# Seasonal and Spatial Variability of Nutrients and Pesticides in Streams of the Willamette Basin, Oregon, 1993–95

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# FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

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## CONVERSION FACTORS AND ABBREVIATIONS

| Multiply | By | To obtain |
|---|---|---|
| | **Length** | |
| inch (in.) | 25.4 | millimeter (mm) |
| inch (in.) | 0.0254 | meter (m) |
| foot (ft) | 0.3048 | meter (m) |
| mile (mi) | 1.609 | kilometer (km) |
| | Area | |
| square mile ($mi^2$) | 2.590 | square kilometer ($km^2$) |
| | **Volume** | |
| cubic feet ($ft^3$) | 0.02832 | cubic meter ($m^3$) |
| | **Flow (volume per unit time)** | |
| cubic feet per second ($ft^3/s$) | 0.02832 | cubic meter per second ($m^3/s$) |
| | **Concentration in water** | |
| milligrams per liter (mg/L) | 1.0 | part per million (ppm) |
| micrograms per liter (µg/L) | 1.0 | parts per billion (ppb) |
| micrograms per liter (µg/L) | 1,000 | nanograms per liter (ηg/L) |
| | **Area** | |
| acre | 0.004047 | square kilometer ($km^2$) |
| | **Mass** | |
| tons, short (2,000 lb) | 0.9072 | megagram (Mg) |
| pounds, avoirdupois (lb) | 0.4536 | kilogram (kg) |

**Abbreviations**

| Abbreviation | Definition |
|---|---|
| < | less than |
| 2,4-D | (2,4-dichlorophenoxy)acetic acid |
| 2,4-DB | 4-(2,4-dichlorophenoxy)butyric acid |
| 2,4,5-T | (2,4,5-trichlorophenoxy)acetic acid |
| censored | concentration below its analytical minimum reporting level or method detection limit |
| DCPA | dimethyltetrachloroterephthalate |
| DDE | dichlorodiphenyldichloroethylene |
| DNOC | 4,6-dinitro-o-cresol |
| E | estimated |
| EPTC | S-ethyl dipropylthiocarbamate |
| FMS | field matrix spike |
| FS | fixed station |
| GC/MS | Gas chromatography/ Mass spectrometry |
| GIRAS | Geographic Information Retrieval and Analysis System land-use data |
| HCH | hexachlorocyclohexane |

## Conversion Factors and Abbreviations—Continued

| Abbreviation | Definition |
|---|---|
| KJDL | total kjeldahl nitrogen (sum of organic and ammonia nitrogen) concentration as N |
| HPLC/DAD | high-performance liquid chromatography/photodiode-array detection |
| LCS | laboratory control spike |
| MCL | maximum contaminant level |
| MCPA | (4-chloro-2-methylphenoxy)acetic acid |
| MCPB | 4-(4-chloro-o-tolyloxy)butyric acid |
| MDL | method detection limit |
| MRL | minimum reporting level |
| N | nitrogen |
| NADP/NTN | National Atmospheric Deposition Program/National Trends Network |
| NAWQA | National Water-Quality Assessment Program |
| $NO_3$-N | filtered nitrite plus nitrate concentration as N |
| NWIS | National Water Information System |
| NWQL | National Water Quality Laboratory |
| P | phosphorus |
| QC | quality control |
| RM | river mile |
| SH | schedule |
| SPE | solid-phase extraction |
| SRP | soluble reactive phosphorus concentration as P |
| STORET | U.S. Environmental Protection Agency Storage and Retrieval System |
| STP | sewage treatment plant |
| SU | Study Unit |
| TN | total nitrogen concentration as N |
| TP | total phosphorus concentration as P |
| USEPA | U.S. Environmental Protection Agency |
| USGS | U.S. Geological Survey |
| WY | water year |

# GLOSSARY

**Accuracy.** A measure of the degree of conformity of the values generated by a specific method or procedure with the true value. The concept of accuracy includes both bias (systematic error) and precision (random error) (Fishman and Friedman, 1989).

**Agricultural site.** Sampling site that receives drainage from an subbasin that has greater than 50-percent agricultural and less than 25-percent urban area.

**Analyte.** A specific compound or element of interest undergoing chemical analysis.

**Background site.** Site at the headwater of a drainage basin that has been minimally impacted by humans.

**Bias.** A persistent positive or negative deviation of the values generated by a specific method or procedure from the true value, expressed as the difference between the true value and the mean value obtained by repetitive testing of the homogeneous sample (Fishman and Friedman, 1989).

**Environmental setting.** Land areas characterized by a unique, homogeneous combination of natural and human-related factors (Gilliom and others, 1995).

**Field equipment blank.** A solution of water that contains analytes of interest below detection limits, and is subjected to all aspects of sample collection, processing, preservation, transportation, and laboratory handling as an environmental sample but is collected at a sampling site immediately before the environmental sample.

**Field-matrix spike sample**. A sample to which a known concentration of specific analytes have been added in such a manner as to minimize the change of the matrix of the original environmental sample. An aliquot of this solution is added to the sample prior to shipment to the laboratory for analysis. This spike sample is analyzed in tandem with the environmental sample at the laboratory.

**Filtered-water sample.** An operational definition referring to the chemical analysis of that portion of a water-suspended sediment sample that passes through a nominal 0.45 micrometer (nutrients) or a 0.7 micrometer (pesticides) filter (Fuhrer and others, 1995).

**Fixed-station network.** Sites on streams at which streamflow is measured and water samples are collected monthly and during periods when extremes in water quality are expected to assess broad-scale seasonal and temporal character and transport of constituents in relation to hydrologic conditions and environmental settings (Shelton, 1994).

**Forested site.** Sampling site that receives drainage from a subbasin that has greater than 90-percent forested area.

**Indicator site.** Stream sampling site located at an outlet of a drainage basin with relatively homogeneous land use and physiographic conditions. Basins are as large and representative as possible, but still encompassing primarily one environmental setting (typically, 50 to 500 $km^2$) (Shelton, 1994).

**Integrator or mixed-use site.** Stream sampling site located at an outlet of a drainage basin that contains multiple environmental settings. Most integrator sites are on major streams with relatively large drainage areas (Shelton, 1994).

