

# RELATION OF PESTICIDE CONCENTRATIONS TO SEASON, STREAMFLOW, AND LAND USE IN SEVEN NEW JERSEY STREAMS



## Abstract

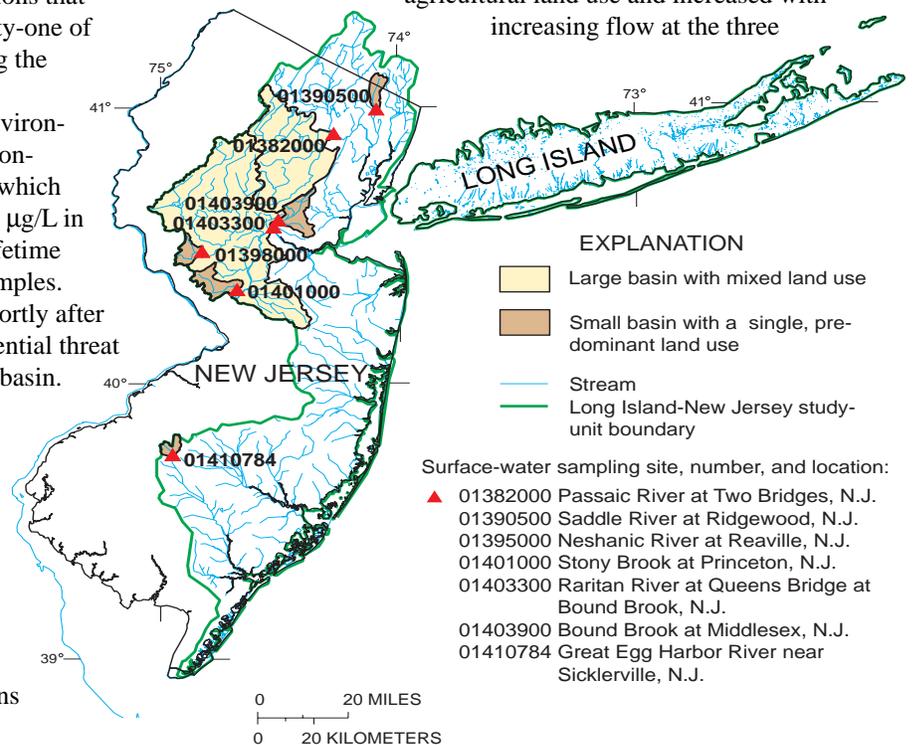
The presence and variability of pesticides in seven New Jersey streams was documented by analyzing 146 samples collected from the streams from April 1996 through June 1998. The samples were analyzed for 85 pesticides, including 50 herbicides, 28 insecticides, and 7 degradation products, at method detection limits that ranged from 0.001 to 0.018  $\mu\text{g/L}$  (micrograms per liter). Pesticides were frequently detected; however, concentrations were generally low. The pesticides most frequently detected were atrazine, in 97 percent of the samples; prometon, 96 percent; metolachlor, 95 percent; desethyl-atrazine, 91 percent; simazine, 88 percent; diazinon, 58 percent; alachlor, 56 percent; and carbaryl, 54 percent. Detection frequencies were highest during the growing season (April-September). At least one pesticide was detected in all but one of these samples, and 49 percent of the samples contained 9 or more pesticides. The numbers of pesticides detected at a given site ranged from 13 to 29.

Ten pesticides were detected at concentrations that exceeded established water-quality criteria. Thirty-one of these detections were in samples collected during the growing season and one during the nongrowing season. The pesticides that exceeded the U.S. Environmental Protection Agency (USEPA) maximum contaminant level for drinking water were atrazine, which exceeded 3  $\mu\text{g/L}$  in four samples, and alachlor, 2  $\mu\text{g/L}$  in two samples. Cyanazine exceeded the USEPA lifetime health advisory level (HAL) of 1  $\mu\text{g/L}$  in two samples. These eight detections occurred during runoff shortly after spring pesticide applications and represent a potential threat to municipal water supplies in the Raritan River basin. Concentrations of chlorpyrifos, chlorthalonil, diazinon, ethyl-parathion, and methyl-azinphos exceeded the chronic life criteria for the protection of aquatic life (AQCR) in 20 samples at four sites during the growing season. Dieldrin was detected in four samples and DDE in two samples at concentrations that exceeded New Jersey Department of Environmental Protection (NJDEP) human health criteria.

Individual and total-pesticide concentrations and total numbers of pesticides detected in the samples varied with season and flow conditions. Median and maximum concentrations of most of the pesticides were highest during runoff in

the growing season. Pesticide concentrations were typically lower and less variable in the nongrowing season than in the growing season, regardless of changes in hydrologic conditions; however, median concentrations of most pesticides were slightly lower during runoff than during base flow. The median total-pesticide concentration and median total number of pesticides detected were highest and most variable in runoff samples in the growing season. In the nongrowing season, the median total-pesticide concentration was lowest in runoff samples and least variable during base-flow conditions. Median total numbers of pesticides were lowest and least variable in the nongrowing season during base-flow conditions at most sites.

The highest total-pesticide concentrations were detected in samples from the two small agricultural basins (greater than 25 percent of land use is agricultural) during runoff in late spring and early summer. In general, insecticides were detected more frequently and in greater concentrations at urban sites. Concentrations of agricultural herbicides generally decreased with increasing flow at the four sites with less than 10 percent agricultural land use and increased with increasing flow at the three



**Figure 1.** Locations of seven stream sites sampled for pesticides from April 1996 through June 1998.

sites with more than 25 percent agricultural land use. Most of the pesticides that correlated positively with streamflow were detected at sites where land use in the basin would indicate the use of those particular pesticides. Most of the pesticides that correlated negatively with streamflow were present at the site in the Coastal Plain or at sites in which the land use in the basin would not indicate heavy use of those particular pesticides.

## Introduction

The U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) program is designed to assess the status of the Nation's water quality, describe trends in water quality, and provide a sound scientific understanding of the primary natural and human factors that affect the quality of the Nation's water resources (Gilliom and others, 1995). One component of the NAWQA program is the study of pesticides to determine their presence, concentrations, and seasonal variability in surface and ground water.

The Long Island-New Jersey coastal drainages study unit (LINJ), one of 59 areas studied as part of the NAWQA program, includes all of Long Island, New York, and New Jersey, except for those areas that drain to the Delaware and Hudson River basins (fig. 1). The 6,000-square-mile study area has a population of more than 10 million people (U.S. Bureau of the Census, 1991) and includes one of the most densely populated areas in the United States. In 1990, 44 percent of the land in the study area was used for residential, commercial, and industrial purposes; 30 percent was forested; 12 percent was used for agriculture; 8 percent was wetlands; and 6 percent was classified as miscellaneous. (Percentages were modified from Fegas and others, 1983, by using the method described by Hitt, 1994.)

The purpose of the study described here was to determine the presence and distribution of dissolved pesticides in seven streams in the LINJ NAWQA study area and to evaluate the variability in concentrations of the pesticides by season, streamflow, and land use. Total numbers and total concentrations of pesticides were included in this study to evaluate the presence and distribution of multiple pesticides. The synergistic effects of multiple pesticides on human and aquatic health is an area of active research. The U.S. Environmental Protection Agency (USEPA) is considering establishing health standards for combinations of triazine pesticides (U.S. Environmental Protection Agency, 1994).

## Purpose and Scope

This report documents the presence and distribution of dissolved pesticides in seven streams in the LINJ NAWQA study area and evaluates the variability in concentrations by season, streamflow, and land use. The results of analyses of 146 stream-water samples collected at the seven sites during April 1996 through June 1998 are presented. Samples from four stream sites were collected only in the growing season (April through September). Samples at the other three sites were collected during both the growing and nongrowing seasons (October through March). Concentrations were determined for 85 pesticides. Total number of pesticides and total concentrations of pesticides were evaluated to determine the presence of multiple pesticides.

## Pesticide Use

Pesticides are chemical substances and biological agents used to control pests. The pesticides analyzed in this study include classes of synthetic organic insecticides, herbicides, and fungicides widely used in the United States. Approximately 1.1 billion pounds of pesticides are used annually in the United States (Ware, 1994). Pesticides are used primarily for agriculture, lawn care, golf course maintenance, termite control, and right-of-way maintenance. In 1991, 76 percent of the pesticides sold in the United States were used for agricultural purposes. Industry and government use represented 18 percent and home and garden use represented 6 percent of total sales (Ware, 1994). The use of herbicides has quadrupled during 1966-91 (Larson and others, 1997).

In New Jersey, licensed applicators applied approximately 2.4 million pounds of pesticides per year during 1992-95 (Curtis Brown, New Jersey Department of Environmental Protection, Pesticide Control Program, written commun., 1992-95). Agricultural use accounted for about 66 percent of the total use in New Jersey. The herbicides atrazine and alachlor were the most heavily applied pesticides in the United States during 1990-91 (Ware, 1994), but ranked sixth and seventh, respectively, in their use in New Jersey. The fungicide chlorthalonil was the most heavily applied pesticide in New Jersey, of those analyzed in this study, but ranked 13th nationwide.

Sixteen of the 25 most heavily applied pesticides used for agriculture and 7 of the top 10 pesticides used for nonagricultural uses in the United States were analyzed for in this study. Some of the most heavily applied pesticides in New Jersey that were not analyzed for in this study include metam sodium, a fumigant; sodium aluminofluoride, an insecticide; glyphosate, a herbicide; and mancozeb, a fungicide.

The herbicides most commonly used in New Jersey, and which were analyzed for in this study, are metolachlor, atrazine, and alachlor used for agriculture; pendimethalin, benfluralin, and trifluralin used for professional lawn care; DCPA, pendimethalin, and benfluralin used for golf courses; and diuron, 2,4-D, and simazine used for weed control along transportation and utility rights-of-way. The most commonly used insecticides analyzed for in this study are methyl-azinphos, carbaryl, and chlorpyrifos used for agriculture; chlorpyrifos, carbaryl, and fonofos used for professional lawn care; chlorpyrifos, carbaryl, and ethoprop used on golf courses; chlorpyrifos and permethrin used for termite control; and malathion and permethrin used for mosquito control. Chlorthalonil, the fungicide most heavily used in lawn care and on golf courses and the most heavily used in agriculture, second to sulfur, was the only fungicide analyzed for in this study. Eight pesticides—acetochlor, alachlor, carbofuran, linuron, methyl-azinphos, metribuzin, pebulate, and terbacil—are used only in agriculture (Curtis Brown written commun., 1992-95).

Pesticide use has significantly increased agricultural productivity, benefiting both farmers and consumers. At the same time, potential adverse effects of pesticides on nontarget organisms and the environment, in general, have become a concern. Organochlorine insecticides such as DDT and dieldrin were banned from use in the United States in 1973 and 1984, respectively, because of bioaccumulation in the foodchain and related adverse health effects on nontarget organisms (Harte and

others, 1991). Some organochlorine insecticides were replaced by less persistent and more water-soluble organophosphate and carbamate pesticides. The higher solubility of the insecticides and herbicides currently used reduces the risk of accumulation in sediments and the food chain, but increases the risk of widespread low levels of dissolved pesticides entering surface- and ground-water systems.

## Previous Investigations

Two previous investigations of pesticides in surface water in the study area focused on relatively small areas. A study of pesticides from agricultural runoff in six New Jersey drainage basins detected low-level concentrations of 10 of the 21 pesticides targeted for analysis (Ivahnenko and Buxton, 1994). Six drainage basins used for public-water supply and considered the most susceptible to pesticide contamination were chosen for study, including Lower Mine Hill Reservoir, South Branch of the Raritan River, the main branch of the Raritan River, Millstone River, Manasquan River, and Matchaponix Brook. All but Lower Mine Hill Reservoir basin lie within the LINJ study unit. Although atrazine and metolachlor were detected in 86 percent of the samples, alachlor in 55 percent, and diazinon in 45 percent, only one concentration, in the 28 samples collected, exceeded the U.S. Environmental Protection Agency (USEPA) recommended Lifetime Health Advisory Limit. Atrazine and metolachlor were detected in the highest concentrations during storms.

The second study assessed the vulnerability of public water supplies to contamination by 20 pesticides in the Millstone and Shark River basins (Buxton and Dunne, 1993). In the Millstone River, the 4 pesticides detected in 8 base-flow and 24 stormflow samples were atrazine, in 66 percent of samples; simazine, in 47 percent; metolachlor, in 38 percent; and alachlor, in 16 percent. No pesticides were detected in 8 base-flow and 13 stormflow samples from Shark River. The method detection limit (MDL) for most pesticides analyzed for in these studies was 0.03 µg/L (micrograms per liter). The MDL's in the present study ranged from 0.001 to 0.03 µg/L.

A study of pesticide data from 463 surface-water sites in the Mid-Atlantic region (Ferrari and others, 1997) detected at

least one compound at more than 90 percent of the sites and frequently detected 16 pesticides, 3 at concentrations greater than the USEPA's maximum contaminant level (MCL).

The LINJ NAWQA project has recently completed two studies of pesticides in surface water and ground water of New Jersey and Long Island, New York. Water-quality data from a 50-site surface-water synoptic network sampled in June 1997 were used to compare pesticide concentrations to land use and pesticide application (Reiser and O'Brien, 1998). Median pesticide concentrations and detection frequencies of some pesticides were related to land use. The 10 most frequently detected pesticides in the synoptic study were also the most frequently detected in this study. Analysis of samples from a network of 72 monitoring wells in southern New Jersey indicated that the 5 most frequently detected pesticides in ground water (Stackelberg and others, 1997) were also the 5 most frequently detected in the 50 stream-water samples.

