams. In many areas, ground water serves as a major source of water for human consumption. The USEPA has established a Federal Maximum Contaminant Level[2] (MCL) for nitrate of 10 mg/L (milligrams per liter) as nitrogen. The consumption of water containing nitrate in excess of this level can cause methemoglobinemia (blue-baby syndrome), a potentially fatal condition in infants (U.S. Environmental Protection Agency, 1991). Elevated nitrate levels in streams can cause eutrophication, a condition in which aquatic plants and algae are over-produced. This algae can block sunlight from the water, consume dissolved oxygen, smother larger plants, and produce toxins that are harmful or fatal to other aquatic species (Allaby, 1989). In 1987, Maryland, Pennsylvania, Virginia, the District of Columbia, and the Federal Government established the goal of reducing nitrogen loads to Chesapeake Bay by 40 percent (based on 1985 levels) by the year 2000.

[2]Maximum Contaminant Levels, established by the U.S. Environmental Protection Agency, are enforceable standards that represent the maximum permissible level of a contaminant in water that is deliverable to any user of a public-water system (U.S. Environmental Protection Agency, 1991).

Figure 2. *Generalized surficial geology in the Mid-Atlantic region (modified from King and Beikman, 1974).*

Pesticides

Approximately 1.1 billion pounds of synthetic organic pesticides are used annually in the United States to control a wide variety of organisms in both agricultural and non-agricultural settings. Agricultural uses of pesticides account for approximately 75 percent of this total (U.S. Environmental Protection Agency, 1994). Most of the pesticides currently registered for use in the United States, such as atrazine and metolachlor, have been designed to be more soluble in water than older pesticides, such as DDT and chlordane. This decreases their persistence in the environment but increases the likelihood that they will leach through the soil and enter the ground-water system. Previous studies have detected at least 143 pesticides and 21 degradates in ground water in 43 states (Barbash, 1995).

Pesticides released into the environment can cause a wide range of ecological and human-health effects. Many pesticides are known or suspected carcinogens and may have toxic effects on humans and aquatic species. Many of the known health effects, however, require exposure to concentrations higher than what is typically found in the environment; the health effects of chronic, long-term exposure to low or trace concentrations of pesticides are unknown. Other concerns include synergistic effects of multiple pesticides as well as the processes of bioaccumulation, bioconcentration, and biomagnification, which entail the uptake and accumulation of chemical substances by organisms through the food chain.

Atrazine, simazine, and prometon are chemically related herbicides known collectively as triazines. Atrazine and simazine are used as selective herbicides to control broadleaf and grassy weeds; atrazine is used mainly on row crops (corn); simazine is used mainly in orchards and vineyards. Atrazine, simazine, and prometon are all used for non-selective weed control, especially in industrial areas.

Metolachlor is a selective chloracetanilide herbicide and is used also for broadleaf weed control in row crops and for non-selective weed control along highway right-of-ways (Meister Publishing Company, 1997).

Approximately 39 million pounds of synthetic organic pesticides are used annually in agricultural applications in the Mid-Atlantic region (Gianessi and Puffer, 1990, 1992a, b). The majority of these pesticides are herbicides, with approximately 25 million pounds used annually; an additional 8.6 million pounds of insecticides and 5.1 million pounds of fungicides are also used in agricultural applications. Atrazine is the most widely applied herbicide (table 1); chlorpyrifos and chlorothalonil are the most widely used insecticide and fungicide (respectively). More pesticides are applied to corn than are used in any other agricultural application, with approximately 17.7 million pounds used annually.

NITRATE AND PESTICIDES IN GROUND WATER

Regional data on ground-water quality are available for a large part of the Mid-Atlantic region but large spatial gaps in available data do exist. Nitrate and pesticide data were collected between 1985 and 1996 by the NAWQA program within five study units in the Mid-Atlantic region: the Albemarle-Pamlico Drainage, the Allegheny-Monongahela River Basins, the Delmarva Peninsula, the Lower Susquehanna River Basin, and the Potomac River Basin (figs. 3 and 4, table 2). Future sampling is planned by the NAWQA program in these areas as well as in the Delaware and Kanawha River Basins (Jones and Sylvester, 1992). Additional nitrate data used in analyses for this report were collected as part of statewide ground-water-quality networks in Maryland (Bolton, 1996), New Jersey (William Bauersfeld, U.S. Geological Survey, *written commun.*, 1997), and West Virginia (Kozar and Brown, 1995) and through other studies in New Jersey (Kozinski and others, 1995; Eric Vowinkel, U.S. Geological Survey, *written commun.*, 1996) and the Elk River Basin of central West Virginia (Mathes and Ward, 1990). Additional pesticide data are available from the Maryland ground-water-quality network and from the other studies in New Jersey. One site within the West Virginia ground-water-quality network has been sampled for pesticides. Large spatial gaps in nitrate and pesticide data compiled for this report include much of Virginia, Pennsylvania, northern North Carolina, and southern New York (figs. 3 and 4). Spatial gaps in compiled pesticide data also include large parts of the Mid-Atlantic region in New Jersey and West Virginia (fig. 4).

Nitrate is present in ground water throughout the sampled areas of the Mid-Atlantic region. Of 868 ground-water samples for which nitrate analyses were compiled for this report, 624 samples (72 percent) contained detectable nitrate and 90 samples (10 percent) contained nitrate in excess of 10 mg/L [3](table 3). Most samples containing nitrate in excess of 10 mg/L were collected in

DATA COMPILATION AND ANALYSIS

Data to support a regional assessment of the occurrence of nitrate and pesticides in ground water were compiled from the set of data collected by the USGS within the Mid-Atlantic region between October 1985 and September 1996 (inclusive), most of which have been previously published. No additional water-quality data were collected specifically for this study. The data were examined to ensure analytical results are not biased toward sites at the same location or sites sampled multiple times during the study period. Only the most recent nitrate and pesticide data from each site were included in analyses for this report. If no sample from a site was analyzed for both nitrate and pesticides, only the most recent data of each type were included. In the case of wells at the same location, only data from the shallowest well were included unless more complete data were available from a deeper well.