**Kjeldahl nitrogen.** Modified Kjeldahl nitrogen (Jirka method) is a a simultaneous digestion/determination analyses.

**Laboratory control spike.** Matrix spike solution added to the stock blank water at the laboratory. This sample is included with each sample set and undergoes the entire extraction, elution, and analysis procedures. Recoveries represent the best possible recoveries for a known matrix and are used to monitor performance of the analytical method.

**Method detection limit.** Minimum concentration of a substance that can be identified, measured, and reported with a 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. Method detection limit is compound dependent and also dependent on sample matrix and instrument performance and other operational sources variation (Zaugg and others, 1995).

**Minimum reporting level.** The smallest measured concentration of a constituent that may be reliably reported given the analytical method. The minimum reporting level is generally higher than the detection limit because of unpredictable matrix effects for different waters (Timme, 1995).

**Nitrate.** One of the primary forms of dissolved nitrogen in natural water. It is a compound of nitrogen in combination with oxygen. Nitrate is highly soluble in water and is stable over a wide range of environmental conditions. It is readily transported in ground water and streams (Mueller and Helsel, 1996).

**Nonpoint source.** A pollution source that cannot be defined as originating from discrete points such as a pipe discharge. Areas of fertilizer and pesticide applications, atmospheric deposition, manure, and natural inputs from plants and trees are types of nonpoint source pollution (Intergovernmental Task Force on Monitoring Water Quality, 1995).

**Nutrients.** Chemical elements that are essential to plant and animal nutrition. Nitrogen and phosphorus are nutrients that are important to aquatic life, but in high concentrations they can be contaminants in water. These nutrients occur in a variety of forms. Both are affected by chemical and biological processes that can change their form and can transfer them to or from water, soil, biological organisms, and the atmosphere (Mueller and Helsel, 1996).

**Occurrence and Distribution Study**. Study of the broad-scale geographic and seasonal distributions of water-quality conditions for surface water of a Study Unit in relation to major contaminant sources and background conditions (Gilliom and others, 1995).

**Pesticide degradation product.** A chemical compound formed by transformation of a pesticide parent compound.

**Phosphates.** Only significant form of dissolved phosphorus in natural water. They are compounds of phosphorus in combination with oxygen and hydrogen. Phosphates are only moderately soluble and, relative to nitrate, are not very mobile in soils and ground water. Phosphates tend to remain attached to soil particles. However, erosion can transport considerable amounts of "particulate" phosphate to streams and lakes (Mueller and Helsel, 1996).

**Point source.** A pollution source is discharge that can flow through a pipe or another discrete source. Municipal wastewater treatment plants, factories, confined animal feedlots, or combined sewers are sources of point-source pollution (Intergovernmental Task Force on Monitoring Water Quality, 1995).

**Precision.** The degree of agreement of repeated measurements by a specific method or procedure, expressed in terms of dispersion of the values generated about the mean values obtained by repetitive testing of the homogeneous samples (Fishman and Friedman, 1989).

**Solid-phase extraction (SPE).** A procedure to isolate specific organic compounds onto a bonded silica extraction column.

**Soluble reactive phosphorus.** A determination of orthophosphate as well as phosphorus adsorbed onto colloidal particles, and approximates "dissolved inorganic phosphorus".

**Split sample.** Sample portions prepared by dividing a sample into two or more equal volumes, where each volume is considered as a separate sample but representative of the entire sample.

**Study unit.** A major hydrologic system of the United States in which NAWQA studies are focused. NAWQA Study Units are geographically defined by a combination of ground- and surface-water features and usually encompass more than 10,000 km$^2$ of land area. The NAWQA design is based on assessment of 60 Study Units, which collectively cover a large part of the Nation, encompass the majority of population and water use, and include diverse hydrologic systems that differ widely in natural and human factors that affect water quality (Shelton, 1994).

**Surrogate solution.** Series of organic compounds of known concentrations which are added to all pesticide samples for laboratory schedules 2010 and 2051. These compounds are not expected to be seen in the environment yet are expected to behave similarly to select targeted analytes found in the environment.

**Synoptic network.** Sites sampled during short time periods (one week or less) to evaluate the spatial distribution of water quality during specified hydrologic conditions.

**Total-water sample**. An operational term referring to the chemical analysis of that portion of a water-suspended sediment sample that has not been not been filtered (analyzing the filtered and suspended phases).

**Urban site.** Sampling site that receives drainage from a subbasin that has greater than 50-percent urbanized and less than 25-percent agricultural area.

**Variability.** The degree of random error in independent measurements of the same quantity. Replicates are quality control samples used to estimate variability.

**Water-quality criteria.** As defined in this report refers to a compilation of commonly used standards or guidelines established by the U.S. Environmental Protection Agency, the Canadian Council of Resource and Environment Ministers, and the National Academy of Sciences/National Academy of Engineering (Gilliom and others, in press). Criteria are established at concentrations at which there normally are some observed risk of adverse effects.

**Water-quality monitoring**. Integrated activity for evaluating physical, chemical and biological character in relation to human health, ecological conditions and designated water uses (Intergovernmental Task Force on Monitoring Water Quality, 1995).

**Water year.** October 1 of one year through September 30 of the next year.

# Seasonal and Spatial Variability of Nutrients and Pesticides in Streams of the Willamette Basin, Oregon, 1993–95

*By* Frank A. Rinella and Mary L. Janet

## Abstract

From April 1993 to September 1995, the U.S. Geological Survey conducted a study of the occurrence and distribution of nutrients and pesticides in surface water of the Willamette and Sandy River Basins, Oregon, as part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program. About 260 samples were collected at 51 sites during the study; of these, more than 60 percent of the pesticide samples and more than 70 percent of the nutrient samples were collected at 7 sites in a fixed-station network (primary sites) to characterize seasonal water-quality variability related to a variety of land-use activities. Samples collected at the remaining 44 sites were used primarily to characterize spatial water-quality variability in agricultural river subbasins located throughout the study area.

This report describes concentrations of 4 nutrient species (total nitrogen, filtered nitrite plus nitrate, total phosphorus, and soluble reactive phosphorus) and 86 pesticides and pesticide degradation products in streams, during high- and low-flow conditions, receiving runoff from urban, agricultural, forested, and mixed-use lands. Although most nutrient and pesticide concentrations were relatively low, some concentrations exceeded maximum contaminant levels for drinking water and water-quality criteria for chronic toxicity established for the protection of freshwater aquatic life. The largest number of exceedances generally occurred at sites receiving predominantly agricultural inputs.