## Study Approach

### Selection of Sampling Sites and Sampling Frequency

Seven stream sites were chosen to represent the variety of land uses, physiographic settings, and other drainage-basin characteristics in the study area (fig. 1; table 1). Five of the sites, all in New Jersey, were chosen to represent water-quality conditions in small basins (less than 50 mi<sup>2</sup>) associated with specific types of land use and physiography. Four of these five sites are in the Piedmont physiographic province; the Great Egg Harbor River site is in the Coastal Plain physiographic province. The Saddle River at Ridgewood site represents a drainage basin that consists predominantly of suburban residential land. The Bound Brook at Middlesex site represents a largely urban drainage basin with older residential, commercial, and industrial areas. Agriculture is the dominant land use in the drainage basin representing the Neshanic River at Reaville site. The Stony Brook at Princeton site represents a basin in transition from a predominantly forested and agricultural area to a suburban residential area. The Great Egg Harbor River near Sicklerville site represents a drainage basin with urban land use in the

**Table 1.** Drainage Basin Characteristics and Sampling Frequency

[1986 Land-use data from New Jersey Department of Environmental Protection, 1996; USGS, U.S. Geological Survey; mi<sup>2</sup>, square miles]

USGS site name	USGS site number	Drainage area (mi <sup>2</sup> )	Number of samples collected		Land use (in percent)				
			Schedule 2001	Schedule 2050	Urban		Forest	Agriculture	Other
					Residential	Non-residential			
Passaic River at Two Bridges, N.J.	01382000	361	8	3	32	15	35	3	15
Saddle River at Ridgewood, N.J.	01390500	21.6	9	5	75	11	11	2	1
Neshanic River at Reaville, N.J.	01398000	25.7	7	5	15	4	27	53	1
Stony Brook at Princeton, N.J.	01401000	44.5	8	5	18	5	46	28	3
Raritan River at Queens Bridge at Bound Brook, N.J.	01403300	804	28	25	19	6	35	30	10
Bound Brook at Middlesex, N.J.	01403900	48.4	44	41	50	23	25	1	1
Great Egg Harbor River near Sicklerville, N.J.	01410784	15.1	46	39	24	8	43	10	15

Coastal Plain. Samples were collected more frequently at the Bound Brook and Great Egg Harbor River sites than at the other sites to investigate the effects of urban land use in relatively small basins in the two major physiographic provinces in the study area (Piedmont and Coastal Plain).

Two of the sites, Passaic River at Two Bridges and Raritan River at Bound Brook, were chosen to represent large drainage areas that integrate the effects of many different types of land uses, physiographic settings (Piedmont, Coastal Plain, and New England), and point-source discharges. No streams on Long Island were chosen for sampling because surface water on the island is not used as a source of public supply and because samples were collected during synoptic studies (O'Brien and others, 1998; Reiser and O'Brien, 1998).

Surface water was sampled at fixed intervals for pesticides at the Bound Brook, Great Egg Harbor River, and Raritan River sites during April 22, 1996, to June 9, 1998. Additional samples were collected during storms. Samples for pesticide analysis were collected monthly only in the growing season of 1996 and once in June 1997 at the Passaic River, Saddle River, Neshanic River, and Stony Brook sites. The data from these samples are available in Reed and others (1997-98) and DeLuca and others (1999).

## Field and Laboratory Methods

Stream samples were collected in teflon bottles using the equal-width-increment (EWI) sampling method (Edwards and Glysson, 1988). The samples were split into equal aliquots by using a teflon cone splitter (Capel and others, 1995). Samples were filtered at the site by using baked glass-fiber filters with 0.7-millimeter pore diameter to remove suspended particulate matter and were shipped on ice to the USGS National Water Quality Laboratory (NWQL).

All 146 samples were analyzed for the 47 pesticides listed in laboratory schedule 2001, which includes 25 herbicides, 20 insecticides, and two degradation products, (Zaugg and others, 1995) as well as nutrients, major ions, suspended sediment, dissolved organic carbon, and suspended organic carbon. An additional 41 pesticides listed in laboratory schedule 2050, which includes 25 herbicides, 10 insecticides, 5 degradation products, and 1 fungicide (Werner and others, 1996) were analyzed for in 119 of the 146 samples. Three pesticides analyzed for are in both schedules, but only concentrations obtained by using the schedule 2001 method are used in this study because this method can detect these pesticides at lower concentrations. The 41 pesticides from schedule 2050 were analyzed for in 91 of the 119 samples collected during the growing season and in all 27 samples from the nongrowing season.

NWQL used C-18 solid-phase extraction (SPE) columns to remove 47 pesticides and metabolites from the filtered water samples by using schedule 2001 methods. The SPE columns were eluted with hexane-isopropanol (3:1). The eluant was evaporated by using a gentle stream of nitrogen. Extracts of the SPE column eluant were analyzed by a capillary-column gas-chromatograph/mass spectrometer operated under a selected-ion monitoring mode (Zaugg and others, 1995).

NWQL uses a 0.5-gram Carboxpak-B graphitized carbon-based SPE cartridge to extract an additional 41 pesticides from the filtered water samples designated for schedule 2050 analysis. Two extract fractions, one containing the adsorbed base and

neutral pesticides and the second containing the acidic pesticides, were eluted from the SPE cartridge. High performance liquid chromatography using ultraviolet spectrometry was performed on each fraction to detect, identify, and quantify the 41 compounds (Werner and others, 1996).

The NWQL techniques allow for the accurate detection and quantification of pesticides at minimum concentrations ranging from 0.001 to 0.018  $\mu\text{g/L}$  for the 47 schedule-2001 pesticides and 0.011 to 0.05  $\mu\text{g/L}$  for an additional 41 schedule-2050 pesticides. Results from the laboratory were censored when concentrations could not be accurately determined because of analytical and other limitations. "Less than" values are reported when a pesticide is either not detected or is not present at a concentration that can be identified and measured by NWQL analytical procedures. Estimated values "E" are reported when the presence of a compound is certain, but there is decreased confidence in accurate quantitation. Four pesticides, azinphos-methyl, carbaryl, carbofuran, and desethylatrazine, were always estimated because of variable quantification performance (Zaugg and others, 1995). For statistical purposes, estimated concentrations were considered to be the same as non-estimated concentrations.

## Quality Assurance

Quality-assurance samples were collected to evaluate the reliability and reproducibility of the data. Three types of quality-assurance samples were evaluated—blanks, replicates, and spikes. Results of 12 field-equipment blank samples documented that no systematic contamination occurred during sampling and processing of the samples. Only 1 of the 12 blank samples had a single detection of a pesticide (0.004  $\mu\text{g/L}$  of trifluralin).

Seven sets of split replicate samples were used to evaluate the reproducibility of the analytical techniques. The environmental and replicate samples were collected and processed simultaneously. Ninety-six percent of the detections occurred in both the environmental and replicate samples. Two detections in the environmental samples were not found in the paired replicates. One pesticide found in a replicate sample was not found in the paired environmental sample. The detected concentrations were within 0.008  $\mu\text{g/L}$  of the MDL. Differences in concentrations detected in both the environmental and replicate samples varied from no difference to 20 percent difference. Environmental and replicate samples with the greatest percentage of difference were those with the lowest pesticide concentrations and differences less than or equal to 0.005  $\mu\text{g/L}$ .

Split spiked samples were used to evaluate potential bias and the ability of the analytical technique to recover analytes from the water-sample matrix. Six spiked environmental samples were analyzed for schedule 2001 pesticides, and five samples were analyzed for schedule 2050 pesticides. The mean percent recoveries for schedule 2001 pesticides ranged from 75 to 150 percent, except for carbaryl which had a mean recovery of 213 percent. The mean percent recoveries for most of the schedule 2050 pesticides detected in this study ranged from 34 to 95 percent; however, aldicarb, which degrades rapidly, had a mean percent recovery of only 7 percent. The degradation products of aldicarb, aldicarb sulfone and aldicarb sulfoxide, had recoveries of 14 and 58 percent, respectively. These results indicated that the schedule 2050 method provides a very conservative estimate of compound concentrations and detection frequencies.

Three pesticides—carbaryl, carbofuran, and linuron—were measured by using both schedule 2001 and schedule 2050 methods. These pesticides were detected more frequently by the 2001 method, which uses an analytical laboratory technique with lower detection levels. The results from the 2001 method are used in this study.

## Statistical Methods

Water samples were categorized by the season and the hydrologic condition in which they were collected. The growing season is April through September, and the nongrowing season is October through March. All samples were grouped into one of two flow categories, base flow or runoff. During base flow, most of the flow in the stream is contributed by water coming out of storage, from lakes, wetlands, and ground-water sources. A sample was considered to be collected during base-flow conditions if flow in the stream did not increase by more than 5 percent from the previous day and if decreases in flow from the previous day were less than 15 percent. This is a rather strict definition of base flow; with this definition some flow conditions are considered runoff that would otherwise be considered base flow when using base-flow separation techniques. A sample was considered to be collected during runoff if the definition of base flow was not met.

To make unbiased comparisons between pesticides, detection frequencies were computed using (1) all pesticide-concentration data and (2) only those pesticide concentrations that exceeded a common threshold of 0.01  $\mu\text{g/L}$ . All pesticide concentration values were censored to 0.01  $\mu\text{g/L}$  because this is a level higher than the MDL for all but four pesticides. Detections of these pesticides below the MDL is common; therefore, potential bias is minimized. Contingency table analysis was used to determine whether detection frequencies at a site were dependent on season or flow condition (Helsel and Hirsch, 1992). Contingency tables also were used to determine whether the number of detections of a pesticide at a site was significantly different among sites. The chi-square test was used to determine significance when the number of expected detections in each category was greater than five. The Fischer's exact test was used when expected detections were less than or equal to five. A significance level of 0.05 was used for this study.

The median and 90th percentile concentrations were used to summarize the data and to make comparisons at each site and among sites by season, flow, and land use. Total-pesticide concentrations in each sample were computed by adding the concentrations of each detected compound and by assigning a concentration of 0  $\mu\text{g/L}$  to all censored values. The inner quartile range (IQR) was used to measure the variability of pesticide concentrations. It measures the range of the central 50 percent of the data and is defined as the 75th percentile minus the 25th percentile (Helsel and Hirsch, 1992). IQR was used instead of variance or standard deviation because it is not influenced by outliers.

One-way analysis of variance (ANOVA) was applied to the ranks of pesticide concentrations to determine whether median concentrations varied among sites by season and flow condition, and whether concentrations at a single site varied by seasons and flow conditions. The null hypothesis ( $H_0$ ) states that mean rank concentrations are equal at each site. The alternate hypothesis states that the mean rank concentration from at least

one site differs from the others. If the null hypothesis is rejected, Tukey's test was used to determine which pairs of mean rank concentration were significantly different at the 0.05 level. Tukey's groups are represented by letters A through C. Sites in group A have the highest mean rank concentration, and those in groups B through C have successively lower rank concentrations. Sites containing one or more of the same letters do not differ significantly (Helsel and Hirsch, 1992).

Multivariate ANOVA (MANOVA) was applied to ranks of pesticide concentrations to simultaneously test the significance of season, flow, and land use as factors contributing to concentrations and numbers of pesticides. MANOVA also was applied to ranks of pesticide concentrations to simultaneously test the significance of season, flow, and season as a function of flow as factors contributing to concentrations and numbers of pesticides at each of the three sites sampled in both seasons.

Relations between instantaneous streamflow and concentration were analyzed at each of the sites. Pesticides detected in more than 50 percent of the samples from a site were analyzed by using tobit regression (Cohn, 1988). The tobit method uses censored data to develop the relation. If censored data accounted for more than 50 percent of the values at a site, the results are not considered reliable and are not discussed in this report. The relation was considered to be significant if the slope of the regression line was different from zero at the 0.05 level of significance. A base-10 logarithm transformation of streamflow was used to normalize the data before using tobit regression.

## Presence and Distribution of Pesticides

Pesticides were detected in 145 of the 146 samples collected from April 1996 through June 1998. Forty-one of the 85 pesticides analyzed for were detected in these samples. More than 97 percent of the samples contained at least five pesticides, and 49 percent contained nine or more pesticides. Detection frequency and median, 90th percentile, and maximum concentrations of detected pesticides from all environmental samples collected are listed in table 2, along with USEPA MCL's and other water-quality criteria. The 44 pesticides not detected in any of the samples are listed in table 3.

## Water-Quality Criteria

Water-quality criteria have been established for 33 of the 41 pesticides detected (table 2). The USEPA has established human-health criteria, including MCL's, health advisory levels (HAL's) for lifetime exposure, and (or) a risk-specific dose (RSD) for drinking water for 30 of the 41 pesticides detected. The NJDEP has established human health criteria (HHC's) for dieldrin and DDE. Water-quality criteria for the protection of aquatic life were established for 21 of the detected pesticides by either the USEPA, NJDEP, Canadian Council of Resource and Environment Ministers, or International Joint Commission of Canada and the United States.