Land-cover data for the Mid-Atlantic region were compiled for comparison to ground-water quality. As part of the Multi-Resolution Land Characterization (MRLC) program, satellite images from 1990 through 1994 were used to classify land cover in the Mid-Atlantic region to a resolution of 30 m (meters) based on spectral analysis of reflected sunlight (Vogelmann and others, 1997). MRLC data within 400 m of 97 wells in the Potomac River Basin were compared to field-mapped land-use data collected from 1993 through 1995 for the same areas (Gerhart and Brakebill, 1997). The two data sets correlated well for percentages of forest, urban land, and total agricultural land around wells. Correlations of cropland and pasture percentages between the two data sets were weaker, possibly because of field rotation within agricultural areas.

Problems of consistency often arise when integrating data from multiple studies for regional analysis. Water-quality data used for analyses cited in this report were collected at various times using various sampling designs and techniques and thus do not represent a random, unbiased sampling of ground water in the Mid-Atlantic region. Although the maximum difference in sample-collection dates for data used in this study (11 years) is relatively small considering typical ground-water-flow velocities, this time difference could be significant in areas where land-cover changes have recently occurred or in aquifers (water-bearing rocks or sediments) such as unconsolidated sediments or carbonate rocks where ground-water-flow velocities may be higher. Unless otherwise indicated, all data cited in this report are considered representative only of the time and site of collection. Although sampling techniques have changed within the USGS since 1985, all data are considered valid unless contemporary quality-assurance sampling suggested otherwise.

agricultural areas in Delaware, central Maryland, south-central Pennsylvania, and southern New Jersey (fig. 3). The maximum nitrate concentration detected in the analyses compiled for this study was 29 mg/L and the median was 0.98 mg/L.

Nitrate concentrations in ground water in some areas of the Mid-Atlantic region are suggestive of anthropogenic sources. Because nitrate occurs naturally, however, its presence in ground water is not always indicative of contamination. The maximum nitrate concentration in natural ground water is not well defined and varies from place to place but has been estimated to be 0.4 mg/L for shallow, unconsolidated sediments of the Delmarva Peninsula (Hamilton and others, 1993) and for consolidated rocks of the Potomac River Basin (Ator and Denis, 1997). On the basis of an analysis of data from the entire United States, Madison and Brunett (1984) estimated that natural ground water in that area may contain as much as 3.0 mg/L, nitrate. In the Mid-Atlantic region, 493 samples (57 percent) in the compiled data set contained nitrate in excess of 0.4 mg/L and 335 samples (39 percent) contained nitrate at concentrations greater than 3.0 mg/L. Most samples containing nitrate at concentrations greater than 3.0 mg/L were collected in agricultural and urban areas in central and eastern parts of the Mid-Atlantic region. Lower concentrations were more commonly detected in samples from the more forested areas of West Virginia and the western parts of Maryland, New York, and Pennsylvania (fig. 3).

Pesticides and degradates also are present in ground water of the Mid-Atlantic region (table 3). Of 543 samples for which pesticide analyses were compiled for this report, 292 samples (54 percent) contained detectable levels of atrazine, desethylatrazine, metolachlor, prometon, or simazine. Atrazine and desethylatrazine were the most commonly detected pesticide compounds — in 39 and 43 percent of samples, respectively. Of 542 samples for which atrazine or desethylatrazine were analyzed, about half (275) contained detectable concentrations of one or both compounds. Metolachlor, prometon, and simazine were each detected in less than 30 percent of samples for which they were analyzed. Other pesticides and degradates detected (in less than 10 percent of samples) include those noted in table 1 as well as acifluorfen; aldicarb; benfluralin; bentazon; bromacil; DCPA; p,p′-DDE; diazinon; dichlobenil; dieldrin; 2,6-diethylaniline; diphenamid; diuron; hexazinone; lindane; metribuzin; naphthalene; napropamide; oryzalin; pebulate; pronamide; propachlor; propazine; propoxur; tebuthiuron; terbacil; and trifluralin.

Concentrations of pesticides in ground water in sampled areas of the Mid-Atlantic region are generally well below established MCL's for drinking water. Only one sample contained atrazine at a concentration greater than 3 μg/L (micrograms per liter), the Federal drinking-water standard. No samples contained simazine at concentrations exceeding the MCL of 4 μg/L. MCL's have not been established for

[3]Nitrate concentrations cited in this report also refer to concentrations of nitrite plus nitrate and are expressed as equivalent masses of elemental nitrogen (mg/L as N). Reported total and dissolved concentrations (of nitrate and pesticide compounds) were considered comparable for the purpose of this study.

Table 1. *Major agricultural pesticides used in the Mid-Atlantic region*

Crops: *A, alfalfa; Ap, apples; C, corn; Cu, cucumbers; D, dry beans; G, grapes; O, onions; Ot, other hay; P, pasture; Pe, peaches; Pn, peanuts; Po, potatoes; S, soybeans; T, tobacco; To, tomatoes; W, watermelons; Wh, wheat;*
Type: *F, fungicide; H, herbicide; I, insecticide* ***Results:*** *D, detected; N, not detected; —, not analyzed for*