Total nitrogen, filtered nitrite plus nitrate, total phosphorus, and soluble reactive phosphorus concentrations were detected in 89 to 98 percent of the samples; atrazine, simazine, metolachlor, and desethylatrazine were detected in 72 to 94 percent of the samples. Fifty different pesticides and degradation products was detected during the 2-1/2 year study.

Seasonally, peak nutrient and pesticide concentrations at the seven primary sites were observed during winter and spring rains. With the exception of soluble reactive phosphorus, peak nutrient concentrations were recorded at agricultural sites during winter rains, whereas peak pesticide concentrations occurred at agricultural sites during spring rains.

Spatially, although nutrients were detected slightly more often in samples from the northern Willamette Basin relative to the southern Willamette Basin, concentration distributions in the two areas were similar. About 75 percent more pesticides were detected in the northern basin; however, two-thirds of the pesticide detections in the southern basin were larger in concentration than for the same pesticides detected in the northern basin.

Nutrient and pesticide concentrations were associated with percent of upstream drainage area in forest, urbanization, and agriculture. Nutrient concentrations at forested sites were among the smallest observed at any of the sites sampled. In addition, only one pesticide and one pesticide degradation product were detected at forested sites, at concentrations near the method detection limits. The highest nutrient concentrations were observed at agricultural sites. Further, the largest numbers of different pesticides detected were at agricultural sites, at concentrations generally larger than at most other land-use sites. Three pesticides—dichlobenil, prometon, and tebuthiuron—were

detected more frequently at a site receiving predominantly urban inputs.

## INTRODUCTION

The Willamette Basin study began in 1991 as 1 of the first 20 study units established nationwide under the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS). The NAWQA Program was designed to characterize status and trends of water quality for most of the Nation's surface- and ground-water resources, and to evaluate natural and human-caused impacts on these resources (Leahy and others, 1990; Leahy and Thompson, 1994). The Willamette Basin Study Unit (SU) encompasses approximately 12,000 square miles in western Oregon and contains the surface-water drainages of the Willamette and Sandy River Basins, referred to collectively as the "Willamette Basin" in this report (fig. 1). The Sandy River Basin was included in this study because its watershed is a major source of drinking water for the city of Portland and its surrounding areas.

### Purpose and Scope

The purpose of this report are (1) to describe the seasonal and spatial variability of nutrients (nitrogen and phosphorus) and pesticides in surface water of the Willamette Basin, and (2) to relate nutrient and pesticide concentrations to streamflow conditions and land-use activities. To this end, surface-water-quality samples were collected at sites selected to allow a temporal and spatial characterization of both nutrient and pesticide dynamics in streams of the basin and analyzed for a suite of nutrient species and pesticide compounds. Sampling sites were selected on the basis of (1) percentages of drainage areas representing forested, agricultural, or urban land use, and (2) specific crop types and pesticide-use patterns in agricultural areas.

### Acknowledgments

The Oregon Department of Environmental Quality provided partial funding for data collection and analysis at seven sites in the basin. In addition, the authors wish to extend their appreciation to many USGS personnel who contributed to this study: Doug Cushman, Mike DeVolder, Martell Kiefer, Greg Olsen, and Roy Wellman conducted much of the fixed-station sampling. Bernie Bonn, Kurt Carpenter, Ben Davis, Ned Gates, Steve Hinkle, Julie Laenen, Dan McClelland, Jennifer Morace, Mark Uhrich, Ian Waite, Dennis Wentz, and Winston Woo assisted with the synoptic sampling. Kathy Kuivila and Kathryn Crepeau (Sacramento, California) provided critical technical and analytical support for the high-flow synoptic sampling in the Pudding River Subbasin in April 1993. This support was instrumental to our understanding of the relations between land use and instream concentrations of nutrients and pesticides during a major storm event. Bernie Bonn provided summary statistics for the pesticide-spike quality-control data. Mark Uhrich created the geographic-information-system (GIS) coverages. Dennis Wentz, Chief of the Willamette Basin NAWQA project, provided guidance and oversight throughout the project. Finally, this report reflects the effort of a team of technical reviewers, illustrators, and editors. Team members included Kathy Kuivila, Doug Lee, Stu McKenzie, Jackie Olson, Donita Parker, Thelma Parks, Joe Rinella, Stewart Rounds, Dennis Wentz, and John Williams.

## DESCRIPTION OF THE WILLAMETTE BASIN

Descriptions of the geographic setting, hydrogeology, surface-water hydrology, major land-use activities, population densities, water use and 1980–90 nitrogen and phosphorus concentrations and loadings for the Willamette Basin are described by Bonn and others (1995). Estimated acreage for most crop types and pounds of pesticides applied for the Willamette Basin in 1987, by county, were described by Anderson and others (1996). Agricultural activities differ between the northern and southern parts of the Willamette Basin. More row crop fields, orchards, vineyards, and nurseries are located in the north, whereas more grains, hays and silages, and grass and legume seeds are produced in the southern part of the basin (Anderson and others, 1996); thus, types of nutrients and pesticides used, rates of