Ten pesticides, including 6 insecticides, 3 herbicides, and 1 fungicide, were detected at concentrations that exceeded established water-quality criteria. Eight pesticides were detected at concentrations that exceeded USEPA drinking-water standards or chronic life criteria for the protection of aquatic life (AQCR), and two pesticides were detected at concentrations that exceeded

**Table 2.** Pesticides detected in samples collected from seven streams in New Jersey April 1996 through June 1998

[Data containing an E suffix are included in the data set of detected values used for statistical analysis. MDL, Method Detection Limit (values listed in parentheses have an increased detection limit as of Dec. 15, 1997; EPA MCL, drinking-water maximum contaminant level (U.S. Environmental Protection Agency, 1996); EPA HAL, health-advisory level, 70 kg adult, lifetime (U.S. Environmental Protection Agency, 1996); NJ HHC, New Jersey human health criteria, (New Jersey Department of Environmental Protection, 1998). Water-quality criteria for aquatic life are as follows: EPA, U.S. freshwater chronic criteria for aquatic life (U.S. Environmental Protection Agency, 1995); EPA2, U. S. freshwater chronic aquatic life criteria (U.S. Environmental Protection Agency, 1991); CAN, Canadian water-quality guidelines (Canadian Council of Resource and Environment Ministers, 1991); GL, Great Lakes Water Quality Objective (International Joint Commission Canada and United States, 1977); RSD5, risk-specific dose at level  $1 \times 10^{-5}$  (U.S. Environmental Protection Agency, 1996); NJ, New Jersey freshwater water quality criteria (New Jersey Department of Environmental Protection, 1998);  $\mu\text{g/L}$ , micrograms per liter; --, criteria do not exist; LD, less than the MDL; E, estimated value; %, percent; #, number; \*, compounds analyzed in only 119 of the 146 samples collected (Schedule 2050); Red, number of detections exceeding criteria; Blue, pesticides not currently applied by licensed applicators in New Jersey.

Compound name	Trade name	MDL ( $\mu\text{g/L}$ )	Detection frequency, % (#)	Median concentration of all samples ( $\mu\text{g/L}$ )	90th percentile of all samples	Maximum concentration detected ( $\mu\text{g/L}$ )	Site of maximum concentration	MCL, HAL, or HHC ( $\mu\text{g/L}$ ), (# in exceedance)	Aquatic Life Criterion ( $\mu\text{g/L}$ )(# in exceedance)
Atrazine	AAtrex, Crisazina	0.001	97 (141)	0.025	0.12	10E	Stony Brook	3 EPA MCL (4)	2 CAN (4)
Prometon	Pramitol, Princep	0.018	96 (140)	0.020	0.06	0.10	Bound Brook	100 EPA HAL	--
Metolachlor	Dual, Pennant	0.002	95 (139)	0.019	0.152	5.2E	Raritan River	70 EPA HAL 50	8 CAN
Atrazine, Desethyl (Atrazine metabolite)		0.002	91 (133)	0.007E	0.034	0.25E	Stony Brook	--	--
Simazine	Aquazine, Princep	0.005	88 (129)	0.009	0.024	0.51	Stony Brook	4 EPA MCL	10 CAN
Diazinon	D.z.n., Sarolex	0.002	58 (84)	0.003	0.063	0.30	Bound Brook	0.6 EPA HAL 50	0.08 GL (12)
Alachlor	Lasso, Bullet	0.002	56 (82)	0.004	0.017	4.7E	Stony Brook	2 EPA MCL(1)	--
Carbaryl	Sevin, Carbamine	0.003	54 (79)	0.008	0.157	1.5E	Bound Brook	700 EPA HAL	--
DCPA	Dacthal	0.002	36 (53)	LD	0.004	0.012	Raritan River	--	--
Chlorpyrifos	Genpest, Eradex	0.004	31 (45)	LD	0.015	0.064	Saddle River	20 EPA HAL	0.041 EPA2 (2)
Diuron	DCMU, Karmex	0.020	*27 (32)	LD	0.17	1.2E	Raritan River	10 EPA HAL	--
Trifluralin	Treflin, Tri-4	0.002	26 (38)	LD	0.005	0.015	Saddle River	5 EPA HAL	0.1 CAN
Tebuthiuron	Spike, Tebusan	0.010	25 (37)	LD	0.008	0.075	Bound Brook	500 EPA HAL	1.6 CAN
2,4-Dichlorophenoxy acetic acid	2,4 D, Lawn-keep, Auqa Kleen	0.035 (0.15)	*20 (24)	LD	0.32	1.7E	Stony Brook	70 EPA MCL	4 CAN
Cyanazine	Bladex, Fortrol	0.004	19 (28)	LD	0.015	1.9E	Stony Brook	1 EPA HAL (2)	2 CAN
Pendimethalin	Prowl, Stomp	0.004	15 (22)	LD	0.012	0.046	Raritan River	--	--
Carbofuran	Furandan, Yaltox	0.003	13 (19)	LD	0.008	0.064E	Raritan River	40 EPA MCL	1.75 CAN
Chlorothalonil	Bravo, Exotherm	0.030 (0.48)	*13 (15)	LD	0.007	0.710E	Great Egg Harbor River	15 RSD5	0.18 CAN (3)
Benfluralin	Benefin, Balan, Bonalan	0.002	12 (18)	LD	0.003	0.007	Bound Brook	--	--
Acetochlor	Harness, Plus	0.002	1 (16)	LD	0.008	4.7	Stony Brook	--	--
Metribuzin	Lexon, Sencor	0.004	8.9 (13)	LD	LD	0.11	Raritan River	100 EPA HAL	1.0 CAN
Malathion	Cythion	0.005	8.9 (13)	LD	LD	0.078	Bound Brook	200 EPA HAL	0.1 EPA2
Fluometuron	Flo-Met, Cotoran	0.035	*3.4 (4)	LD	LD	0.11E	Raritan River	90 EPA HAL	--
Fonofos	Dyfonate, Tycap	0.008	3.4 (5)	LD	LD	0.054	Bound Brook	10 EPA HAL	--
Dieldrin	Panoram D-31, Octalox	0.001	2.7 (4)	LD	LD	0.005	Saddle River	0.02 RSD5 0.000135 NJ HHC (4)	0.0625 EPA2 0.0019 NJ (4)
4-Chloro-2-methylphenoxy acetic acid	MCPA, Metaxon	0.050 (0.17)	*2.5 (3)	LD	LD	0.20	Bound Brook	10 EPA HAL	2.6 CAN
Linuron	Lorex, Linex	0.002	2.1 (3)	LD	LD	0.62	Stony Brook	--	7 CAN
Napropamide	Devrinol	0.003	2.1 (3)	LD	LD	0.019	Raritan River	--	--
Azinphos,Methyl-	Guthion	0.001	1.4 (2)	LD	LD	0.039E	Great Egg Harbor River	--	0.01 EPA2 (1)
HCH, gamma-	Lindane	0.004	1.4 (2)	LD	LD	0.014	Bound Brook	0.2 EPA MCL	0.08 EPA2
DDE,p,p-		0.006	1.4 (2)	LD	LD	0.003E	Raritan River	0.1 RSD5 0.000588 NJ HHC (2)	0.000588 NJ (2)
Acifluorfen	Blazer, Tackle 2S	0.035	*0.8 (1)	LD	LD	0.130	Raritan River	10 RSD5	--
Aldicarb	Temik, Ambush	0.016 (0.55)	*0.8 (1)	LD	LD	0.130	Bound Brook	7 EPA MCL	1.0 CAN
Bentazon	Basagran, Bentazone	0.014	*0.8 (1)	LD	LD	0.070	Stony Brook	200 EPA HAL	--
Bromocil	Bromax, Urox B	0.035	*0.8 (1)	LD	LD	0.050	Bound Brook	90 EPA HAL	--
Dicamba	Banval, Dianat	0.035	*0.8 (1)	LD	LD	0.040	Bound Brook	200 EPA HAL	10 CAN
Molinate	Ordram	0.004	0.7 (1)	LD	LD	0.017	Neshanic River	--	--
Parathion, Ethyl-	Roethyl-P, Alkron	0.004	0.7 (1)	LD	LD	0.018	Bound Brook	--	0.013 EPA2 (1)
Propachlor	Ramrod, Satecid	0.007	0.7 (1)	LD	LD	0.018	Bound Brook	90 EPA HAL	--
Propanil	Stampede, Wham	0.004	0.7 (1)	LD	LD	0.005	Raritan River	--	--
Terbufos	Counter, Pilarfox	0.013	0.7 (1)	LD	LD	0.033	Bound Brook	0.9 EPA HAL	--

NJDEP HHC's and (or) AQCR's. Thirty-two detections in samples collected during April 23, 1996, to August 22, 1996; May 26, 1997 to July 25, 1997; and November 11, 1997, exceeded criteria. There were 10 detections at concentrations greater than USEPA and NJDEP human health criteria—MCL's, HAL's, and HHC's—and 22 detections at concentrations greater than USEPA and NJDEP AQCR's (table 2) in the 146 samples collected. Seven detections of herbicides exceeded the criteria and 12 detections of the insecticide diazinon exceeded the criteria; all were present in samples collected during runoff events. Eight of 10 detections of the other 5 insecticides that exceeded criteria occurred during base-flow conditions. Two of the three detections of the fungicide chlorthalonil that exceeded a criterion occurred during base-flow conditions.

Concentrations of atrazine, alachlor, and cyanazine exceeded the USEPA human health criteria in samples collected during runoff shortly after spring applications of these pesticides; these concentrations represent a potential threat to municipal water supplies in the Raritan River basin. Concentrations of alachlor, atrazine, and cyanazine exceeded HHC at three sites in the basin. Concentrations of atrazine exceeded the USEPA's MCL (3.0 µg/L) in four samples collected during runoff in June 1996 and May 1997 from the Neshanic River, Stony Brook, and Raritan River sites. The concentration of alachlor exceeded the MCL (2.0 µg/L) in one sample collected during runoff in June 1996 at the Stony Brook site. Concentrations of cyanazine exceeded the HAL (1.0 µg/L) in two samples collected during runoff in June 1996 and May 1997, one at the Stony Brook site and one at the Raritan River site.

Concentrations of chlorpyrifos, chlorthalonil, diazinon, ethyl-parathion, and methyl-azinphos exceeded AQCR's in samples from four sites. Diazinon exceeded the Great Lakes Water Quality Objective (GL) AQCR of 0.08 µg/L in 10 samples collected during runoff conditions during June and July 1996 and 1997, and September 1996 at the Bound Brook site and in 2 samples collected during runoff conditions in July 1996 and 1997 at the Raritan River site. Chlorthalonil exceeded the Canadian fresh-water chronic aquatic-life criteria of 0.18 µg/L in two samples collected in July 1997 samples—one during base flow and one during runoff—at Bound Brook and in one July 1997 base-flow sample at Great Egg Harbor River. Chlorpyrifos exceeded the USEPA criteria of 0.041 µg/L in a June base-flow sample at Saddle River and a June runoff sample at Bound Brook. Ethyl-parathion exceeded the EPA AQCR (0.013 µg/L) in an April base-flow sample at Bound Brook. Methyl-azinphos exceeded the EPA AQCR (0.01 µg/L) in a June base-flow sample at Great Egg Harbor River.

Dieldrin was detected in four samples and DDE in two samples at concentrations that exceeded NJDEP human health criteria; because the MDL is greater than the HHC, other samples also may have exceeded the criteria. Dieldrin concentrations exceeded the HHC (0.000135 µg/L) and the AQCR (0.0019 µg/L) in four samples collected during base flow during May 30 to August 22, 1996, three samples at the Saddle River site and one at the Stony Brook site. DDE concentrations exceeded the HHC (0.000588 µg/L) in two samples, one collected during the receding limb of the hydrograph in August 1996 at the Raritan River site and one collected during base-flow conditions in November 1997 at the Great Egg Harbor River site.

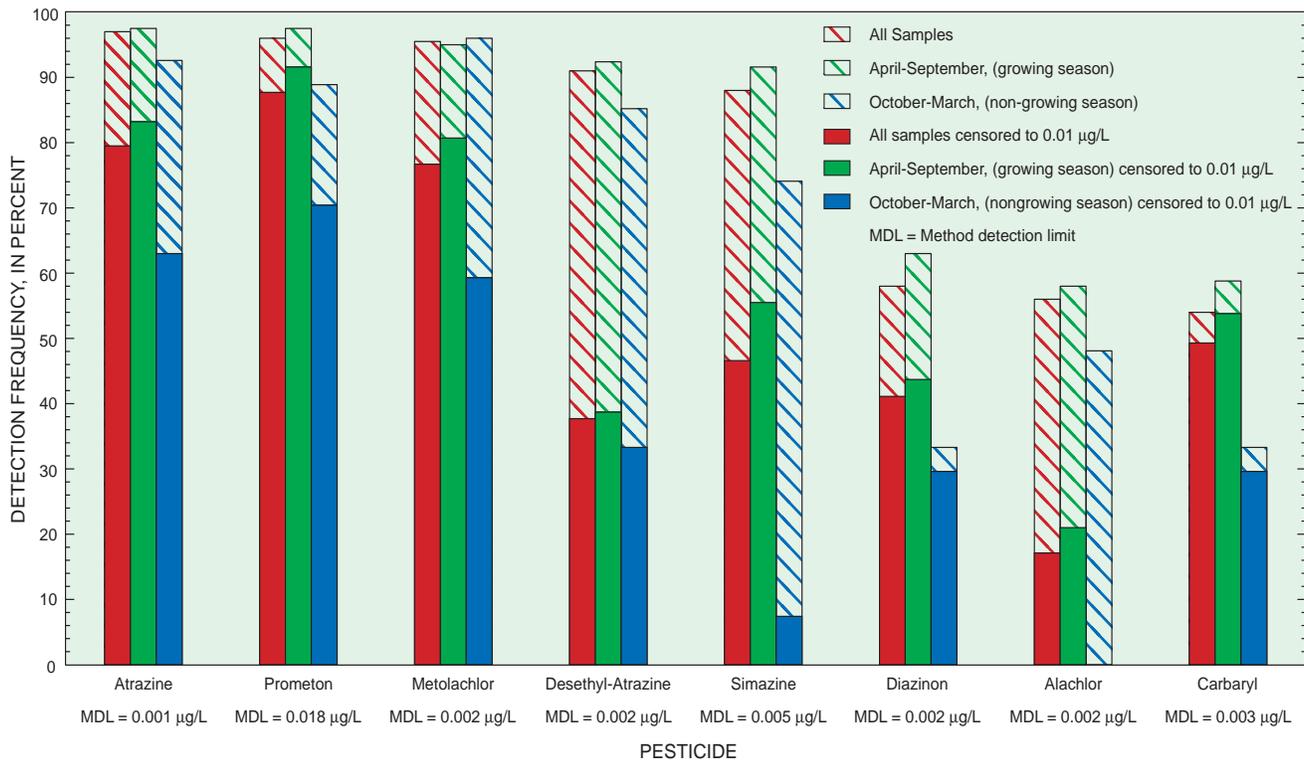
**Table 3.** Pesticides analyzed for but not detected in stream samples from seven stream sites in New Jersey April 1996 through June 1998 [IUPAC, International Union of Pure and Applied Chemistry; Blue indicates pesticides and degradates of pesticides applied by licensed applicators in New Jersey; \*, compounds analyzed in only 119 of the 146 samples collected (schedule 2050); MDL, Method Detection Limit (values listed in parentheses have an increased detection limit as of Dec. 15, 1997; µg/L, micrograms per liter; --, no trade name.]