PESTICIDE (TRADE NAMES[1])	SAMPLE RESULT	TYPE	ESTIMATED ACTIVE INGREDIENT APPLIED[2] (lbs/year)	ESTIMATED AREA TREATED[2] (acres)	MAJOR TARGET CROPS[2]
Atrazine (AAtrex, Gesaprim)	D	H	4,900,000	3,610,000	C
Metolachlor (Dual, Pennant)	D	H	4,270,000	2,500,000	C, S
Alachlor (Lasso, Alanox)	D	H	3,630,000	2,010,000	C, S, Pn
Chlorpyrifos (Dursban, Lorsban)	D	I	2,340,000	2,000,000	C, A, Pn, T
Glyphosate (Roundup, Rattler)	—	H	1,420,000	1,310,000	C, P, S
Chlorothalonil (Bravo, Daconil)	N	F	1,350,000	314,000	P, To, Cu
Butylate (Genate Plus, Sutan)	D	H	1,260,000	300,000	C
Mancozeb (Dithane DF, Nemispor)	—	F	1,180,000	247,000	Ap, Po, G, To, O, Cu, W
2,4-D (Weed-B-Gon, Chloroxone)	D	H	1,130,000	2,180,000	P, C, Ot, Wh
Cyanazine (Bladex, Fortrol)	D	H	1,090,000	716,000	C
EPTC (Eptam, Alirox)	D	H	1,070,000	257,000	C, A, Po, D
Carbofuran (Furadan, Curaterr)	D	I	992,000	923,000	C, A, S, T
Pendimethalin (Prowl, Stomp)	D	H	975,000	1,030,000	C, S, T
Captan (Clomitane, Captanex)	—	F	802,000	101,000	Ap, Pe
Simazine (Aquazine, Princep)	D	H	730,000	523,000	C, Ap, A, G
Paraquat (Cyclone, Total)	—	H	705,000	1,820,000	C, S, A
Linuron (Lorox, Linex)	D	H	485,000	795,000	S
Dimethoate (Cygon, Devigon)	N	I	485,000	928,000	A, S, Ap
Carbaryl (Sevin, Savit)	D	I	453,000	312,000	G, Pn, S, C, Ap, Wh
Dicamba (Banvel, Metambane)	D	H	410,000	1,290,000	P, C, Ot, Wh

[1]*Use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.*
[2]*from Gianessi and Puffer, 1990, 1992a,b*

Table 2. U.S. Geological Survey projects from which regional ground-water-quality data were compiled for this report

PROJECT	NUMBER OF GROUND-WATER SITES COMPILED
National Water-Quality Assessment (NAWQA):	
Albemarle-Pamlico Drainage	71
Allegheny-Monongahela River Basins	60
Delmarva Peninsula	140
Lower Susquehanna River Basin	169
Potomac River Basin	105
State Water-Quality Networks:	
Maryland (Phases 1 and 2)	108
New Jersey	160[1]
West Virginia	26
Ground-Water Pesticide Vulnerability, NJ	90[1]
Natural Radioactivity in Ground Water of the Kirkwood-Cohansey Aquifer System, NJ	140[1]
Water Resources of the Elk River Basin, WVa	99

[1]*Some sites from New Jersey projects are outside of the Mid-Atlantic region.*

desethylatrazine, metolachlor, or prometon. Individual pesticide concentrations exceeded 0.3 µg/L in less than 10 percent of samples for each compound (table 3).

The highest pesticide concentrations within ground water of sampled areas of the Mid-Atlantic region were most commonly detected in samples from Maryland and south-central Pennsylvania. Atrazine (fig. 4) and simazine concentrations greater than 0.1 µg/L and desethylatrazine, prometon, and metolachlor concentrations greater than 0.2 µg/L were most often measured in samples from agricultural areas of this part of the region. Similar levels of prometon also were detected in some urban areas. It is difficult to compare detection frequencies or very low concentrations of pesticides from different areas of the Mid-Atlantic region because minimum laboratory reporting levels for pesticides vary widely among and even within different projects from which the data were compiled.

RELATION OF NITRATE AND PESTICIDES IN GROUND WATER TO LAND COVER AND ROCK TYPE

The occurrence of nitrate and pesticides in ground water of the Mid-Atlantic region is related to land cover and rock type. Predominant rock types were identified for each sampled site from information supplied by original investigators. Sites were assigned to land-cover groups on the basis of the predominant land cover (from MRLC data) within 100 m of each. Data from sites with no predominant land cover within 100 m and sites with a predominant land cover other than urban, forested, cropland, or pasture were excluded from statistical comparisons among land-cover groups. Data from sites in North Carolina were also excluded from land-cover comparisons because MRLC data for that area were not available at the time of data analysis.

Concentrations of nitrate and detection frequencies of pesticide compounds were compared and contrasted among four major land covers (urban, forested, cropland, and pasture) and rock types (crystalline, siliciclastic, carbonate, and unconsolidated sediments) of the Mid-Atlantic region. Nitrate concentrations were compared among land covers and rock types using rank-transform analysis-of-variance (ANOVA) and Tukey tests. Pesticide-detection frequencies were compared using multiple exact Kruskal-Wallis contingency-table analyses (Helsel and Hirsch, 1992). Null hypotheses were rejected at the 95-percent confidence level (alpha=0.05).

Nitrate concentrations were censored at a common minimum-detection level prior to statistical testing. Because of the difficulty involved in comparing heavily censored data with multiple detection levels, all statistical tests on pesticides were performed using only those data from projects with the lowest common detection level for each compound. Tests on pesticides thus included only the data from NAWQA projects in the Allegheny-Monongahela, Lower Susquehanna, and Potomac River Basins — about 60 percent of compiled pesticide data.

Because shallow ground water may be more susceptible than deep ground water to surficial contamination by nitrate and pesticides in some areas, any differences in well depths and ground-water levels among land covers and rock types in the compiled data set should be considered when comparing these environmental variables to ground-water quality. Rank-transform ANOVA and Tukey test results indicate no significant difference in total depths or ground-water levels among wells in the four land-cover groups. Among rock types, wells in unconsolidated aquifers are significantly shallower than those in siliciclastic aquifers; wells in carbonate and crystalline rocks are the deepest. Ground-water levels are likewise significantly nearer the land surface in wells in unconsolidated aquifers than in those in any other type.