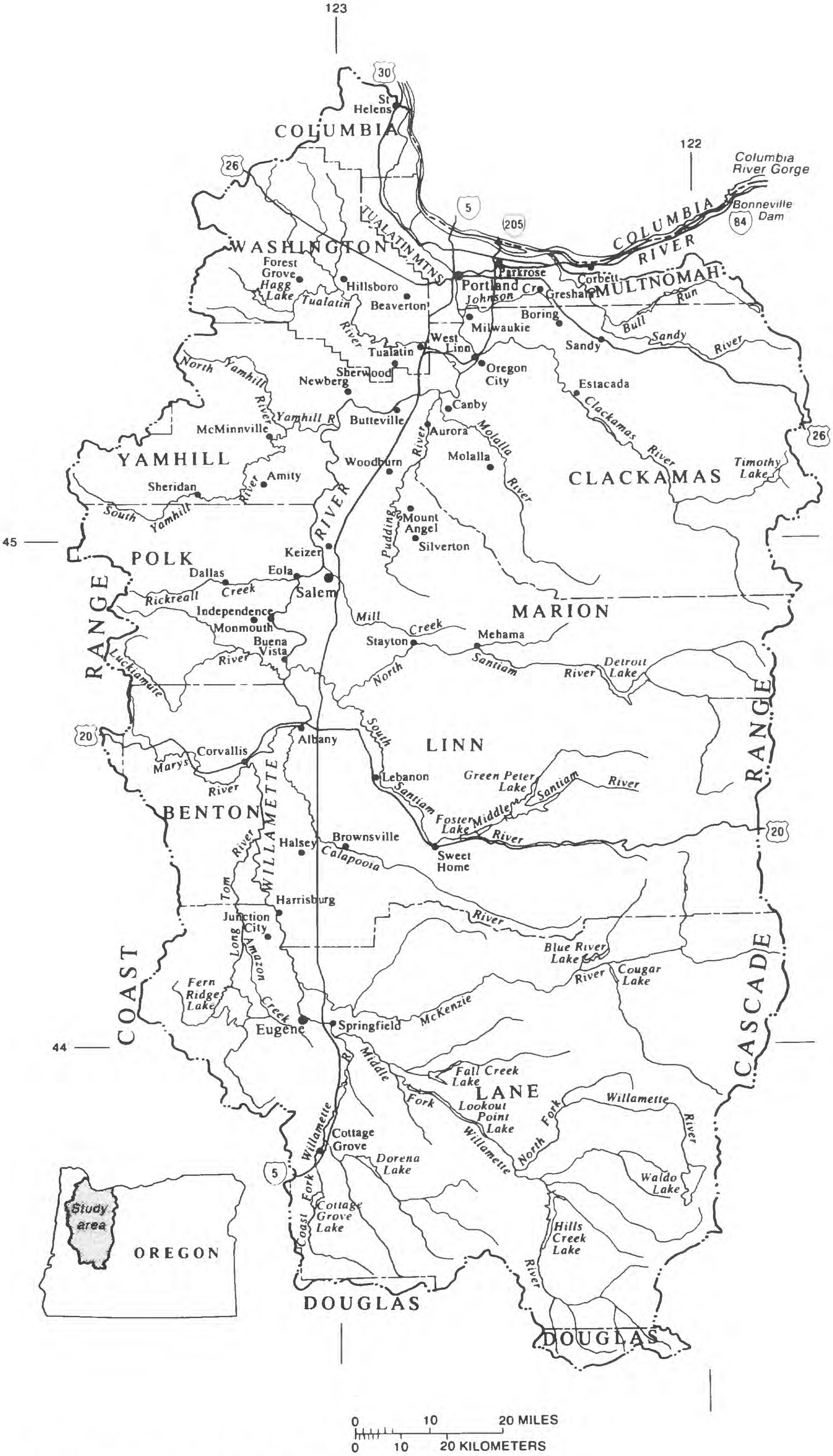

**Figure 1**. Willamette River Basin, Oregon.

application, and timing of usage are different throughout the basin.

### Sources of Nutrients

Nutrient inputs to the Willamette Basin are generally categorized as atmospheric deposition, fertilizer applications, animal manure deposits, and other sources, such as industrial/municipal discharge, runoff and leachate from septic systems and landfills, and natural inputs from plants and trees (Bonn and others, 1995). Updated estimates have been provided in this report, where possible, for the contribution of nitrogen and phosphorus loadings from atmospheric deposition, fertilizer applications, and manure deposits; insufficient information was available to summarize nutrient loadings from other sources (Bonn and others, 1995).

The average annual atmospheric deposition (wet) for nitrogen on the Willamette Basin, on the basis of data from the National Trends Network of the National Atmospheric Deposition Program (NADP/NTN) for the 1980–90 period, was estimated at 4,100 tons per year as nitrogen (this estimate was based on averaging atmospheric depositional amounts for the 11,200 square-mile drainage area upstream of the monitoring site located on the Willamette River at Portland [Bonn and others, 1995]). No data were available in the NADP/NTN database that would enable an estimate to be made of the average annual atmospheric deposition for phosphorus.

Annual loadings for nitrogen and phosphorus from fertilizer applied to agricultural areas in the Willamette Basin for 1991 (most recent data available) were estimated in this study to be 63,100 tons as nitrogen and 20,400 tons as phosphorus. These estimates represent a 21 and 220 percent increase, respectively, in the annual nitrogen and phosphorus fertilizer loadings estimated for 1985 (Bonn and others, 1995). The 1985 and 1991 estimates were calculated from county estimates of total nitrogen and phosphorus fertilizer sales for 1985 and 1991 (W.A. Battaglin, USGS, written commun., 1996).

Annual loadings for nitrogen and phosphorus from animal livestock (manure) in the Willamette Basin for 1992 (most recent data available) were estimated as 16,100 and 3,800 tons, respectively. These estimates represent a 17 and 22 percent reduction, respectively, in the annual nitrogen and phosphorus manure loadings estimated for 1982 (Bonn and others, 1995). These estimates were calculated from county estimates of animal populations for 1982 and 1992 from the 1992 Census of Agriculture (U.S. Bureau of the Census, 1995) multiplied by estimated nitrogen and phosphorus amounts contributed by animal wastes (L.J. Puckett, USGS, written commun., 1996).

### Sources of Pesticides

Pesticide inputs to the Willamette Basin have been estimated from data that include applications to agricultural crops, industrial and residential properties, rights of way, and disease-vector control. Basinwide usage rates for the top 30 most used pesticides in 1987 (Rinehold and Witt, 1989), along with rates of pesticide use between the northern and southern parts of the basin, are listed in table 1. Because current pesticide-use estimates are now available only for particular agricultural crops, no current estimates of all pesticide use throughout the Willamette Basin similar to the 1987 estimates was available. In addition, several pesticides, such as ethoprop, prometon, and tebuthiuron, frequently detected in the basin were not included in table 1 because usage rates were unavailable.

## STUDY DESIGN AND METHODS

### Study Design

The design of the surface-water-quality monitoring program involved the selection of sites to increase our understanding of seasonal and spatial variability of runoff of nutrients and pesticides in the Willamette Basin. Two types of sampling programs—the fixed-station network and the synoptic network—were designed to accomplish this goal.