Compound name (IUPAC)	Trade name	MDL (µg/L)
*Aldicarb Sulfone	Standak, Aldoxycad	0.016 (0.100)
*Aldicarb Sulfoxide	--	0.021
*Bromoxynil	Torch, Buctril	0.035
Butylate	Genate Plus, Suntan+	0.002
*3-hydrxy-carbofuran	--	0.014
*Chloramben	Amiben,methyl	0.011 (0.42)
*Chlorpyralid	Stringer	0.050
*Dichlobenil	Barrier, Casoron	0.020 (1.20)
*2,4-Dichlorophenoxy butyric acid	2,4 DB, Butyrac	0.035 (0.24)
*Dachthal, MA	--	0.017
*Dichlorprop	2,4 DP, Sertux 50	0.032
Diethylaniline	Metabolite of Alachlor	0.003
*Dinitroresol	DNOC, Trifocide	0.035 (0.42)
*Dinoseb	DNPB, Dinosebe	0.035
Disulfoton	Disyston, Solvinex	0.017
EPTC	Eptam, Alirox	0.002
*Esfenvalerate	Asana, Sumi-alpha	0.019
Ethalfuralin	Sonalan, Curbit	0.004
Ethoprop	Mocap, ethoprophos	0.003
*Fenuron	Beet-Klean, Fenulon	0.013
HCH, alpha-	alpha-Lindane, alpha-BHC	0.002
*Methiocarb	Mesuroil, Slug-Geta	0.026
*Methomyl	Lannate, Lanox	0.017
*4-2-Methyl-4-chlorphenoxy butyric acid	MCPB, Tropotox	0.050
*1-Naphthol	Alpha Naphthol	0.007
*Neburon	Neburea, Neburyl	0.015
*Norflurazon	Euitol, Predict	0.024
*Oryzalin	Surflan, Dirimal	0.019 (0.31)
*Oxyamyl	Vydate, Pratt	0.018
Parathion, Methyl-	Penncap-M	0.006
Pebulate	Tillam, PEBL	0.004
Permethrin,cis-	Ambush, Astro	0.005
Phorate	Thimet, Rampart	0.002
*Picloram	Grazon, Tordon	0.035
Pronamide	Kerb, Propyzamid	0.003
Propargite	Omite, Ornamite	0.013
*Propam	Tuberite	0.035
*Propoxur	Baygon, Blattanex	0.035
*Silvex	2,4,5-TP, Fenoprop	0.021
Terbacil	Counter, Sinbar	0.013
Thiobencarb	Bolero, Saturn	0.002
Triallate	Avadex BW, Far-Go	0.001
*2,4,5-Trichlorophenoxy acetic acid	2,4,5 T	0.035
*Triclopyr	Garlon, Grandstand	0.050 (0.25)

## Detection Frequency

Pesticides were detected in 145 of the 146 samples collected. The only sample without any pesticide detections was from the Great Egg Harbor River and was collected during the receding limb of the hydrograph in October 1996. Detection frequencies were computed using (1) all pesticide-concentration data and (2) only those concentrations that exceeded a common threshold of 0.01 µg/L in order to make unbiased comparisons between pesticides (fig. 2).

The 41 pesticides detected in the 146 stream samples collected for this study consist of 26 herbicides, 13 insecticides, 1 fungicide, and 1 degradation product. The pesticides most frequently detected in the 146 samples were atrazine, in 97 percent of the samples; prometon, in 96 percent; metolachlor, in 95 percent; desethyl-atrazine, in 91 percent; simazine, in 88



**Figure 2.** Pesticides most frequently detected in all samples and in samples collected during growing and nongrowing seasons at seven sites in New Jersey during April 1996 to June 1998.

percent; diazinon, in 58 percent; alachlor, in 56 percent; and carbaryl, in 54 percent. Seven of the eight most frequently detected pesticides remained the same regardless of the method used. Prometon replaced atrazine as the most frequently detected compound, carbaryl moved from eighth to fourth place, and diuron replaced alachlor in the top eight when a common threshold of 0.01 µg/L was used to compute detection frequencies. Five of the eight most frequently detected pesticides are herbicides, two are insecticides and one is a degradation product of atrazine. Ten pesticides, including the eight most frequently detected, DCPA, and cyanazine, were detected at least once at all seven sites. The Bound Brook site had the most pesticides detected (29), and Passaic River at Two Bridges had the least (13).

### Relation to Season

Seasonal variability in detection frequencies of pesticides was analyzed by comparing results from the growing season with results from the nongrowing season for the Raritan River, Bound Brook, and Great Egg Harbor River sites. The detection of pesticides in the growing season was significantly higher than in the nongrowing season at each of the three sites. Detection frequencies of 38 of the 41 pesticides detected during this study were higher at each of the three sites during the growing season. Detection frequencies of most of these pesticides, however, were not found to be significantly higher in the growing season. Six of the eight most frequently detected pesticides were detected at equally high frequencies during both seasons at each of the three sites. None of the 41 pesticides detected had significantly higher frequencies in the nongrowing season.

Thirty-nine pesticides were detected during the growing season and 20 pesticides were detected during the nongrowing season. Twenty-one pesticides were detected only during the growing season; however, three of these compounds—dieldrin,

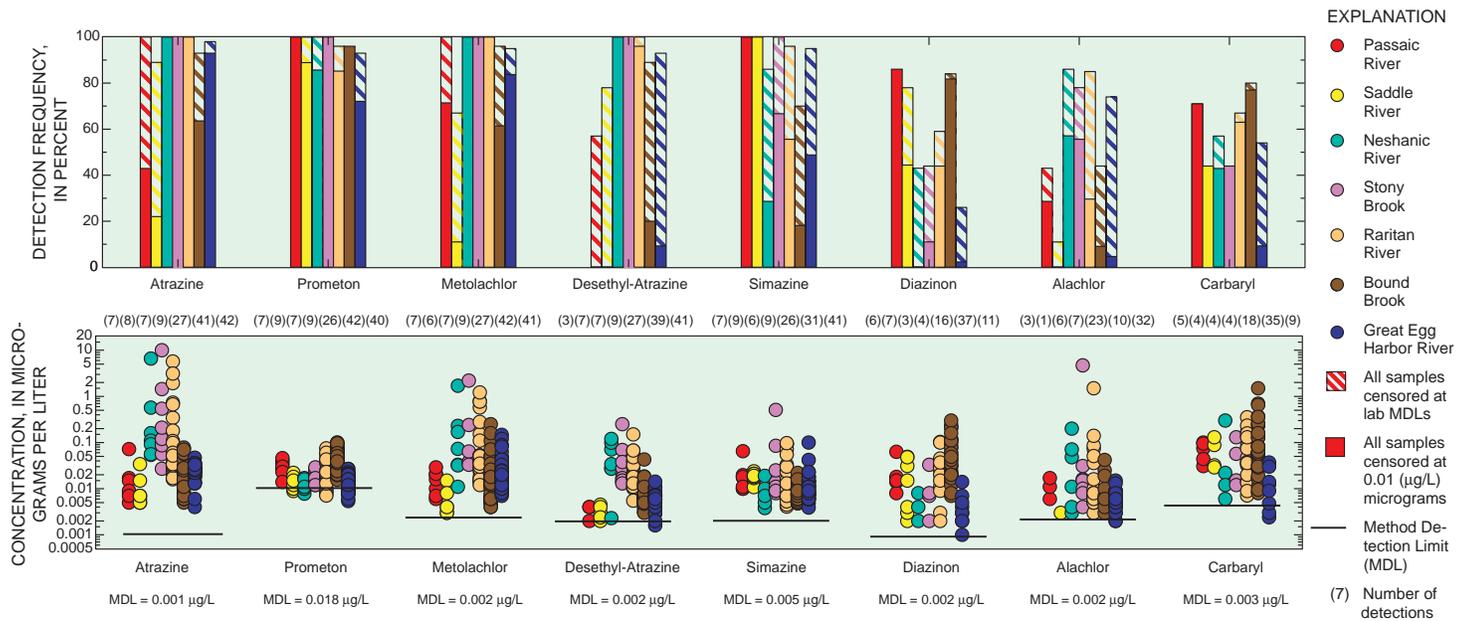
bentazon, and molinate—were detected at sites sampled exclusively during the growing season. Two herbicides—acifluorfen and propanil—were detected only during the nongrowing season and only at the Raritan River site.

Detection frequencies of the eight most frequently detected pesticides were compared among the seven sites (fig. 3). On the basis of contingency table analysis, high detection frequencies of atrazine and prometon at each site were not significantly different between sites. Detections of the other six pesticides were significantly higher at one or more sites than at the other sites. Detections of three pesticides used in or associated almost exclusively with agricultural practices—metolachlor, desethyl-atrazine, and alachlor—were higher than expected at the three sites located in the basins with greater than 25 percent agricultural land use. Carbaryl and diazinon detections were highest at the four most urbanized sites. The number of simazine detections was significantly higher at the Bound Brook and Neshanic River sites than at the other sites.

Detection frequencies of all but four pesticides were higher at the seven sites sampled during this study than those sampled during the June 1997 synoptic study when streams were sampled at or near base-flow conditions (Reiser and O'Brien, 1998). DCPA had the same frequency of detection in both studies, and dieldrin, linuron, and malathion had higher detection frequencies during the synoptic study. Fonofos, gamma-HCH, p,p-DDE, molinate, ethyl-parathion, propachlor, propanil, and terbufos were detected during routine sampling at the seven sites but were not detected during the synoptic study sampling. Terbacil and pebulate were detected during the synoptic study but not during routine sampling at the seven sites.

### Relation to Pesticide Use

Sixty-six of the 85 pesticides analyzed for in this study are currently used by licensed applicators in New Jersey to control



**Figure 3.** Detection frequencies and measured concentrations of the most frequently detected pesticides in the 146 samples collected by stream site.

pests. Thirty-six (55 percent) of these 66 pesticides were detected in samples collected during this study. An additional five pesticides—aldicarb; DDE, p,p-; dieldrin; molinate; and propanil—were detected but are not presently applied in New Jersey by licensed applicators (N.J. Department of Environmental Protection, 1994).

The pesticides most commonly used are not always the most frequently detected (Reiser and O'Brien, 1998). Atrazine, metolachlor, alachlor, and carbaryl are the only pesticides among the eight most frequently detected that are also among the eight most commonly used in New Jersey. Prometon and simazine were detected in 96 and 88 percent of the samples, respectively, but ranked 36th and 23d in pounds of active ingredient applied. Diazinon, the seventh most frequently detected pesticide in the study, ranked 14th in pounds of active ingredient applied. Diazinon and prometon, however, are active ingredients in products used by unlicensed applicators for home and garden use.

Physical and chemical properties and application rates of pesticides affect their detection frequencies in streams. Prometon may be detected more frequently than expected because of its high solubility in water, low soil-adsorption coefficient, and long half-life in soil (U.S. Department of Agriculture, 1995). Higher than expected detection frequencies of simazine, despite its low solubility in water and short half-life in soil, might be explained by its low soil-adsorption coefficient. Larson and others (1995) found a larger percentage of simazine than any other pesticide in streamwater based on the amount of pesticide applied within a drainage basin in five of the nine basins studied within the Mississippi River basin. Pendamethalin and chlorpyrifos are among the four most heavily applied pesticides of those studied (Reiser and O'Brien, 1998); however, detections were minimal, due in part to their low water solubility and high soil-adsorption coefficient.