Nitrate concentrations and pesticide-detection frequencies are significantly higher in samples from ground water in urban and agricultural areas of the Mid-Atlantic region than in samples from forested areas (table 4). Nitrate concentrations are significantly higher in ground water from sites in agricultural areas than from sites in urban or forested areas. Although nitrogen and pesticide compounds typically are applied in greater quantities to crops than to pastures, nitrate concentrations and detection frequencies of pesticides in ground water are statistically indistinguishable between row crops and pastures for all compounds (table 4). This may indicate that field rotation or the close proximity of crops and pastures within agricultural areas leads to a mixed-agricultural effect on ground-water quality or that distinctions between row crops and pasture in the MRLC data are imprecise. Prometon, which is commonly used to control weeds in urban areas, was most often detected at urban sites (table 4).

Pesticides in ground-water samples from urban areas of the Mid-Atlantic region may be derived from urban sources or from surrounding agriculture. Detection frequencies for atrazine, desethylatrazine, and simazine are statistically indistinguishable among urban, row crop, and pasture sites, although only 20 urban sites were included in pesticide analyses. All urban samples containing detectable pesticide compounds were collected in carbonate-rock areas of the Lower Susquehanna Basin where urban centers are surrounded by agricultural land. The relatively large solution channels that are typical of carbonate rocks can allow for relatively rapid transport of surficial contaminants throughout the ground-water system (White, 1993; Barbash and Resek, 1996). Concentrations of atrazine (fig. 5; $p<0.0001$) and desethylatrazine ($p<0.0001$) in ground water in this area of the Lower Susquehanna Basin are significantly higher in agricultural areas (row crops or pasture) than in urban areas, although the detection frequencies are similar. Simazine concentrations in this area are not significantly different among agricultural and urban areas ($p=0.3027$).

Nitrate concentrations and pesticide-detection frequencies in ground water of sampled areas of the Mid-Atlantic region are related to rock type as well as to land cover. Concentrations of nitrate and detection fre-

Table 3. Sampling frequency, detection frequency, summary statistics, and water-quality criteria for nitrate and selected pesticide compounds

COMPOUND	NUMBER OF SAMPLES	NUMBER OF DETECTIONS[1]	PERCENTAGE OF SAMPLES IN WHICH DETECTED[1]	MEDIAN[2]	90th PERCENTILE[2]	MAXIMUM[2]	MAXIMUM CONTAMINANT LEVEL[2] (MCL)	NUMBER OF SAMPLES EXCEEDING MCL	PERCENTAGE OF SAMPLES EXCEEDING MCL
Nitrate (as Nitrogen)	868	624	72	0.98	11	29	10	90	10
Atrazine	542	213	39	≤ .009	.25	11.6	3	1	.2
Desethylatrazine	500	215	43	≤ .019	.22	1.4	---	---	---
Metolachlor	542	148	27	≤ .005	≤ .093	5.0	---	---	---
Prometon	537	97	18	< .018	< .15	1.4	---	---	---
Simazine	537	124	23	< .007	≤ .083	1.3	4	0	0

[1]*Minimum detection levels varied for each compound.*
[2]*Concentrations listed are in milligrams per liter (as nitrogen) for nitrate and micrograms per liter for all other listed constituents.*

quencies of pesticides are significantly higher in ground-water samples from sites in carbonate rocks than in aquifers of any other type (table 4). Most areas of the Mid-Atlantic region that are underlain by carbonate rocks have been heavily developed for agricultural or urban use (figs. 1 and 2), and carbonate aquifers are particularly susceptible to surficial contamination. Ground-water samples from crystalline rocks also contain higher concentrations of nitrate and are more likely to contain detectable atrazine, desethylatrazine, or metolachlor than samples from unconsolidated or siliciclastic aquifers (table 4). Most samples from crystalline aquifers in the compiled data set represent ground water in agricultural and urban areas; samples from heavily forested, crystalline-rock areas would likely contain lower nitrate and pesticide concentrations. Among samples from crystalline aquifers in the compiled data set, nitrate concentrations are positively correlated with the percentage of agricultural land (based on MRLC data) within 400 m of sampled sites (Spearman's rho=0.520, p<0.0001) and negatively correlated with percent forest (rho=-0.529, p<0.0001).

Nitrate concentrations and pesticide-detection frequencies in unconsolidated aquifers are among the lowest of any rock type. Nitrate concentrations in samples from these aquifers are highly variable, however, ranging from less than 0.02 mg/L (the minimum detection level) to 29 mg/L. Much of this variability is likely due to local differences in soil properties and abundances of wooded areas within and around agricultural fields (Mueller and others, 1995). Some of the lower nitrate concentrations were measured in samples from the deepest wells; these wells may be completed in confined aquifers that are less vulnerable to contamination than are surficial aquifers. Lower nitrate concentrations also may be related to areally extensive denitrification[4] in subsoils, which has been demonstrated in areas of unconsolidated deposits in the southeastern United States, where soils and shallow sediments typically contain abundant organic matter (Hallberg and Keeney, 1993). Nitrate concentrations in samples from the Albemarle-Pamlico Drainages in North Carolina and Virginia and from glacial and alluvial deposits