The fixed-station monitoring network consisted of seven stations distributed throughout the northern Willamette Basin (table 2 and fig. 2); these stations were sampled for 2-1/2 years to monitor seasonal changes in water quality resulting from a variety of land-use activities, whose

**Table 1.** Annual usage rates for the top 30 pesticides applied in the Willamette Basin, Oregon, 1987
[Data for 1987 from Rinehold and Witt, 1989; lbs/yr, pounds per year; - -, not available; 2,4-D, (2,4-dichlorophenoxy) acetic acid; EPTC, S-ethyl dipropylthiocarbamate; MCPA, (4-chloro-2-methylphenoxy) acetic acid; the northern Willamette Basin area includes Clackamas, Marion, Multnomah, Polk, Washington, and Yamhill Counties; the southern Willamette Basin area includes Benton, Lane, and Linn Counties]

| Compound | 1987 Rank | 1987 Total usage (lb/yr) | 1987 Northern basin (lb/yr) | 1987 Southern basin (lb/yr) |
|---|---|---|---|---|
| 2,4-D | 4 | 4 | 330,700 | 145,000 |
| Alachlor | 25 | 25 | 63,540 | 19,500 |
| Atrazine | 2 | 2 | 409,400 | 209,000 |
| Benomyl | 30 | 30 | 37,100 | 9,900 |
| Calcium polysulfide | 3 | 3 | 401,900 | 26,900 |
| Captan | 27 | 27 | 51,960 | 14,660 |
| Carbaryl | 14 | 14 | 119,500 | 26,000 |
| Chlorothalonil | 16 | 16 | 112,000 | 52,400 |
| Chlorpyrifos | 13 | 13 | 120,710 | 46,100 |
| Copper | 6 | 6 | 316,300 | 16,300 |
| Diazinon | 12 | 12 | 122,400 | 22,500 |
| Dicamba | 22 | 22 | 72,230 | 30,500 |
| Dichlobenil | 28 | 28 | 46,080 | 5,680 |
| Dichloropropene | 26 | 26 | 55,500 | - - |
| Dichlofop | 18 | 18 | 108,380 | 38,000 |
| Dinoseb | 17 | 17 | 108,800 | 40,400 |
| Diuron | 1 | 1 | 552,500 | 240,000 |
| EPTC | 20 | 20 | 78,600 | 39,000 |
| Ethofumesate | 24 | 24 | 69,040 | 58,500 |
| Fonofos | 15 | 15 | 114,100 | 34,600 |
| Glyphosate | 10 | 10 | 158,300 | 40,700 |
| MCPA | 11 | 11 | 133,900 | 43,000 |
| Malathion | 23 | 23 | 71,680 | 1,080 |
| Maneb | 7 | 7 | 279,200 | 153,000 |
| Metaldehyde | 19 | 19 | 80,140 | 4,640 |
| Metolachlor | 29 | 29 | 42,450 | 24,100 |
| Napropamide | 21 | 21 | 74,790 | 5,490 |
| Oil | 5 | 5 | 319,800 | 42,800 |
| Simazine | 9 | 9 | 166,600 | 65,700 |
| Sulfur | 8 | 8 | 240,400 | 21,000 |

categories were agricultural, urban, forested, and mixtures of these. The sites generally were sampled monthly, and additional water-quality samples were collected during periods when extremes in water quality were expected. Additional water samples were collected during spring runoff (late March through early June) following application of pesticides and fertilizers, and fall/winter runoff (October through January) following the heaviest seasonal rains. Three sites were located in the Tualatin River Subbasin (map reference numbers 4–6) and three sites were located within the Pudding River Subbasin (map reference numbers 1–3) in a nested design. Both subbasins included a forested site selected to reflect background water-quality conditions, an “indicator” site, selected to represent one predominant land use (urban or agricultural), and an “integrator” site (located near the terminus of the subbasin) selected to represent an integration of water-quality conditions from a mix-

**Table 2.** Description of surface-water-quality sampling sites and sampling frequencies for nutrients and pesticides, Willamette Basin, Oregon, April 1993 through September 1995

[Sites are listed by subbasins, tributaries or main-stem basin in downstream order within a subbasin; - -, not analyzed; abv, above; Ave, Avenue; blw; below; Br, Bridge; Cr, Creek; Dr, Drive; Hwy, Highway; L, Little; Ln, Lane; Mt, Mount; NF, North Fork; nr, near; R, River; Rd, Road; SH, Schedule; STP, sewage treatment plant; Trib, tributary; minimum reporting levels for nutrients, Appendix 3; method detection limits for SH 2010, Appendix 1; method detection limits for SH 2051, Appendix 2; land-use estimates, Fegeas and others, 1983; major land-use designations in bold; no bold number in land-use columns represents mixed land-use or industrial designation]