## Concentrations

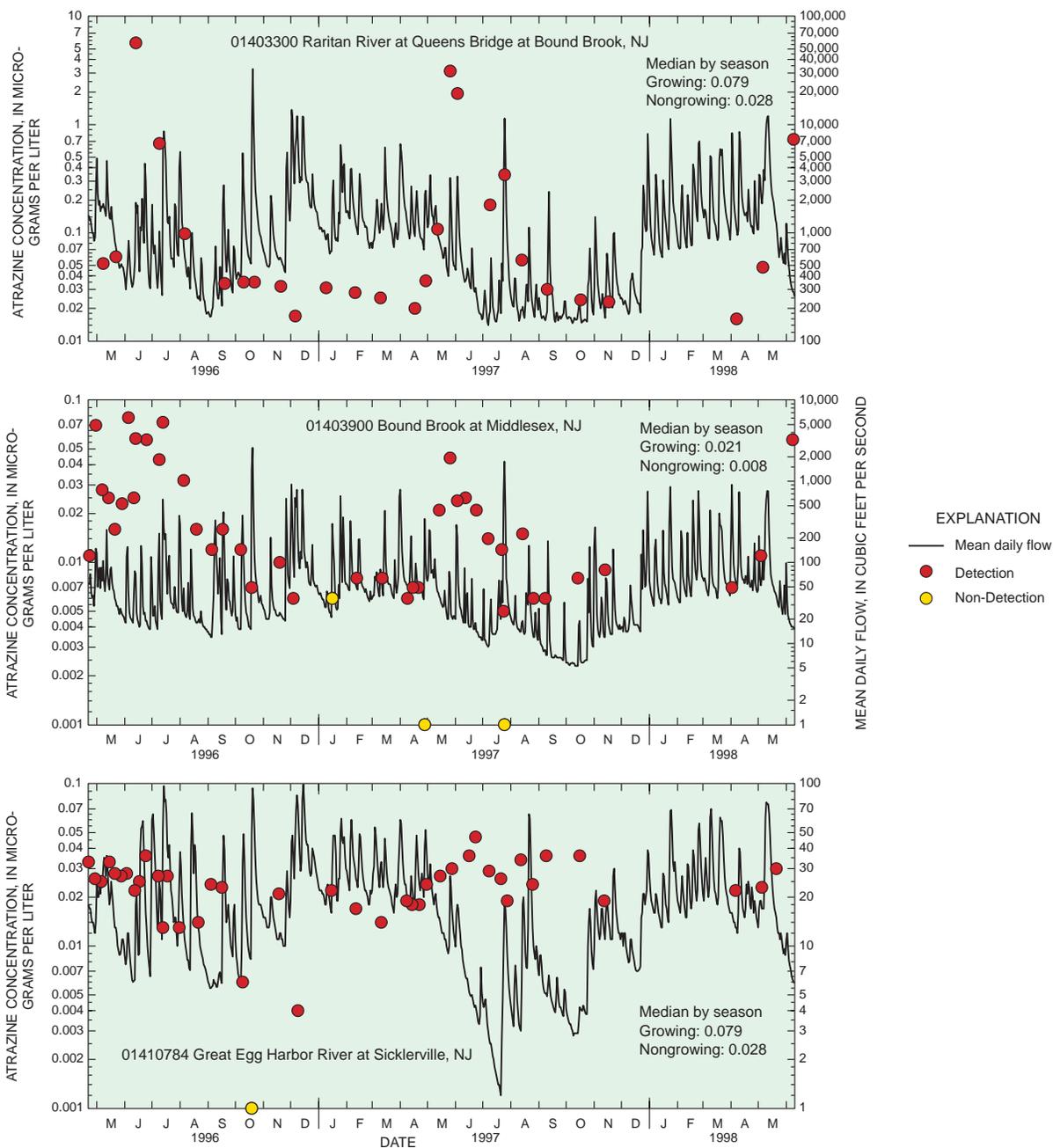
Concentrations of individual pesticide compounds ranged from less than 0.001 to 10.0 µg/L. Median concentrations of the pesticides detected ranged from < 0.001 µg/L for dieldrin and azinphos, methyl to 0.025 µg/L for atrazine (table 2) for all samples collected during this study. The 90th percentile values ranged from less than the MDL to 0.32 µg/L for 2,4-D (table 2). The maximum concentrations of 37 of the 41 pesticides detected occurred during the growing season. The maximum concentrations of 24 of these 37 pesticides occurred during runoff conditions. The four pesticides with maximum concentrations occurring during the nongrowing season were collected during base-flow conditions.

The maximum concentrations of 10 pesticides were detected in samples collected after a night of heavy rain on June 13, 1996—atrazine, 10 µg/L; acetochlor, 4.7 µg/L; desethyl atrazine, 0.25 µg/L; alachlor, 4.7 µg/L; 2,4-D, 1.7 µg/L; cyanazine, 1.9 µg/L; and linuron, 0.62 µg/L—at Stony Brook at Princeton (01401000) and metolachlor, 5.2 µg/L; metribuzin, 0.11 µg/L; and pendimethalin, 0.046 µg/L at Raritan River at Queen's Bridge (01403300).

The maximum concentrations for all but four pesticides detected in this study are higher than those detected in the June 1997 synoptic study (Reiser and O'Brien, 1998). The four pesticides—carbofuran, dieldrin, simazine, and tebuthiuron—occurred at maximum concentrations in this study during the same time of year and same hydrologic conditions, in late May and June at or near base-flow conditions. A comparison of the concentrations of pesticides detected in both studies indicated that only dieldrin and tebuthiuron had lower median concentrations in this study. All of the dieldrin detections and 80 percent of tebuthiuron detections occurred during base-flow conditions.

## Relation to land use

The highest median, 90th percentile, and maximum concentrations of a particular pesticide typically occurred at a site where land use in the drainage basin upstream from the site



**Figure 4.** Measured atrazine concentrations and mean daily flow at the three sites sampled during growing and nongrowing seasons from April 1996 to June 1998 (Method detection limit is 0.001 micrograms per liter).

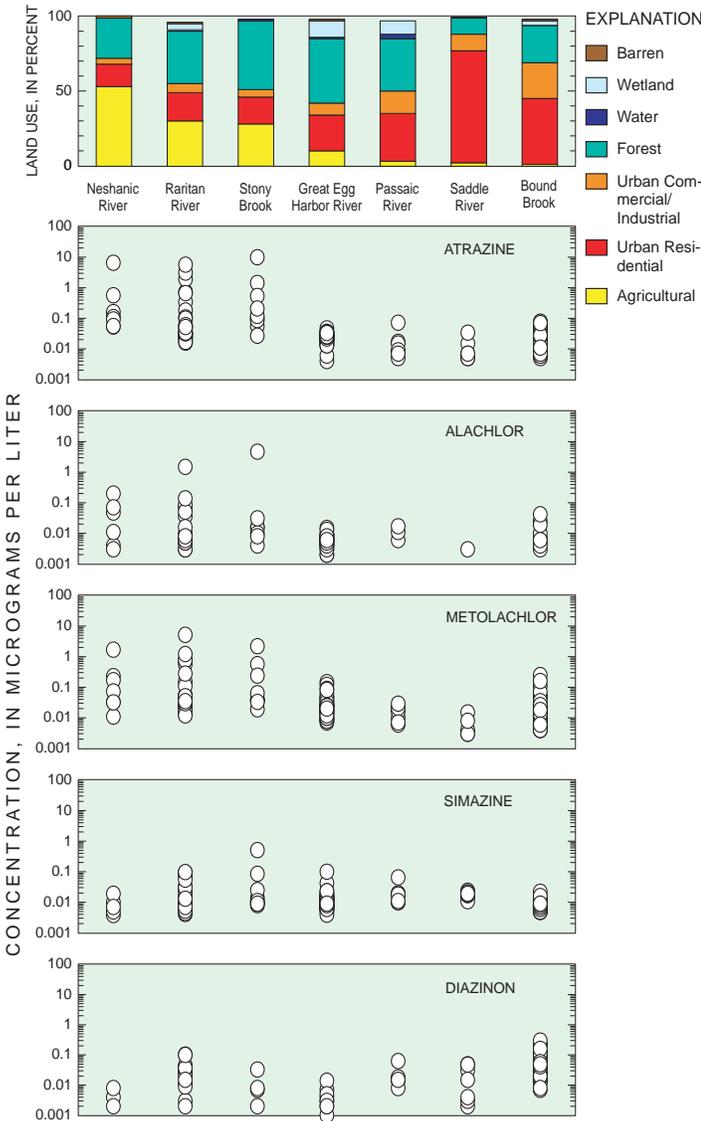
would indicate the use of that particular pesticide. Five herbicides used almost exclusively for agriculture — acetochlor, alachlor, atrazine, cyanazine, and metolachlor — and another herbicide — 2,4-D — used for multiple purposes were the only pesticides with 90th percentile concentrations that exceeded 1.0 µg/L. All the detections that exceeded 1.0 µg/L were at the three sites with the most agricultural land use (01398000, 01401000, and 01403300). These same herbicides also showed the largest variations in concentration with season and flow condition. Concentrations of atrazine in relation to mean daily flow are shown in figure 4. Concentrations varied by more than two orders of magnitude at the three sites with greater than 25 percent agricultural land use. Concentrations of agricultural herbicides increased as much as 500 percent during spring runoff. The largest inner quartile ranges (IQR's) observed were

for atrazine and metolachlor at these three sites. Median concentrations of the insecticides, diazinon and carbaryl, were detected at significantly higher concentrations at one or more of the most urbanized sites.

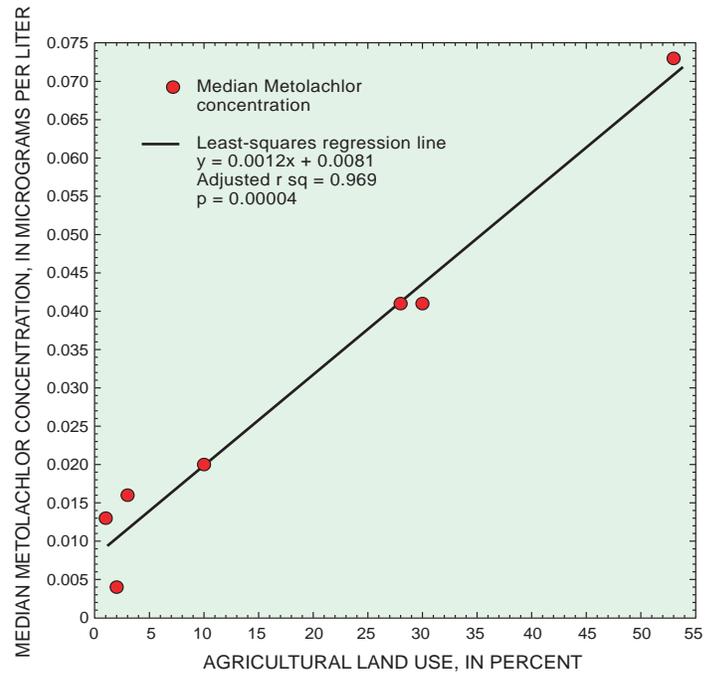
The median concentrations of six herbicides—atrazine, metolachlor, desethyl-atrazine, alachlor, cyanazine and acetochlor—used almost exclusively in agriculture were significantly higher at the three sites with greater than 25 percent agricultural land use than the concentrations at the other four sites. The distribution of detected concentrations of four herbicides and one insecticide at each site ordered by percent agricultural land use is shown in figure 5. Eleven of the 15 pesticides present in maximum concentrations at the urban Bound Brook site are associated primarily with lawn care, rights-of-way maintenance and mosquito control. Two pesticides are used for

agriculture only; the other two are not applied by licensed applicators in New Jersey, and their uses are unknown. Water samples from the urban-residential site on the Saddle River contained the maximum individual and (or) 90th percentile concentrations of three herbicides associated primarily with lawn care, two insecticides used formerly or presently for termite control, and one insecticide used for mosquito control. Six of the nine pesticides found in maximum concentrations at the Stony Brook site, whose drainage basin is changing from agriculture to urban land use, are used exclusively for agriculture, and the other three are used primarily for agriculture. (Reiser and O'Brien, 1998).

Median and 90th percentile concentrations of the eight most frequently detected pesticides from each of the seven sites were evaluated with respect to land use at the sites by using least squares linear regression (Ott, 1988). Median concentrations of metolachlor, desethyl-atrazine, alachlor and atrazine (adjusted  $r^2$  ranged from 0.97 to 0.62) increased significantly as the percentage of agricultural land increased (fig. 6). In contrast, median concentrations of metolachlor and desethyl atrazine decreased



**Figure 5.** Land use distribution in the drainage basins of the seven streams and concentrations of five of the most frequently detected pesticides in stream samples collected during April 1996 to June 1998.



**Figure 6.** Relation of median concentration of metolachlor to percent of agricultural land use at each of the seven sites.

significantly with an increase in percentage of urban land (adjusted  $r^2= 0.59$  and  $0.46$ , respectively) and median concentrations of metolachlor decreased significantly with an increase in population density. Concentrations of diazinon at the 90th percentile increased significantly with increased commercial/industrial land use and population density (adjusted  $r^2= 0.81$  and  $0.74$  respectively). Concentrations of prometon at the 90th percentile were also found to increase with an increase in commercial/industrial land use and population density.