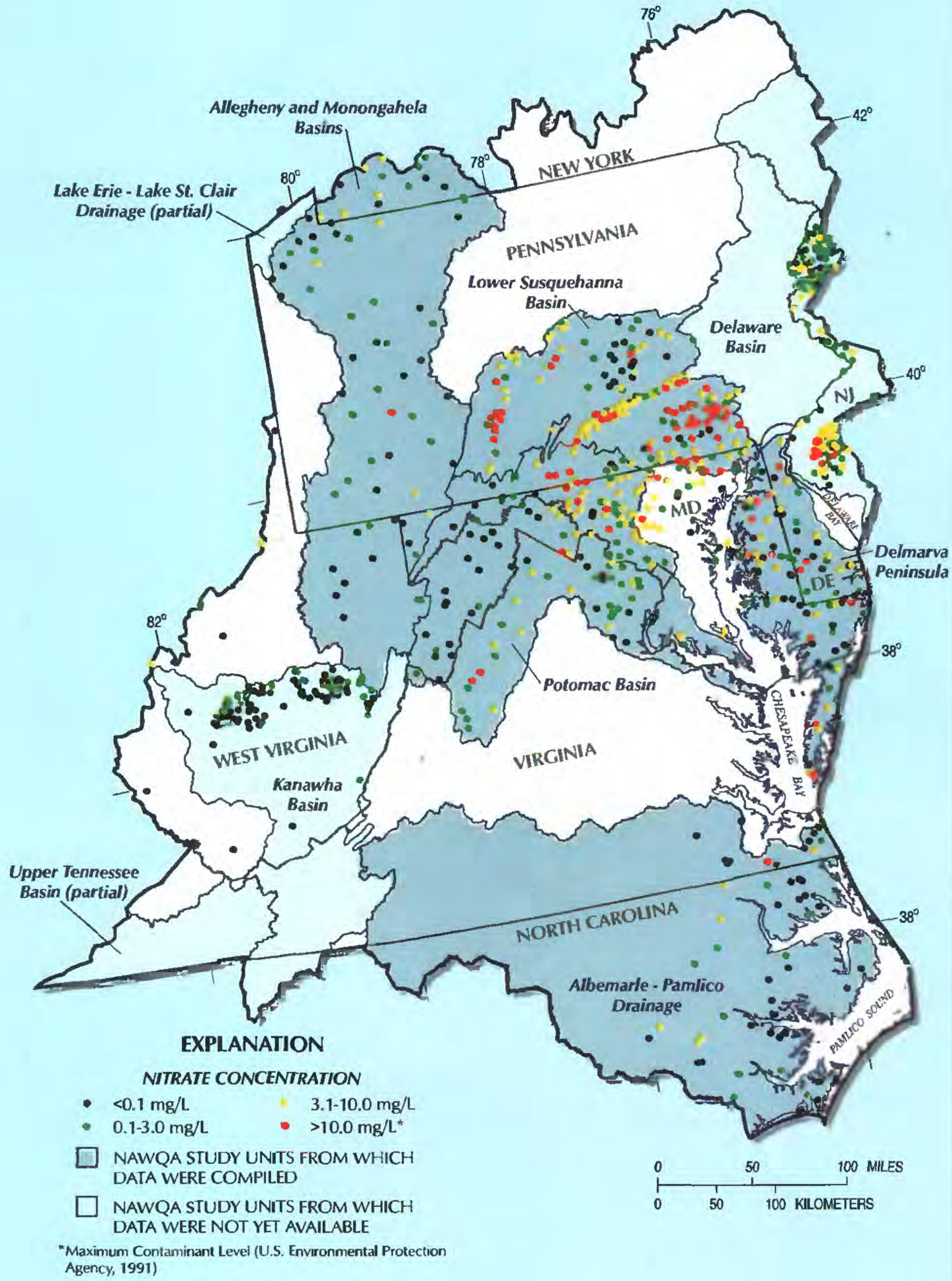

Figure 3. *Map of the Mid-Atlantic region showing location of available regional nitrate data and distribution of nitrate concentrations.*

Table 4. *Median nitrate concentrations and detection frequencies of pesticides and degradates in sampled ground water of the Mid-Atlantic region, in decreasing order by land use and rock type.* [Colored bars indicate results of multiple comparison tests among land uses or rock types (alpha = 0.05)[1].]

	Nitrate (median, in mg/L as N)	Atrazine (percent detected)[2]	Desethylatrazine (percent detected)[2]	Metolachlor (percent detected)[2]	Prometon (percent detected)[2]	Simazine (percent detected)[2]
Land Use	Pasture/Hay (5.5)	Urban (70)[3]	Row Crops (70)	Urban (70)[3]	Urban (70)[3]	Urban (60)[3]
	Row Crops (4.8)	Row Crops (67)	Urban (70)[3]	Row Crops (44)	Row Crops (31)	Pasture/Hay (42)
	Urban (2.0)	Pasture/Hay (59)	Pasture/Hay (63)	Pasture/Hay (37)	Pasture/Hay (30)	Row Crops (39)
	Forested (<0.1)	Forested (9)	Forested (12)	Forested (4)	Forested (2)	Forested (2)
Rock Type	Carbonate (6.4)	Carbonate (94)	Carbonate (93)	Carbonate (66)	Carbonate (62)	Carbonate (71)
	Crystalline (4.0)	Crystalline (43)	Crystalline (55)	Crystalline (29)	Crystalline (0)	Crystalline (9)
	Unconsolidated (0.79)	Unconsolidated (13)	Unconsolidated (29)	Unconsolidated (3)	Unconsolidated (0)	Unconsolidated (3)
	Siliciclastic (<0.1)	Siliciclastic (7)	Siliciclastic (9)	Siliciclastic (2)	Siliciclastic (0)	Siliciclastic (1)

[1] **Bars shaded with the same intensity indicate no significant difference in median concentration (for nitrate) or detection frequency (for pesticides and degradates).**
[2] *Pesticide and degradate results include only data with common reporting limits for each compound (NAWQA data from the Allegheny/Monongahela, Lower Susquehanna, and Potomac study units).*
[3] *Statistical tests on pesticides in urban areas were limited to only 20 sites, most of which represent one bedrock type that may be particularly vulnerable to contamination.*