| | | | | Number and types of samples collected | | | | | Land use (percent) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Map reference number | Station number | Station name | Sampling period | Nutrients SH 2702 | Pesticides SH 2010 | Pesticides SH 2051 | Selected nutrients | Selected pesticides | Urban | Agriculture | Forest | Drainage area (square miles) |
| **FIXED-STATION NETWORK** | | | | | | | | | | | | |
| **Pudding River Subbasin** | | | | | | | | | | | | |
| 1 | 14200400 | Little Abiqua Cr nr Scotts Mills | 04/93–08/95 | 22 | 3 | 1 | - - | - - | 0 | 4 | **96** | 9.84 |
| 2 | 14201300 | Zollner Cr nr Mt Angel | 04/93–08/95 | 32 | 30 | 29 | - - | - - | 1 | **99** | 0 | 15.0 |
| 3 | 14202000 | Pudding R at Aurora | 04/93–08/95 | 30 | 30 | 30 | - - | - - | 5 | **58** | 36 | 487 |
| **Tualatin River Subbasin** | | | | | | | | | | | | |
| 4 | 14203750 | Gales Cr nr Glenwood | 04/93–08/95 | 23 | 4 | 1 | - - | - - | 0 | 0 | **100** | 7.10 |
| 5 | 14206950 | Fanno Cr at Durham | 04/93–08/95 | 29 | 29 | 25 | - - | - - | **92** | 2 | 5 | 31.0 |
| 6 | 14207500 | Tualatin R at West Linn | 04/93–08/95 | 26 | 5 | 3 | - - | - - | 17 | 35 | 48 | 709 |
| **Main Stem Willamette River** | | | | | | | | | | | | |
| 7 | 14211720 | Willamette R at Portland | 04/93–09/95 | 31 | 20 | 7 | - - | - - | 6 | 22 | 70 | 1,200 |
| **SYNOPTIC NETWORK** | | | | | | | | | | | | |
| **Long Tom River Subbasin** | | | | | | | | | | | | |
| 8 | 441549123232503 | Ferguson Cr at Ferguson Rd nr Junction City | 05/94 & 07/94 | 2 | 2 | 2 | - - | - - | 0 | 0 | **100** | 5.49 |
| 9 | 441307123171003 | Bear Cr at Territorial Hwy nr Junction City | 05/94 & 07/94 | 2 | 2 | 2 | - - | - - | 1 | 30 | 69 | 26.5 |
| 10 | 441451123170903 | Ferguson Cr at Territorial Hwy nr Junction City | 05/94 & 07/94 | 2 | 2 | 2 | - - | - - | 0 | 21 | 79 | 20.5 |
| 11 | 441745123141603 | Flat Cr at Noraton Rd nr Monroe | 05/94 | 1 | 1 | 1 | - - | - - | 13 | **87** | 0 | 32.5 |
| 12 | 442223123153703 | Long Tom R at Bundy Bridge nr Monroe | 05/94–11/94 | 4 | 4 | 4 | - - | - - | 10 | 29 | 57 | 403 |
| **Muddy Creek Subbasin** | | | | | | | | | | | | |
| 13 | 441430123054803 | Muddy Cr at Weatherford Ln nr Harrisburg | 06/94 & 07/94 | 2 | 2 | 2 | - - | - - | 3 | 40 | 57 | 30.9 |
| 14 | 442107123082903 | Muddy Cr at Nixon Rd nr Halsey | 06/94 & 07/94 | 2 | 2 | 2 | - - | - - | 2 | **59** | 38 | 46.8 |

**Table 2.** Description of surface-water-quality sampling sites and sampling frequencies for nutrients and pesticides, Willamette Basin, Oregon, April 1993 through September 1995—Continued

| | | | | Number and types of samples collected | | | | | Land use (percent) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Map reference number | Station number | Station name | Sampling period | Nutrients SH 2702 | Pesticides SH 2010 | Pesticides SH 2051 | Selected nutrients | Selected pesticides | Urban | Agriculture | Forest | Drainage area (square miles) |
| | | | | **SYNOPTIC NETWORK—Continued** | | | | | | | | |
| | | | | **Muddy Creek Subbasin—Continued** | | | | | | | | |
| 15 | 442108123082403 | Little Muddy Cr at Nixon Rd nr Halsey | 07/94 | 1 | 1 | 1 | - - | - - | 1 | **62** | 37 | 59.8 |
| 16 | 443138123120901 | Muddy Cr nr Peoria | 05/94–11/94 | 9 | 9 | 9 | - - | - - | 2 | **71** | 27 | 146 |
| | | | | **Calapooia River Subbasin** | | | | | | | | |
| 17 | 14173500 | Calapooia R at Albany | 05/94–11/94 | 4 | 4 | 4 | - - | - - | 3 | 47 | 50 | 369 |
| | | | | **Pudding River Subbasin** | | | | | | | | |
| 18 | 445300122360103 | NF Silver Cr at Van Handle Rd nr Stayton | 08/94 | 1 | - - | - - | - - | - - | 0 | 0 | **100** | 12.9 |
| 19 | 445322122475303 | Pudding R Trib at Cascade Hwy nr Silverton | 08/94 | 1 | - - | - - | - - | - - | 3 | **94** | 3 | 4.71 |
| 20 | 445633122485103 | Beaver Cr at Sunnyview Rd nr Silverton | 08/94 | 1 | - - | - - | - - | - - | 0 | **100** | 0 | 3.26 |
| 21 | 445814122505602 | Pudding R at Kaufman Rd | 04/93 & 08/94 | 1 | - - | - - | 1 | 1 | 1 | **90** | 9 | 25.3 |
| 22 | 445811122503503 | Beaver Cr at Kaufman Rd nr Silverton | 08/94 | 1 | - - | - - | - - | - - | 0 | **98** | 2 | 7.82 |
| 23 | 450024122492503 | Silver Cr nr Silverton | 08/94 | 1 | - - | - - | - - | - - | 6 | 17 | 77 | 50.2 |
| 24 | 14200300 | Silver Cr at Silverton | 04/93 | - - | - - | - - | 1 | 1 | 4 | 15 | 80 | 47.8 |
| 25 | 450215122484702 | Abiqua Cr at Mt Angel Hwy | 04/93 | - - | - - | - - | 1 | 1 | 2 | 29 | 68 | 77.3 |
| 26 | 14201000 | Pudding R nr Mt Angel | 04/93 & 08/94 | 1 | - - | - - | 1 | 2 | 3 | 47 | 50 | 203 |
| 27 | 445724122551102 | L Pudding R at Sunnyview Rd | 04/93 | - - | - - | - - | 1 | 1 | 10 | **89** | 1 | 11.1 |
| 28 | 450245122542202 | Lake Labish Ditch at 75th Ave | 04/93 & 08/94 | 1 | - - | - - | 2 | 2 | 18 | **82** | 0 | 18.1 |
| 29 | 450241122534102 | L Pudding R nr Rambler Dr | 04/93 & 08/94 | 1 | - - | - - | 1 | 1 | 22 | **74** | 3 | 40.8 |
| 30 | 450602122494503 | Pudding R nr Zollner Cr nr Mt Angel | 08/94 | 3 | - - | - - | - - | - - | 7 | **57** | 36 | 288 |
| 31 | 450735122491003 | Agripac Discharge Pipe by Hwy 214 at Woodburn | 08/94 | 3 | - - | - - | - - | - - | - - | - - | - - | - - |
| 32 | 450734122490902 | Pudding R at Hwy 214 | 04/93 & 08/94 | 3 | - - | - - | 1 | 1 | 6 | **61** | 33 | 316 |
| 33 | 450904122480903 | Woodburn STP Discharge Outflow nr Woodburn | 08/94 | 1 | - - | - - | - - | - - | - - | - - | - - | - - |