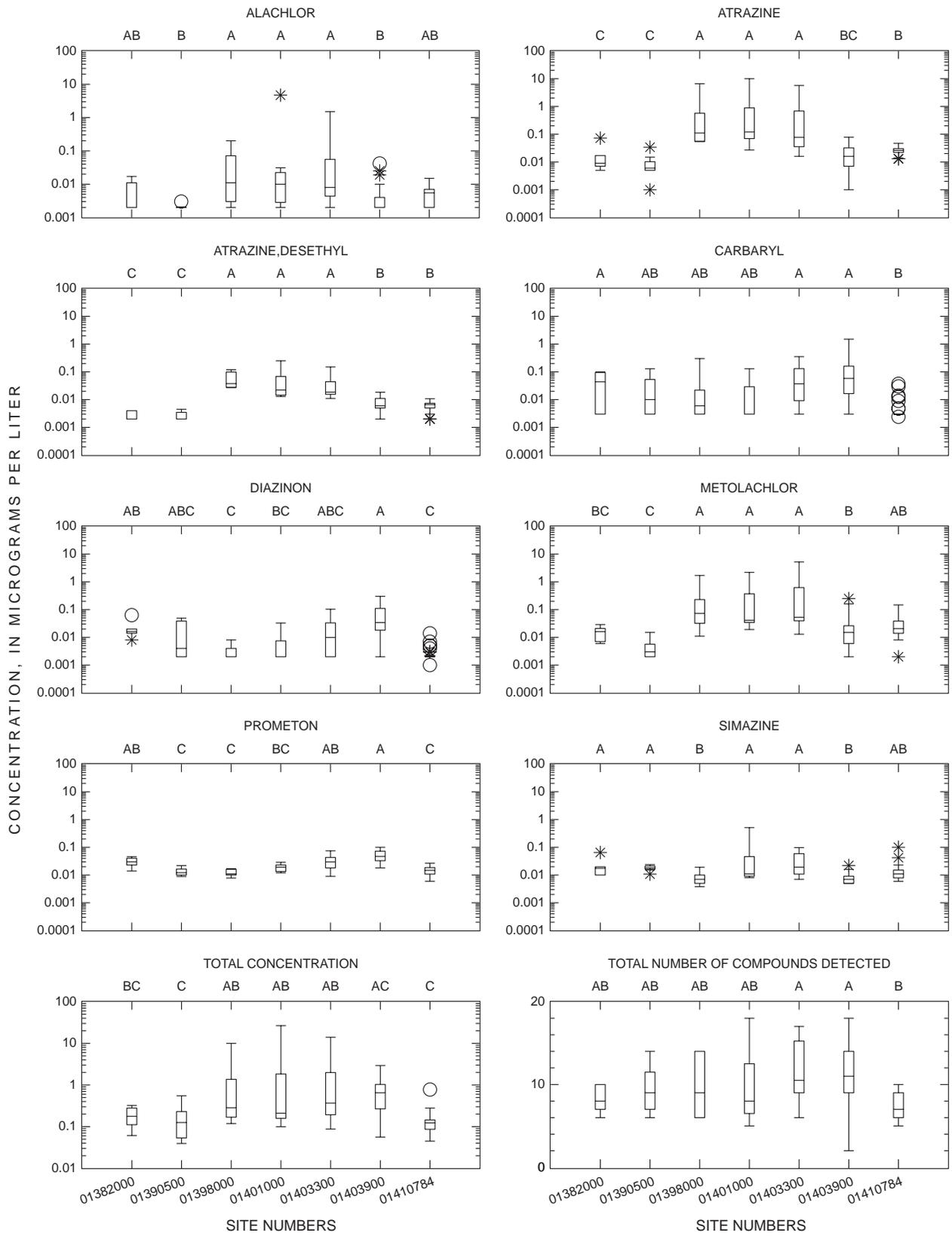
The variability of pesticide concentrations as defined by the IQR was typically greatest at sites in which land use in the drainage basin upstream from the site is generally associated with expected pesticide applications. The IQR of eight herbicides and one insecticide associated with agricultural use was highest at either Neshanic River or Raritan River, the two sites with the most agricultural land use. The IQR's of six herbicides used primarily for lawn care or rights-of-way maintenance and of three insecticides used in urban areas were highest at the Bound Brook site. The IQR of dieldrin was highest at Saddle River, the basin with the highest percentage of urban-residential land use.

## Variation in Pesticide Concentrations

### Relation to Season

Pesticides with median concentrations greater than the MDL were compared by season at each of the three sites sampled throughout the year. Median concentrations of the eight most frequently detected pesticides were significantly higher in the growing season than in the nongrowing season at all three sites. Sixteen pesticides had median concentrations greater than the MDL in at least one season at one site. Tebuthiuron was the only pesticide of the 16 with a median concentration greater than the MDL in the nongrowing season only and only at the Bound Brook site. Median concentrations of tebuthiuron at other sites were less than the MDL in both seasons.

The median concentrations of the eight most frequently



**Figure 7.** Distribution of pesticide concentrations in the growing season and results of Tukey's test at the seven stream sites in New Jersey. [Boxplots consist of a center line (median) splitting a rectangle defined by the 75th and 25th percentiles, whiskers are drawn to 10th and 90th percentiles, circles and asterisks are outliers (Helsel and Hirsch, 1992). Significant differences in mean rank concentration between sites from Tukey's test: from A, the highest, to C, the lowest].

detected pesticides during the growing season were compared among the seven sites. (fig 7). The median concentrations of atrazine, desethyl atrazine, metolachlor, and alachlor, compounds used or associated almost exclusively with agricultural use, were significantly higher at the Neshanic River, Raritan River, and Stony Brook sites than at the other four sites. The drainage basins represented by these sites contain greater than 25 percent agricultural land use. The median concentrations of prometon, carbaryl, and diazinon, pesticides used in urban areas, were significantly higher at the Bound Brook site than at the other sites. The Bound Brook drainage basin contains 73 percent urban land use. Simazine was found to be significantly higher at Saddle River, Raritan River, Passaic River, and Stony Brook than at the other three sites. The highest median concentrations appear to be related to mixed land uses at these sites. Simazine is used primarily for agriculture, but also for lawn care and rights-of-way maintenance.

Results of ANOVA and Tukey's test at the three sites sampled in the nongrowing season were similar to the results from the growing season. The median concentrations of atrazine, desethyl atrazine, and metolachlor were significantly higher at the Raritan River site than at the other two sites. Alachlor was significantly higher at Raritan River and Great Egg Harbor River than at Bound Brook. Prometon, diazinon and carbaryl were significantly higher at Bound Brook than the other two sites. No significant differences in median simazine concentrations were determined to exist between the three sites.

The variability of individual pesticide concentrations was generally greater during the growing season than the nongrowing season at each of the three sites (fig. 4). Tebuthiuron was the only pesticide with a higher IQR in the nongrowing season at the Bound Brook and Great Egg Harbor River sites. Both atrazine and desethyl atrazine have a higher IQR in the nongrowing season at the Great Egg Harbor River site.

### **Relation to Flow Condition**

Samples collected at base-flow conditions were compared to those collected during storms. The median concentrations of the 8 most frequently detected pesticides in all 70 base-flow samples were compared by season to those in all 76 runoff samples collected in this study. ANOVA indicated that the median concentrations of atrazine, prometon, metolachlor, desethyl-atrazine, diazinon, alachlor, and carbaryl were highest during runoff conditions in the growing season. The median simazine concentration was highest during the growing season regardless of flow condition. The lowest median concentrations of atrazine, prometon, metolachlor, simazine and alachlor occurred during runoff conditions in the nongrowing season. Both desethyl atrazine and diazinon are equally low during base-flow and runoff conditions in the nongrowing season. Median carbaryl concentrations are less than the detection limit (<0.003 µg/L) during all hydrologic conditions, except during runoff conditions in the growing season when the median concentration was 0.045 µg/L.

A comparison between sites of median concentrations of the eight most frequently detected compounds indicated that, in general, concentrations were lower during base-flow conditions than during runoff conditions at all sites. The three most urbanized sites had significantly higher median concentrations of prometon, diazinon, and carbaryl than the other sites regardless

of flow conditions. The only exception was that samples from the Saddle River had significantly lower concentrations of carbaryl than those from all other sites during base flow. Median concentrations of the agricultural herbicides and the metabolite desethyl atrazine were consistently higher at the three most agricultural sites than at the other sites during all flow conditions and seasons. The only exception was the median concentration of alachlor during base-flow conditions in the growing season, which was higher at the Great Egg Harbor River site than at two of the three sites with the most agricultural land use. Significantly higher concentrations of the four pesticides associated with agriculture were present in samples from one or more of the agricultural sites than in samples from the other sites during each flow condition in each season.

### **Simultaneous comparison to season, streamflow, and land use**

Concentrations of pesticides from all samples were evaluated simultaneously by the predominant land use at each site, season, and flow condition using MANOVA. The concentrations of each of the eight most frequently detected pesticides varied as a function of season and land use. Flow condition was significant only in predicting variability in concentrations of diazinon and carbaryl. Forty-eight percent of the variability of concentrations of diazinon and carbaryl was related to season, flow, and land use. Twenty-seven to 59 percent of the variability in concentrations of the other six pesticides was related to season and land use only. Concentrations of some pesticides were significantly higher in runoff during the growing season at specific sites, but when concentrations from both seasons were analyzed, flow became insignificant.

Concentrations of pesticides were evaluated simultaneously by season, flow condition, and flow condition as a function of season at each of the three sites with samples collected during both seasons. At the Raritan River site, 83 percent of the variability in the concentrations of simazine was related to flow and season. Twenty-nine to 52 percent of the variability in carbaryl and prometon concentrations was related significantly to flow only. Forty-two percent of the variability in atrazine concentrations was attributed to flow as a function of season. The other four compounds did not relate significantly to any of the three variables in the model.

At Bound Brook, five of the eight pesticides related significantly to season only, accounting for 15 to 24 percent of the variability in concentration. Diazinon and carbaryl related significantly to flow and season, accounting for 38 percent of variability in concentration. At Great Egg Harbor River diazinon and prometon concentrations were related to season only, accounting for 18 to 21 percent of variability. Flow and season accounted for 38 to 42 percent of the variability in atrazine and simazine concentrations. Metolachlor was significantly related to season and flow as a function of season, and desethyl atrazine was related to flow, accounting for 21 and 18 percent of variability, respectively.

### **Total-Pesticide Concentration and Numbers of Pesticides Detected**

Total-pesticide concentrations in each sample were computed by adding the concentrations of each detected com-

pound and by assigning a concentration of 0  $\mu\text{g/L}$  to all censored values. Total-pesticide concentrations and total numbers of pesticides in all samples at a site were compared among sites. Total concentrations in a sample ranged from 26.4  $\mu\text{g/L}$  at the Stony Brook site during runoff in June 1996 to 0.00  $\mu\text{g/L}$  at the Great Egg Harbor River site during runoff in October 1997 when no pesticide concentrations exceeded the detection limit. The highest number of pesticides detected (18) were present in four samples collected during spring runoff; three samples were from Bound Brook and one from Stony Brook. The highest total concentrations and numbers of pesticides occurred at each of the seven sites during runoff in the growing season. The smallest total concentrations and numbers of pesticides at each site typically occurred during runoff events in the nongrowing season. The number of pesticides detected at each site over the 2-year sampling period ranged from 29 at Bound Brook to 13 at Passaic River.

Median total-pesticide concentrations and median total number of pesticides from all 70 base-flow samples were compared to those from 76 runoff samples, by season. The median total-pesticide concentration was highest (0.41  $\mu\text{g/L}$ ) in runoff samples in the growing season and lowest (0.087  $\mu\text{g/L}$ ) in the nongrowing season regardless of flow condition. The median total-pesticide concentrations in base-flow and runoff samples increased in the growing season. The median total number of pesticides was highest (10) in runoff samples in the growing season and lowest (6) in runoff samples in the nongrowing season. The median total number of pesticides in base-flow and

runoff samples also increased significantly in the growing season.

### Relation to Season and Flow Condition

Total-pesticide concentrations and total numbers of pesticides at the three sites sampled throughout the year were compared by seasons using ANOVA. Median total concentrations and median total numbers of pesticides were significantly higher in the growing season at each of the three sites ( $p < 0.05$ ). A seasonal pattern was observed at each site (fig. 8). The median total-pesticide concentration during the nongrowing season, however, was the same as that during base-flow and runoff conditions at the Raritan River and Bound Brook sites and decreased slightly during runoff conditions at the Great Egg Harbor River site. The median total number of pesticides during runoff conditions in the nongrowing season was larger than during base flow at the Raritan River site, remained the same at the Bound Brook site, and was smaller at the Great Egg Harbor River site.

Total-pesticide concentration and total number of pesticides in all samples collected during the growing season were compared among the seven sites. The median total concentration and median total number of pesticides were higher during runoff conditions than during base flow at each site during the growing season (table 4). The median total-pesticide concentration was highest at the Bound Brook site (0.65  $\mu\text{g/L}$ ) and smallest at the Saddle River and Great Egg Harbor River sites (0.12  $\mu\text{g/L}$ ). Tukey's test showed that samples from the Bound Brook site