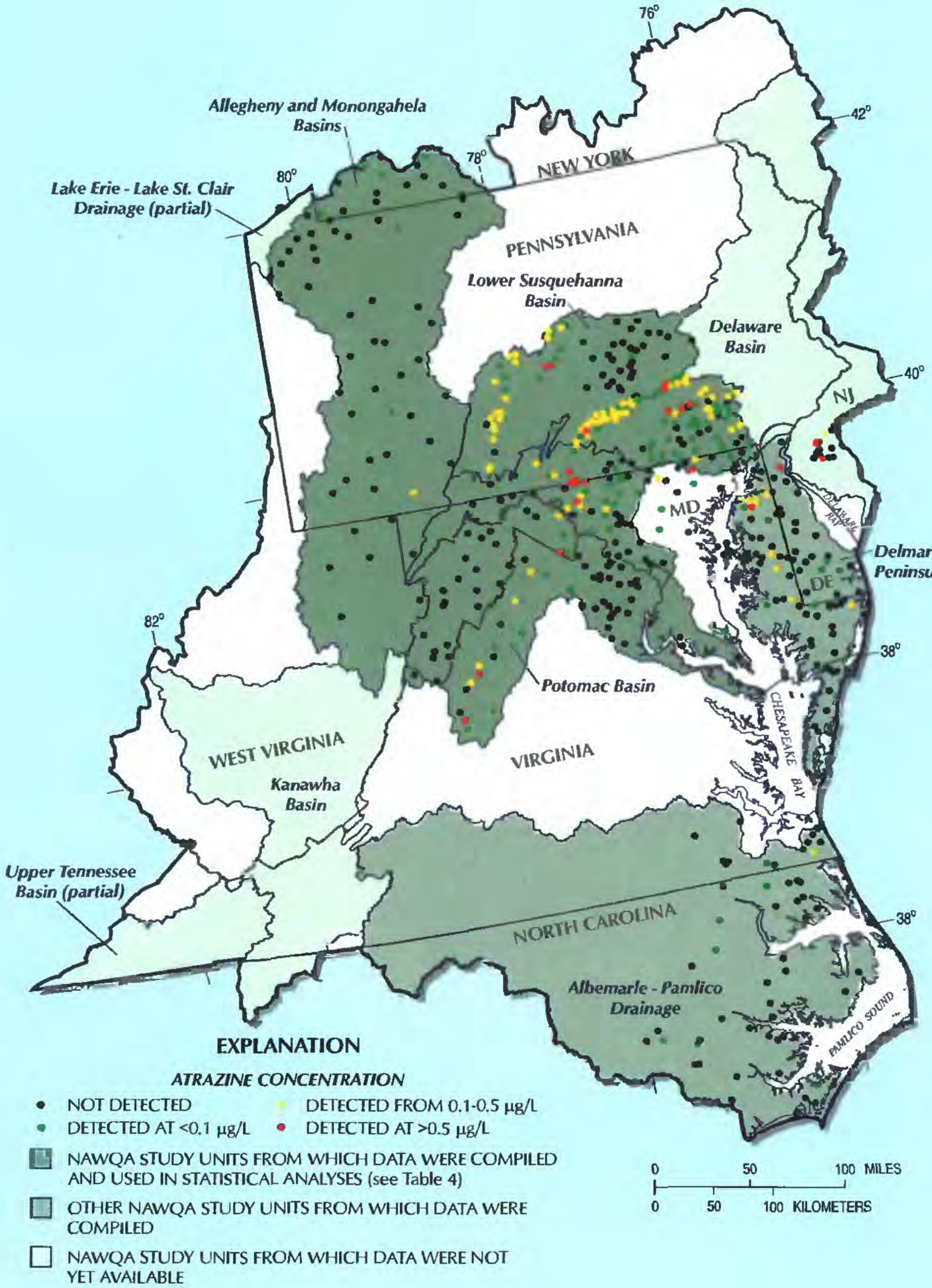

Figure 4. *Map of the Mid-Atlantic region showing location of available regional atrazine data and distribution of atrazine concentrations.*

in West Virginia and Pennsylvania are significantly lower ($p<0.0001$) than those from unconsolidated aquifers in the rest of the Mid-Atlantic region. Although statistical tests on nitrate in the unconsolidated aquifers were performed using all compiled data, tests on pesticides were limited to samples from sites in glacial and alluvial deposits in the northern and western parts of the Mid-Atlantic region and do not reflect any possible effects of intensive agriculture in areas of unconsolidated aquifers in coastal areas of Delaware, Maryland, North Carolina, Virginia, or southern New Jersey.

Because land cover is related to rock type in sampled areas of the Mid-Atlantic region, both variables must be considered simultaneously when using the compiled data set to compare ground-water quality from different areas. A rank-transform, two-way ANOVA test indicates a significant interaction effect ($p<0.0001$) between the land-cover and rock-type variables in the compiled data set when comparing ground-water nitrate concentrations to environmental settings. Statistical tests comparing nitrate concentrations and pesticide-detection frequencies among different land covers within each rock type showed similar results to that for all rock types combined (table 4), although statistically significant differences among land-cover groups were less common. Comparisons of nitrate concentrations and pesticide-detection frequencies among different rock types within each land-cover group yielded similar results. Targeted sampling of different land covers within a single rock type (or of different rock types within a single land cover) may show which variable has the greater effect on the occurrence of nitrate and pesticides in ground water. Analysis of nitrate data collected in the Lower Susquehanna Basin using such a design, however, showed rock-type and land-cover effects remain difficult to separate (Bruce Lindsey, U.S. Geological Survey, *written commun.*, 1997).