**Table 2.** Description of surface-water-quality sampling sites and sampling frequencies for nutrients and pesticides, Willamette Basin, Oregon, April 1993 through September 1995—Continued

| | | | | Number and types of samples collected | | | | | Land use (percent) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Map reference number | Station number | Station name | Sampling period | Nutrients SH 2702 | Pesticides SH 2010 | Pesticides SH 2051 | Selected nutrients | Selected pesticides | Urban | Agriculture | Forest | Drainage area (square miles) |
| | | | SYNOPTIC NETWORK—Continued | | | | | | | | | |
| | | | **Pudding River Subbasin—Continued** | | | | | | | | | |
| 34 | 450901122473202 | Pudding R at Hwy 211 | 04/93 & 08/94 | 3 | -- | -- | 1 | 2 | 6 | **61** | 33 | 320 |
| 35 | 450758122470302 | Butte Cr at Elliott Prairie Rd | 04/93 | -- | -- | -- | 1 | 1 | 1 | 24 | 75 | 66.6 |
| 36 | 451138122431702 | Bear Cr at Barlow-Monitor Rd | 04/93 & 08/94 | 1 | 1 | 1 | 1 | 1 | 12 | **86** | 2 | 19.8 |
| 37 | 450956122440202 | Rock Cr at Miller Rd | 04/93 | -- | -- | -- | 1 | 1 | 2 | **63** | 35 | 61.1 |
| 38 | 451259122481902 | Senecal Cr at Donald Rd | 04/93 & 08/94 | 1 | -- | -- | 1 | 1 | 8 | **89** | 3 | 10.4 |
| 39 | 451403122452101 | Mill Cr at Aurora | 04/93 | -- | -- | -- | 1 | 1 | 13 | **84** | 3 | 39.7 |
| | | | **Zollner Tributary to Pudding River** | | | | | | | | | |
| 40 | 450343122443203 | Zollner Cr at Meridian Rd nr Mt Angel | 08/94 | 1 | 1 | 1 | -- | -- | 0 | **100** | 0 | 1.92 |
| 41 | 450417122461603 | Zollner Cr Trib at Marquam Rd nr Mt Angel | 08/94 | 1 | 1 | 1 | -- | -- | 2 | **96** | 2 | 1.76 |
| 42 | 450431122454602 | Zollner Cr at Boehmer Rd | 04/93 & 08/94 | 1 | 1 | 1 | 1 | 1 | 0 | **100** | 0 | 3.40 |
| 43 | 450517122471503 | Zollner Cr at Hwy 214 nr Mt Angel | 08/94 | 1 | 1 | 1 | -- | -- | 1 | **98** | 1 | 6.75 |
| | | | **Molalla River Subbasin** | | | | | | | | | |
| 44 | 14198500 | Molalla R abv Pine Cr nr Wilhoit | 04/93 | -- | -- | -- | 1 | 1 | 0 | 0 | **100** | 96.9 |
| 45 | 14200000 | Molalla R nr Canby | 04/93 | -- | -- | -- | 1 | 1 | 3 | 15 | 81 | 344 |
| 46 | 451350122415603 | Gribble Cr nr Canby | 08/94 | 1 | 1 | 1 | -- | -- | 9 | **89** | 2 | 9.60 |
| 47 | 451603122423301 | Molalla R at Knights Br nr Canby | 04/93 & 05/94 | 3 | 3 | 1 | -- | 1 | 3 | 15 | 81 | 325 |
| | | | **Johnson Creek Subbasin** | | | | | | | | | |
| 48 | 452823122240900 | Johnson Cr at Palmblad Rd nr Gresham | 05/94 & 10–11/94 | 4 | 6 | 6 | -- | 2 | 27 | **59** | 14 | 12.6 |
| | | | **Champoeg Creek Subbasin** | | | | | | | | | |
| 49 | 451502122524700 | Champoeg Cr blw Mission Cr nr Butteville | 05/94 & 11/94 | 1 | 2 | 2 | -- | 1 | 1 | **95** | 3 | 45.0 |
| | | | **Sandy River Basin** | | | | | | | | | |
| 50 | 453205122223701 | Beaver Cr nr Troutdale | 05/94 & 08/94 | 2 | 2 | 2 | -- | -- | **67** | 29 | 4 | 14.2 |
| | | | **Luckiamute River Subbasin** | | | | | | | | | |
| 51 | 444002123163603 | Soap Cr nr Corvallis | 08/94 | 1 | 1 | 1 | -- | -- | 0 | 6 | **94** | 10.1 |