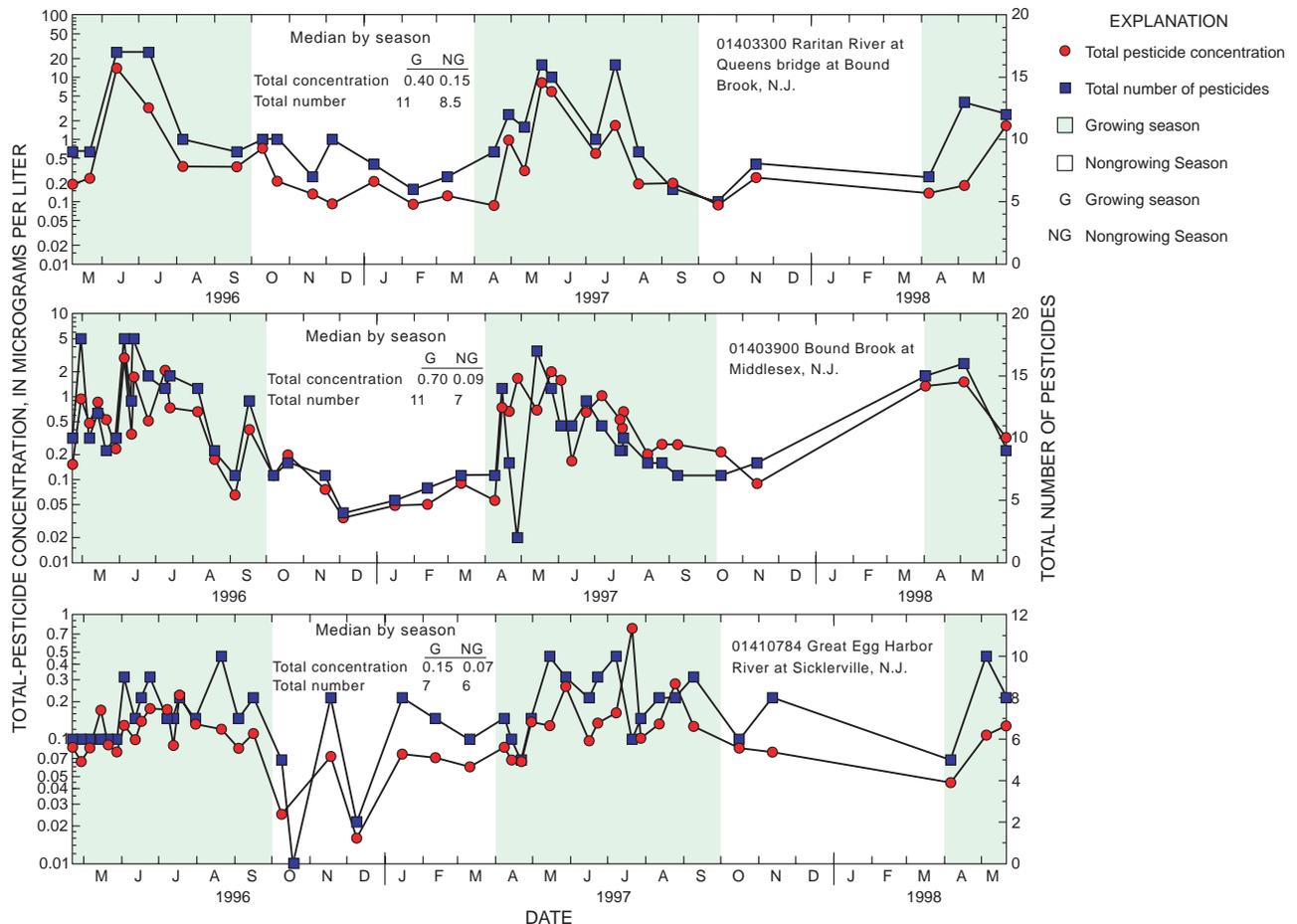


Figure 8. Total-pesticide concentration and total number of pesticides in all samples collected during April 1996 to June 1998.

**Table 4.** Median total pesticide concentration and total number of pesticides by season and flow condition for each sampling site [Significant differences in mean rank concentration between sites by season, from Tukey's test: **A**=highest, **AB**=middle, **B**=lowest, **N**=no significant difference. Significant differences between flow conditions by site: \* significantly higher at this flow condition. Inner quartile range is the 25th percentile minus the 75th percentile; **Brown** indicates value is less during runoff than during base flow;  $\mu\text{g/L}$ , micrograms per liter]

Station name	Total number of pesticides per sample				Total pesticide concentration per sample ( $\mu\text{g/L}$ )			
	Median		Inner-quartile range		Median		Inner-quartile range	
	Base flow	Runoff	Base flow	Runoff	Base flow	Runoff	Base flow	Runoff
<b>Growing Season</b>								
Passaic River	7 (N)	10 (AB)	1	0	0.11 (AB)	0.28 (AB)	0.07	0.008
Saddle River	8 (N)	11 (AB)	2	5.5	0.06 (B)	* 0.23 (AB)	0.02	0.21
Neshanic River	6.5 (N)	14 (A)	2	5	0.25 (A)	1.37 (AB)	0.20	9.8
Stony Brook	7.5 (N)	10 (AB)	5	12	0.20 (A)	0.43 (AB)	0.89	26
Raritan River	8 (N)	11.5 (A)	2	6.5	0.19 (A)	0.48 (AB)	0.10	2.3
Bound Brook	9 (N)	13.5 (A)	3	4.5	0.27 (A)	0.80 (A)	0.35	1.0
Great Egg Harbor River	7 (N)	8 (B)	2.5	2	0.10 (AB)	0.13 (B)	0.04	0.08
<b>Nongrowing Season</b>								
Raritan River	7 (N)	10 (A)	2	3	0.13 (A)	0.13 (A)	0.12	0.12
Bound Brook	7 (N)	7 (AB)	0	1	0.09 (AB)	0.09 (AB)	0.03	0.06
Great Egg Harbor River	* 8 (N)	6 (B)	1	3	* 0.08 (B)	0.07 (B)	0.006	0.06
<b>Both Seasons</b>								
Raritan River	7 (N)	* 10 (A)	1	4	0.14 (A)	0.34 (A)	0.08	1.5
Bound Brook	8 (N)	* 13 (A)	3	6	0.22 (A)	0.74 (A)	0.26	1.2
Great Egg Harbor River	7 (N)	7 (B)	2	2	0.09 (B)	* 0.11 (B)	0.05	0.07

contained significantly higher total-pesticide concentrations than those at other sites, and samples from the Saddle River and Great Egg Harbor River sites contained significantly lower total concentrations. Tukey's test showed that the median total numbers of pesticides at the Bound Brook and Raritan River sites were significantly higher than those at the other sites and the total number was significantly lower at the Great Egg Harbor River site.

Total-pesticide concentration and total number of pesticides in all samples collected during the nongrowing season were compared between the three sites. The median total concentration at the Raritan River site was significantly greater than that at the Bound Brook and Great Egg Harbor River sites. The medians of total numbers of pesticides were not significantly different between sites.

Variability, as determined by the IQR of observations, in total-pesticide concentrations and total numbers of pesticides detected in samples collected during the growing season was compared among the seven sites (table 4). Variability in total-pesticide concentrations for all growing season samples was highest at the Raritan River site (1.49  $\mu\text{g/L}$ ) and lowest at the Great Egg Harbor River site (0.05  $\mu\text{g/L}$ ). Variability in total numbers of pesticides detected in a sample was highest at the Neshanic River site (8) and lowest at the Passaic River, Saddle River and Great Egg Harbor River sites (3).

During the nongrowing season, the IQR in total-pesticide concentration was essentially the same at each site (0.04-0.06

$\mu\text{g/L}$ ). The IQR of total numbers of pesticides detected was one at Bound Brook and three at Raritan River and Great Egg Harbor River. Variability was substantially lower in the nongrowing season than in the growing season at the Bound Brook and Raritan River sites, but remained the same at the Great Egg Harbor River site. (table 4).

### Relation to Flow Condition

Median total-pesticide concentrations of pesticides in base-flow and runoff samples in the growing and nongrowing seasons were compared among sites. Median total-pesticide concentrations were highest during runoff in the growing season at the Neshanic River site (table 4), the site with the most agricultural land use, and significantly higher than at the other sites. The second highest total-pesticide concentration was at the Bound Brook site, a site with 68 percent urban land use and 24 percent commercial/industrial land use. The highest median total-pesticide concentrations at base-flow conditions during the growing season ranged from 0.19 to 0.27  $\mu\text{g/L}$  at the Bound Brook, Neshanic River, Raritan River, and Stony Brook sites. The lowest median at Saddle River (0.06  $\mu\text{g/L}$ ) was significantly lower than that at all the other sites. Median total concentrations ranged from 0.07 to 0.13  $\mu\text{g/L}$  in the nongrowing season and did not vary with flow conditions. The Raritan River site had the highest median concentration, which was significantly higher than that at the Great Egg Harbor River site.

Median total numbers of pesticides in base-flow and runoff

samples were compared among sites. Total numbers of pesticides at Bound Brook and Raritan River during runoff were significantly higher than those at Great Egg Harbor River. No other significant differences were found between sites during runoff conditions. Total numbers of pesticides detected at base-flow conditions did not vary significantly among sites.

The differences in median total numbers between sites also were compared by flow and season. Numbers were not significantly different between sites at base-flow conditions in the nongrowing or growing season. The highest median number of pesticides (14) occurred during runoff conditions in the growing season at the Neshanic River site (table 4) and was significantly higher than the median at Great Egg Harbor River. The Great Egg Harbor River site had the lowest median number (8), which was significantly lower than the Neshanic River, Raritan River, and Bound Brook sites. During runoff conditions in the nongrowing season, the median total number of pesticides at the Raritan River site (10) was significantly higher than the lowest number (6) at Great Egg Harbor River.

Variability in total-pesticide concentrations and total numbers, as defined by the IQR, was compared between base-flow and runoff samples at each site. Variability in total numbers was greatest during runoff conditions at each site except for the Passaic River and the Great Egg Harbor River in the growing season (table 4). In addition, variability in total concentrations was greater during runoff conditions at all sites, except Passaic River.

Variability in total-pesticide concentrations and total numbers was compared among sites. Pesticide concentrations at the three sites with the most agricultural land use had the greatest variability in samples collected during runoff conditions (table 4). Variability at base-flow conditions was greatest at the Raritan River site during the nongrowing season and at the Stony Brook and Bound Brook sites during the growing season. Variability in total numbers was generally greatest in runoff samples at the agricultural sites in the growing season. Variability in total numbers at base-flow conditions was nearly equal between sites.

### **Simultaneous Comparison to Season, Stream flow, and Land use**

Total-pesticide concentrations and total numbers of pesticides from all samples were compared simultaneously to the predominant land use at each site, the season, and the flow condition by using MANOVA. Both totals varied as a function of season, land use, and flow condition. Forty-seven percent of the variability in total concentration and 35 percent of the variability in total numbers resulted from a combination of season, flow condition, and land use.

Total concentrations and total numbers of pesticides were compared simultaneously to season, flow condition, and flow condition as a function of season at the three sites with samples collected in both seasons. At Raritan River, total concentrations did not relate significantly to any of the three variables. Total concentrations related significantly to season, however, when flow was removed from the model. Total concentrations were significantly related to season at Bound Brook and Great Egg Harbor River, with 61 percent and 32 percent of the variability at these sites, respectively, accounted for by season only. Total numbers differed significantly in relation to flow at Raritan

River, to season at Bound Brook, and to flow as a function of season at Great Egg Harbor River. These factors accounted for 24 to 51 percent of the variability in total numbers at these sites.

### **Relation of Concentration to Streamflow**

Relations between pesticide concentrations and streamflow were evaluated for 16 of the 41 pesticides detected in this study. Pesticides detected in more than 50 percent of the samples from a site were analyzed by using tobit regression (Cohn, 1988). All data, including censored values, are used with the tobit method to develop a relation between concentration and flow. If censored data accounted for more than 50 percent of the values at a site, the results are not considered reliable and are not discussed in this report. The relation was considered to be significant if the slope was different from zero at the 0.05 level of significance. A base-10 logarithm transformation of streamflow was used to normalize the data before using tobit regression.

Concentrations of at least four pesticides were significantly correlated to streamflow at each of the three sites sampled routinely throughout the year (table 5). Concentrations of four of the eight most frequently detected pesticides in this study decreased significantly with flow during both seasons at the Great Egg Harbor River site. At the urban Bound Brook site, eight pesticides were significantly related to streamflow, more than at any other site. Atrazine, desethyl atrazine, and simazine, associated primarily with agricultural use, decreased significantly as stream flow increased. Three insecticides and two herbicides associated with mixed uses increased significantly with stream flow. Four pesticides increased significantly with flow at the Raritan River site. Diazinon, an insecticide used for agriculture and lawn care, increased as streamflow increased during both seasons. Simazine concentrations increased as streamflow increased only during the growing season, and alachlor and carbaryl increased only when concentrations from both seasons were analyzed.

Pesticide concentrations also were correlated with streamflow at three of the four sites sampled only during the growing season. Concentrations of prometon, metolachlor, trifluralin, and pendimethalin, herbicides used for lawn care, increased with increasing streamflow, and simazine, used primarily for agriculture, decreased with increasing streamflow at the Saddle River site. Concentrations of desethyl-atrazine, a metabolite of atrazine, and DCPA, used in agriculture, golf course, and lawn care, increased with increasing streamflow; simazine decreased with increasing streamflow at the Passaic River site. Simazine was also found to decrease successively in downstream order at three sites in the Passaic River basin during base-flow conditions in June 1997 (Reiser and O'Brien, 1998). Metolachlor, alachlor, and cyanazine, herbicides used primarily in agriculture, increased significantly with increasing streamflow at the Stony Brook site. No pesticide concentrations were related to streamflow at the Neshanic River site.

Total-pesticide concentrations increased significantly with increasing streamflow at Saddle River, Stony Brook, and Bound Brook and decreased significantly with increasing streamflow at Great Egg Harbor River (table 5). Total concentrations, in general, increased with increasing streamflow at the Passaic River, Neshanic River, and Raritan River sites, but the relations were not statistically significant.