SUMMARY AND IMPLICATIONS

Ground-water-quality data were collected by the U.S. Geological Survey between October 1985 and September 1996 in much of the Mid-Atlantic region. Nitrate and pesticides are present in ground water throughout the sampled areas. Nitrate was detected in most samples, commonly at levels suggestive of anthropogenic sources. Ten percent of samples contained nitrate at concentrations greater than 10 mg/L, the MCL for drinking water. Pesticide compounds (including atrazine, metolachlor, prometon, simazine, and desethylatrazine, an atrazine degradate) were detected in about half of the samples for which they were analyzed; only one sample contained concentrations of any pesticide in excess of an MCL. Atrazine, the most commonly used pesticide in the Mid-Atlantic region, and desethylatrazine were the most commonly detected pesticide compounds.

Likely sources of nitrate and pesticides to ground water of the Mid-Atlantic region include urban and agricultural practices. Nitrate concentrations are higher in ground water in agricultural areas than in urban areas. Nitrate concentrations and pesticide-detection frequencies are statistically indistinguishable among ground-water samples from sites near row crops and pastures, possibly because of field rotation in agricultural areas. Detection frequencies of atrazine, desethylatrazine, and simazine are statistically indistinguishable among cropland, pasture, and urban areas, although the presence of pesticides in the few

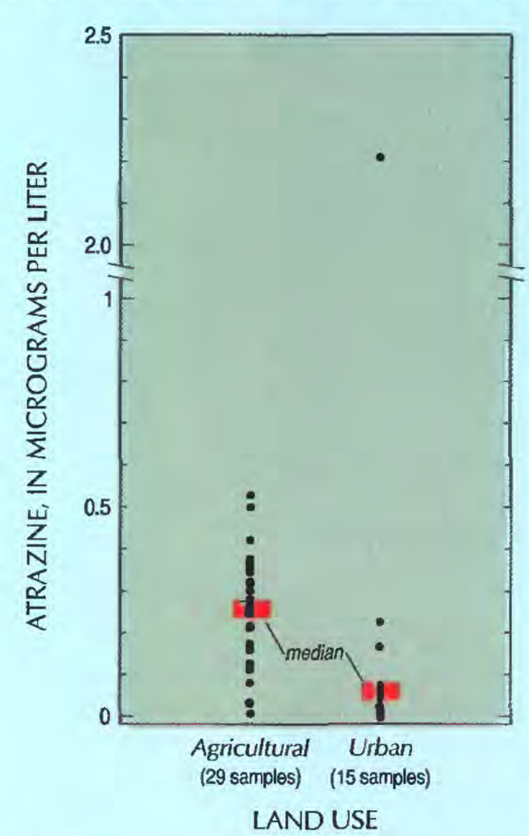

Figure 5. *Atrazine concentrations in samples from wells in carbonate aquifers near urban areas in the Lower Susquehanna Basin.*

[4]The conversion of nitrogen from nitrate to more reduced forms such as nitrous oxide, nitrogen gas, or, less commonly, ammonium (Freeze and Cherry, 1979).

urban sites included in this study may be related to the application of pesticides on surrounding agricultural land. Prometon was most often detected in urban areas. Nitrate concentrations and pesticide-detection frequencies in ground water of the region are lower in forested areas than in urban or agricultural areas.

The occurrence of nitrate and pesticides in ground water of the Mid-Atlantic region is related to rock type as well as to land cover. Rock type affects how quickly and easily surficial contaminants are transported through the ground and must be considered along with sources when analyzing the occurrence of these compounds in ground water. Areas underlain by carbonate rocks are particularly vulnerable to ground-water contamination because the relatively large solution cavities that are typical of these rocks allow for rapid movement of water throughout the ground-water system. Samples from carbonate-rock areas typically contained the highest detected nitrate and pesticide concentrations of any rock type in the Mid-Atlantic region. These concentrations are likely a result of the carbonate rock type as well as the intensive agricultural and urban development that is typical of carbonate-rock areas of the Mid-Atlantic region. Ground-water samples from crystalline rocks in the combined data set also contained higher concentrations of nitrate and pesticides than did those from unconsolidated or siliciclastic aquifers, although relatively few data from forested, crystalline areas were available for analysis.

A more thorough understanding of the occurrence of nitrate and pesticides in ground water of the Mid-Atlantic region could be obtained with further study. Spatial gaps in existing regional data include much of Virginia, northern and eastern Pennsylvania, and southern New York, although future sampling is planned in some of these areas. A random, unbiased sampling of ground water from various depths throughout the region, using consistent methods, would be necessary to conclusively compare nitrate and pesticide concentrations in ground water from different parts of the region. Constituent-concentration data from such a study would likely have consistent detection levels and therefore provide more statistical power for comparisons of water quality among land covers and rock types. Periodic sampling could clarify how ground-water nitrate and pesticide concentrations vary seasonally and over time.

REFERENCES CITED

Allaby, Michael, 1989, Dictionary of the environment (3d ed.): New York, New York University Press, 423 p.

Ator, S.W., and Denis, J.M., 1997, Relation of nitrogen and phosphorus in ground water to land use in four subunits of the Potomac River Basin: U.S. Geological Survey Water-Resources Investigations Report 96-4268, 26 p.

Barbash, J.E., 1995, Pesticides in ground water - current understanding of distribution and major influences: U.S. Geological Survey Fact Sheet FS-244-95, 4 p.

Barbash, J.E., and Resek, E.A., 1996, Pesticides in ground water: distribution, trends, and governing factors: Ann Arbor Press, Chelsea, Michigan, 588 p.

Battaglin, W.A., and Goolsby, D.A., 1994, Spatial data in a geographic information system format on agricultural chemical use, land use, and cropping practices in the United States: U.S. Geological Survey Water-Resources Investigations Report 94-4176, 87 p.

Bennison, A.P., comp, 1989, Geologic highway map of the Mid-Atlantic Region: Tulsa, Ok., The American Association of Petroleum Geologists, 1 sheet.

____, 1995, Geologic highway map of the Northeastern Region: Tulsa, Ok., The American Association of Petroleum Geologists, 1 sheet.

Bolton, D.W., 1996, Network description and initial water-quality data from a statewide ground-water-quality network in Maryland: Maryland Geological Survey Report of Investigations No. 60, 167 p.

Cardwell, D.H., Erwin, R.B., and Woodward H.P., comps., 1968 (slightly revised 1986), Geologic map of West Virginia: West Virginia Geological and Economic Survey, 2 sheets, scale 1:250,000.

Cleaves, E.T., Edwards, Jonathan, Jr., and Glaser, J.D. comps., 1968, Geologic map of Maryland: Maryland Geological Survey, 1 sheet, scale 1:250,000.

Freeze, R.A. and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, N.J., Prentice Hall, 604 p.

Gerhart, J.M., and Brakebill, J.W., 1997, Design and implementation of a sampling strategy for a water-quality assessment of the Potomac River Basin: U.S. Geological Survey Water-Resources Investigations Report 96-4034, 31 p.

Gianessi, L.P, and Puffer, C., 1990 (revised 1991), Herbicide use in the United States: Resources for the Future, Quality of the Environment Division, Washington, D.C., 128 p.

____1992a., Fungicide use in U.S. crop production: Resources for the Future, Washington, D.C., [variously paged]

____1992b., Insecticide use in U.S. crop production: Resources for the Future, Washington, D.C., [variously paged]

Hallberg, G.R., and Keeney, D.R., 1993, Nitrate, in Alley, W.M., ed., Regional ground-water quality: New York, Van Norstrand Publishing Company, p. 297-322.

Hamilton, P.A., Denver, J.M., Phillips, P.J., and Shedlock, R.J., 1993, Water-quality assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia — Effects of agricultural activities on, and distribution of, nitrate and other inorganic constituents in the surficial aquifer: U.S. Geological Survey Open-File Report 93-40, 87 p.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: New York, Elsevier Science Publishing Company, Inc., 522 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water Supply Paper 2254, 263 p.

Jones, D.R., and Sylvester, M.A., 1992, The national water-quality assessment (NAWQA) program: U.S. Geological Survey Open-File Report 92-145, 1 p.

King, P.B., and Beikman, H.M., 1974, Geologic map of the United States: U.S. Geological Survey, 3 sheets, scale 1:2,500,000.

Kozar, M.D., and Brown, D.P., 1995, Location and site characteristics of the ambient ground-water-quality-monitoring network in West Virginia: U.S. Geological Survey Open-File Report 95-130, 48 p.

Kozinski, Jane, Szabo, Zoltan, Zapecza, O.S., and Barringer, T.H., 1995, Natural radioactivity in, and inorganic chemistry of, ground water in the Kirkwood-Cohansey aquifer system, southern New Jersey, 1983-89: U.S. Geological Survey Water-Resources Investigations Report 92-4144, 130 p.

Madison, R.J., and Brunett, J.O., 1984, Overview of the occurrence of nitrate in ground water of the United States in national water summary 1984 — hydrologic events, selected water-quality trends, and ground-water resources: U.S. Geological Survey Water-Supply Paper 2275, p. 93-105.

Mathes, M.V., and Ward S.M., 1990, Water resources of the Elk River Basin, West Virginia: U.S. Geological Survey River Basin Bulletin 6, 37 p.

Meister Publishing Company, 1997, Farm Chemicals Handbook 97, Willoughby, Ohio, [variously paged].

Mueller, D.K, Hamilton, P.A., Helsel, D.R., Hitt, K.J., and Ruddy, B.C., 1995, Nutrients in ground water and surface water of the United States — An analysis of data through 1992: U.S. Geological Survey Water-Resources Investigations Report 95-4031, 74 p.

Puckett, L.J., 1995, Identifying the major sources of nutrient water pollution: Environmental Science and Technology, v. 29, no. 9, p. 408-414.

Sisterson, D.L., 1990, Detailed SOx-S and NOx-N mass budgets for the United States and Canada: in Venkatram, Akula, principal author, Relationships between atmospheric emissions and deposition/air quality: National Acid Precipitation Assessment Program Report 8, Appendix A, 10 p.

U.S. Environmental Protection Agency, 1990, National pesticide survey — Glossary: Washington,D.C., U.S. Government Printing Office, 7 p.

____ 1991, Fact Sheet: National primary drinking water standards: Washington, D.C., U.S. Government Printing Office, 8 p.

____1994, Pesticides industry sales and usage: 1992 and 1993 market estimates: EPA 733-K-94-001.

U.S. Department of Commerce, 1995, 1992 Census of Agriculture — Geographic Series 1B: Bureau of the Census, Washington, D.C.

Virginia Division of Mineral Resources, 1993, Geologic map of Virginia: Virginia Division of Mineral Resources, 1 sheet, scale 1:500,000.

Vogelmann, J.E., Sohl, T.L, Campbell, P.V., and Shaw, D.M, 1997, Regional land cover characterization using Landsat and other spatial data input [abs.]: Developing the tools to meet the Nation's monitoring needs — the evolution of EMAP, p. 10.

White, W.B., 1993, Analysis of karst aquifers, in Alley, W.M., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 471-489.

ACKNOWLEDGMENTS

Many people participated in the production of this report.Thoughtful reviews and comments were provided by Bruce Lindsey, Fred Tenbus, Mark Ayers, Tom Pheiffer, Chester Zenone, Pixie Hamilton, and Valerie Gaine. GIS maps were produced by Sarah Kelley. Layout and camera-ready illustrations were designed by Tim Auer. The authors also wish to thank the many people who collected, checked, and otherwise provided the data used in our analyses, without whom our work would have been impossible.

The preparation of this document has been funded wholly or in part by the EPA under assistance agreement DW14937692-01-0 to the USGS. The document has been subjected to the USGS publications review process, and was reviewed by representatives of the EPA Office of Research and Development.

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