**Table 5.** Tobit regression slopes of significant relations between pesticide concentrations and stream flow, and total numbers of pesticides and streamflow, April 1996 to June 1998, by season  
 [+ , positive regression slope indicates concentration increases with increasing flow; - , negative regression slope indicates concentration decreases with increasing flow; NSR, no significant relation at 0.05 level; ---, less than 50 percent detections, therefore, no results given]

Pesticide	Passaic River	Saddle River	Neshanic River	Stony Brook	Raritan River			Bound Brook			Great Egg Harbor River		
	Growing	Growing	Growing	Growing	All	Growing	Non-growing	All	Growing	Non-growing	All	Growing	Non-growing
Atrazine	NSR	NSR	NSR	NSR	NSR	NSR	NSR	NSR	NSR	- 0.09	- 0.42	- 0.16	- 0.98
Prometon	NSR	+ 0.28	NSR	NSR	NSR	NSR	NSR	NSR	NSR	NSR	- 0.24	- 0.20	- 0.38
Metolachlor	NSR	+ 0.96	NSR	+ 0.75	NSR	NSR	NSR	NSR	NSR	NSR	NSR	+ 0.39	NSR
Atrazine, Desethyl	+ 0.33	NSR	NSR	NSR	NSR	NSR	NSR	NSR	NSR	- 0.26	- 0.31	- 0.20	- 0.66
Simazine	- 0.32	- 0.19	NSR	NSR	NSR	+ 0.36	NSR	- 0.12	- 0.12	NSR	- 0.32	NSR	- 0.46
Diazinon	NSR	NSR	---	---	+ 1.15	+ 1.12	+ 1.19	+ 0.38	+ 0.41	---	NSR	---	---
Alachlor	---	---	NSR	+ 1.27	+ 0.59	NSR	NSR	---	---	---	- 0.52	- 0.42	- 0.72
Carbaryl	NSR	---	NSR	---	+ 0.73	NSR	---	+ 0.50	+ 0.46	NSR	---	---	---
DCPA	+ 0.39	---	---	---	NSR	NSR	---	+ 0.20	+ 0.20	---	NSR	---	---
Chlorpyrifos	NSR	NSR	---	---	---	---	---	+ 0.23	NSR	---	---	---	---
Diuron	---	---	---	---	---	---	---	NSR	NSR	---	---	---	---
Trifluralin	---	+ 0.51	---	---	---	---	---	---	+ 0.40	---	---	---	---
Tebuthiuron	---	---	---	---	---	---	---	---	---	NSR	---	---	---
Cyanazine	---	---	---	+ 1.72	---	NSR	---	---	---	---	---	---	---
Pendimethalin	---	+ 1.10	---	---	---	---	---	---	---	---	---	---	---
Acetochlor	---	---	NSR	---	---	---	---	---	---	---	---	---	---
Total Concentration	NSR	+ 0.88	NSR	+ 0.86	NSR	NSR	NSR	NSR	+ 0.28	NSR	- 0.53	- 0.20	NSR
Total Number	NSR	NSR	NSR	NSR	+ 0.15	+ 0.15	+ 0.16	NSR	NSR	NSR	- 0.22	NSR	NSR

The numbers of pesticides detected significantly increased with streamflow at the Raritan River site and decreased significantly at the Great Egg Harbor River site. For four of the five other sites, numbers of pesticides detected, in general, increased as streamflow increased, but the relations were not statistically significant.

## Summary and Conclusions

Pesticides were frequently detected in water samples collected from seven New Jersey streams from April 1996 through June 1998. Pesticides were present in streams throughout the year, but rarely at concentrations that exceeded established water-quality criteria. The pesticides most frequently detected were atrazine, in 97 percent of the samples; prometon, in 96 percent; metolachlor, in 95 percent; desethyl-atrazine, in 91 percent; simazine, in 88 percent; diazinon, in 58 percent; alachlor, in 56 percent; and carbaryl, in 54 percent. More than 97 percent of the samples contained at least five pesticides. Twenty-nine pesticides were detected at the highly urbanized Bound Brook site throughout the sampling period, the most detected at any site, and 13 pesticides were detected at the Passaic River site, which drains a large basin of mixed land uses, the fewest at any site.

Pesticides were detected more frequently during the growing season than during the nongrowing season. Thirty-nine pesticides were detected during the growing season and 20 pesticides during the nongrowing season. Twenty-one pesticides were detected only during the growing season; however, three of these—dieldrin, bentazon and molinate—were detected only at sites sampled exclusively in the growing season.

The concentrations of 10 pesticides infrequently exceeded

established water-quality criteria. Thirty-one detections occurred during the growing season and one during the nongrowing season. Concentrations of atrazine, alachlor, and cyanazine exceeded the U.S. Environmental Protection Agency human health criteria during runoff shortly after spring applications of these pesticides, and represent a potential threat to municipal water supplies in the Raritan River basin. Concentrations of chlorpyrifos, chlorthalonil, diazinon, ethyl-parathion, and methyl-azinphos exceeded chronic life criteria for the protection of aquatic life (AQCR) at four sites during the growing season. Dieldrin was detected in four samples and DDE in two samples at concentrations that exceeded New Jersey Department of Environmental Protection (NJDEP) health advisory levels. Dieldrin concentrations also exceeded the NJDEP AQCR.

The highest individual concentrations and highest median concentrations of most of the pesticides detected occurred during runoff in the growing season, and the lowest typically occurred during runoff in the nongrowing season. The median concentrations of most pesticides at most sites were equally low during base flow and runoff in the nongrowing season. Typically, concentrations were least variable during base-flow conditions in the nongrowing season. All 24 pesticides with the highest concentrations during runoff were sampled in the growing season. The four pesticides with highest concentrations during the nongrowing season were sampled during base-flow conditions.

Pesticide concentrations were related to land use in the drainage basin upstream from the sampling site. The highest median concentration and the maximum concentration of a pesticide were typically found at a site where land use in the drainage basin upstream from the site is generally associated with applications of that pesticide. Herbicides associated with

agricultural land use, such as atrazine, generally were detected in higher concentrations than other pesticides, showed the strongest correlation to land use, and had the largest variability in concentration with season and streamflow. In general, insecticides were detected more frequently and in greater concentrations at urban sites than at other sites. The highest individual and median concentrations of 10 of the 13 insecticides detected were present in samples from the two sites with the highest urban land use. Ten of the 13 insecticides were detected at the highest frequencies at the three most urbanized sites.

Concentrations of 13 pesticides were significantly correlated with streamflow at one or more sites. The strongest relations were (1) concentrations of two herbicides used for lawn care at a suburban site and two herbicides used for agriculture at a site in a small basin with 28 percent agricultural land use correlated positively with streamflow during the growing season and (2) concentrations of the insecticide diazinon correlated positively with streamflow during both seasons at the site that drains the large Raritan River basin. Concentrations of five pesticides, total concentration, and total number of pesticides decreased significantly with flow at the Great Egg Harbor River site, a mixed land-use site in the Coastal Plain. In general, most of the pesticides that correlated positively with streamflow were detected at sites where the predominant land use is associated with the use of the detected pesticide. Most of the pesticides with a negative relation to streamflow were detected at sites where the land use in the basin would not indicate use of the detected pesticide.

The highest total concentrations of pesticides occurred during runoff in late spring and early summer in small agricultural basins (greater than 25 percent agricultural land use). The smallest total concentrations and numbers of pesticides at each site typically occurred during runoff in the nongrowing season, with the smallest values occurring at the Great Egg Harbor River and Bound Brook sites. The highest number of pesticides detected in a sample (18) occurred during the growing season at both Bound Brook and Stony Brook sites. Total-pesticide concentrations and total number of pesticides generally increased as streamflow increased at all sites except Great Egg Harbor River. The number of pesticides detected was found to increase significantly as streamflow increased at the Raritan River site and to decrease with increased streamflow at the Great Egg Harbor River site. Numbers of pesticides generally increased with increased streamflow at four of the five other sites; the exception was the Passaic River site.

The median total-pesticide concentrations were highest in runoff samples in the growing season at all sites and lowest in the nongrowing season regardless of flow conditions at all sites. The median total number of pesticides was highest in runoff samples collected in the growing season at all sites and lowest in runoff samples collected in the nongrowing season at all sites, except the Raritan River site. Variability in total-pesticide concentrations and total numbers of pesticides was greatest during runoff in the growing season and least during base-flow conditions in the nongrowing season at most sites.

—Robert G. Reiser

## References Cited

- Buxton, D.E., and Dunne, Paul, 1993, Water-quality data for the Millstone River at Weston, New Jersey, and the Shark River at Remson Mill, New Jersey, March - September 1992: U.S. Geological Survey Open-File Report 93-444, 16 p.
- Canadian Council of Resource and Environmental Ministers, 1991, Canadian water quality guidelines: Ottawa, Ontario, Environment Canada, Inland Waters Directorate, Water Quality Branch (updated May 1996), variously paged.
- Capel, P.D., Nacionales, F.C., and Larson, S.J., 1995, Precision of a splitting device for water samples: U.S. Geological Survey Open-File Report 95-293, 6 p.
- Cohn, T.A., 1988, Adjusted maximum estimation of the moments of lognormal populations from type 1 censored samples: U.S. Geological Survey Open-File Report 88-350, 34 p.
- DeLuca, M.J., Oden, J.H., Romanok, K.M., and Riskin, M.L., 1999, Water resources data for New Jersey—Water year 1998, Volume 3. Water-quality data: U.S. Geological Survey Water-Data Report NJ-98-3, 450 p.
- Edwards, T.K., and Glysson, D.G., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.
- Fegeas, R.G., Claire, R.W., Guptill, S.C., Anderson, K.E., and Hallam, C.A., 1983, Land use and land cover digital data: U.S. Geological Survey Circular 895-E, 21 p.
- Ferrari, M.J., Ator, S.W., Blomquist, J.D., and Dryart, J.E., 1997, Pesticides in surface water of the Mid-Atlantic region, 1997: U.S. Geological Survey Water-Resources Investigations Report 97-4280, 12 p.
- Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program: Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33p.
- Harte, John, Holdren, Cheryl, Schneider, Richard, Shirley, Christine, 1991, Toxics A to Z: A guide to everyday pollution hazards: Berkeley and Los Angeles, Calif., University of California Press, 479 p.
- Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: New York, Elsevier Science Publishing Company Inc., 522 p.
- Hitt, K.J., 1994, Refining 1970's land-use data with 1990 population data to indicate new residential development: U.S. Geological Survey Water-Resources Investigations Report 94 4250, 15 p.
- International Joint Commission Canada and United States, 1977, New and revised Great Lakes water quality objectives, Volume II, An IJC report to the governments of the United States and Canada: Windsor, Ontario, Canada, IJC.
- Ivahnenco, Tamara, and Buxton, D.E., 1994, Agricultural pesticides in six drainage basins used for public water supply in New Jersey, 1990: U.S. Geological Survey Water-Resources Investigations Report 93-4101, 56 p.
- Larson, S.J., Capel, P.D., Goolsby, D.A., Zaugg, S.D., and Sandstrom, M.W., 1995, Relations between pesticide use and riverine flux in the Mississippi River basin: *Chemosphere*, v. 31, no. 5, p. 3305-3321.

- Larson, S.J., Capel, P.D., and Majewski, M.S., 1997, Pesticides in surface waters - Distribution, trends, and governing factors: Chelsea, Michigan, Ann Arbor Press, 373 p.
- New Jersey Department of Environmental Protection, 1996, New Jersey geographic information system: Trenton, N.J., CD-ROM series 1, v. 2.
- \_\_\_\_\_. 1998, Surface water quality standards: N.J.A.C. 7:9B: Trenton, N.J., New Jersey Department of Environmental Protection, Office of Environmental Planning, April 1998, 122 p.
- O'Brien, A.K., Reiser, R.G., and Gylling, Helle, 1998, Volatile organic compounds in New Jersey and Long Island streams: U.S. Geological Survey Fact Sheet 194-97, 6 p.
- Ott, L., 1988, An introduction to statistical methods and data analysis: Boston, Mass., PWS-Kent Publishing Company, 835 p.
- Reed, T.J., Centinaro, G.L., DeLuca, M.J., Hutchinson, J.T., and Scudder, Jeffrey, 1997, Water resources data for New Jersey—Water year 1996, Volume 1. Surface-water data: U.S. Geological Survey Water-Data Report NJ-96-1, 562 p.
- Reed, T.J., Centinaro, G.L., DeLuca, M.J., and Oden, J.H., 1998, Water resources data for New Jersey—Water year 1997, Volume 1. Surface-water data: U.S. Geological Survey Water-Data Report NJ-97-1, 608 p.
- Reiser, R.G., and O'Brien, A.K., 1998, Occurrence of pesticides in streams in New Jersey and Long Island, New York, and relation to land use: U.S. Geological Survey Water-Resources Investigation Report 98-4261, 12 p.
- Stackelberg, P.E., Hopple, J.A., and Kaufman, L.J., 1997, Occurrence of nitrate, pesticides, and volatile organic compounds in the Kirkwood-Cohansey aquifer system, southern New Jersey: U.S. Geological Survey Water-Resources Investigations Report 97-4241, 8 p.
- U.S. Bureau of the Census, 1991, Census of population and housing, 1990: Public Law 94-171 data for New Jersey: Washington, D.C., U.S. Bureau of the Census [machine readable data files (CD ROM)].
- U.S. Department of Agriculture, 1995, ARS Pesticide Properties Database (Last update: May 1995): U.S. Department of Agriculture, Agricultural Research Service. (Accessed July 1, 1998, on the World Wide Web at URL <http://www.arsusda.gov/rsml/ppdb2.html>.)
- U. S. Environmental Protection Agency, 1991, Water-quality criteria summary Office of Water, Office of Science and Tech., Health and Ecological Effects Division (poster).
- \_\_\_\_\_. 1994, Atrazine, simazine, cyanazine; notice of initiation of special review: Federal Register, v.59, p. 60412-60443 (Accessed July 8, 1998, on the world wide web at URL <http://www.epa.gov/fedrgstr/EPA-PEST/1994/November/Day-23/pr-54.html>).
- \_\_\_\_\_. 1995, Guidance for assessing chemical contaminant data for use in fish advisories: Volume 1, Fish sampling and analysis, 2d ed.: Office of Water, EPA 823-R-95-007, 436 p.
- \_\_\_\_\_. 1996, Drinking water regulations and health advisories: Office of water, EPA 822-B-96-002, Washington, D.C., Oct., 1996, 16 p.
- Ware, G.W., 1994, The pesticide book: Fresno, Calif., Thomson Publications, 386 p.
- Werner, S.L., Burkhardt, M.R., and DeRusseau, S.N., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96-216, 42 p.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 49 p.

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