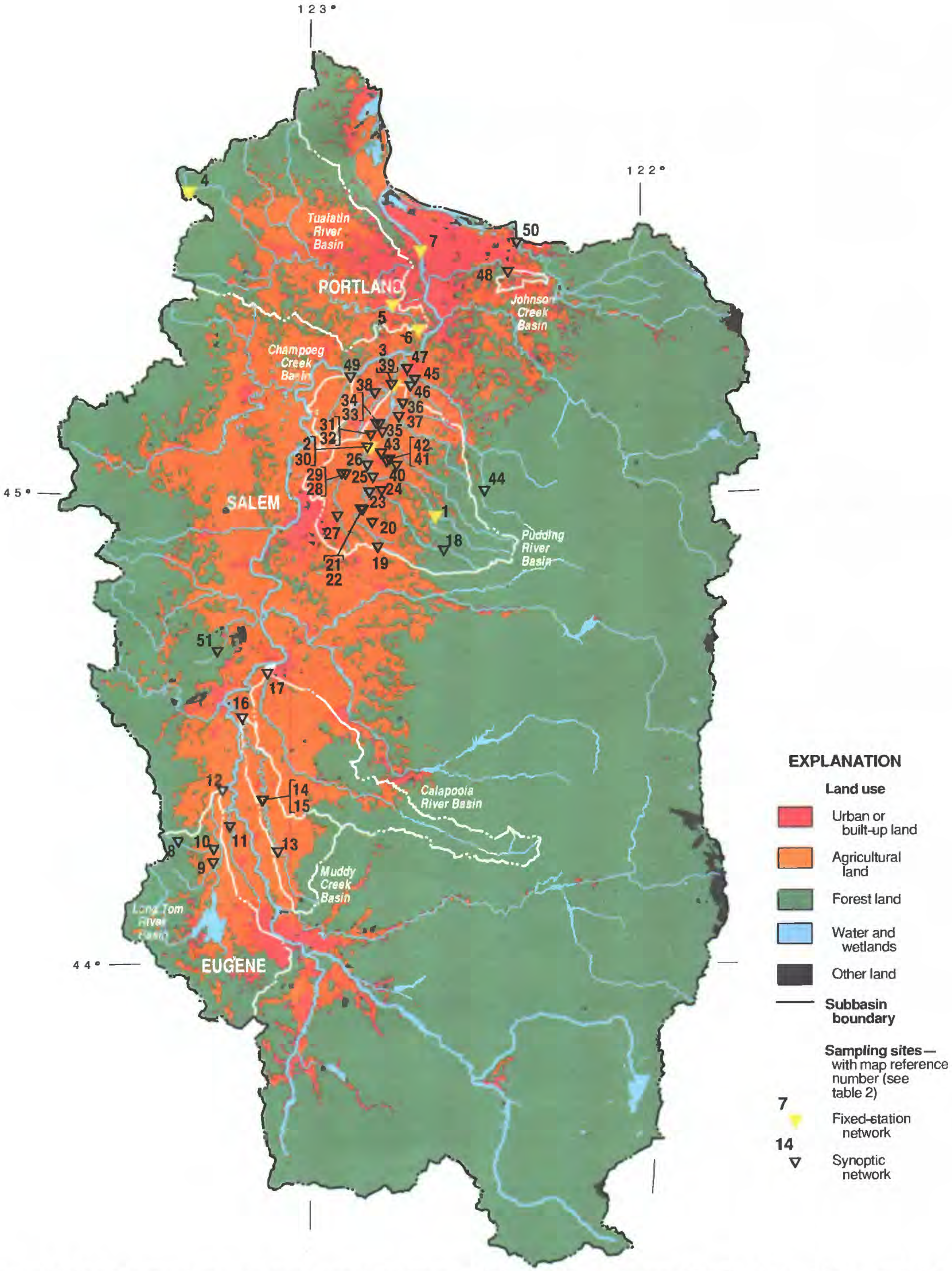

**Figure 2.** Location of surface-water-quality sampling sites in the Willamette Basin, Oregon, April 1993 through September 1995.

ture of land uses (agricultural, forested, and urban). The seventh fixed-station monitoring site was also an "integrator" site located on the Willamette River near the mouth (map reference number 7) to monitor the integrated outflow from nearly the entire Willamette River.

The synoptic monitoring network included 44 additional sites that were located in selected agricultural settings and sampled during periods of 1 week or less (table 2 and fig. 2). The synoptic sites mostly were clustered in areas in the southern portion of the basin and were sampled primarily to evaluate spatial distribution of water quality during extreme hydrologic conditions (high flow or low flow). Three of the synoptic sites (Long Tom River at Bundy Bridge near Monroe [station number 442223123153703], Muddy Creek near Peoria [station number 443138123120901], and Calapooia River at Albany [station number 14173500]) also were used to evaluate the ability of the fixed-station monitoring sites to characterize water quality from agricultural areas in other parts of the basin.

The fixed-station and the synoptic sampling sites were designated forested, agricultural, urban, or mixed on the basis of percentages of the subbasin's upstream land use by using superimposed Geographic Information Retrieval and Analysis System (GIRAS) land-use data (Fegeas and others, 1983). If a subbasin's drainage area was greater than 90 percent forested, it was designated as "forested"; if its area was greater than 50 percent agricultural and less than 25 percent urban, it was designated as "agricultural"; and, if its area was greater than 50 percent urban and less than 25 percent agricultural, it was designated as "urban." Sites that did not fall into any of the above categories were designated as "mixed-use," with the exception of two sites that were downstream of municipal or industrial sources. In all, 6 sites were designated as "forested," 27 sites were designated as "agricultural," 2 sites were designated as "urban," 14 sites were designated as "mixed-use", and 2 sites were designated "municipal/industrial" (fig. 3). The use of the coarse land-use classification scheme was an attempt to categorize individual subbasin areas according to what was generally considered to be its predominant land use; however, many activities in other land uses in a subbasin can influence instream water quality depending on their locations within the subbasin and time of year. For example, the subbasin drainage area upstream of the Pudding River at Aurora site is classified as agricultural; however, discharge from an sewage treatment plant located upstream of the site influences instream nutrient concentrations during the summer low-flow months.

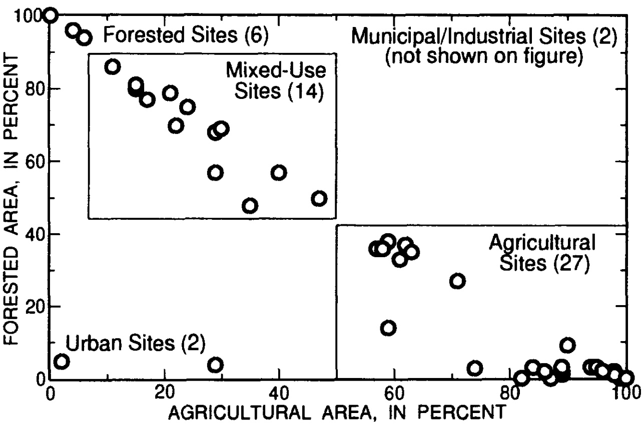

**Figure 3.** Percentage of agricultural and forested land upstream from surface-water-quality sites in the Willamette Basin, Oregon. (Number in parenthesis indicates number of sites in each category; some sites are hidden.)

## Field and Laboratory Methods

Streamflow measurements were made in accordance with standard USGS procedures (Rantz and others, 1982), or streamflows were calculated from stage-discharge relations. Water-quality samples for nutrients and pesticides analysis were collected, transported, and processed according to methods described by Shelton (1994). Water samples were processed at the Oregon District USGS laboratory in Portland, Oregon, within 4–6 hours of sample collection. Laboratory processing included sample filtration and preservation, and extraction of filtered samples for analysis of organic compounds (schedules 2010 and 2051; app. 1 and 2) through solid-phase extraction (SPE) cartridges (Zaugg and others, 1995; Werner and others, 1996). The processed nutrient and pesticide samples were shipped on ice to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado, where the samples were analyzed. Nutrient samples (schedule 2702, app. 3) were analyzed according to methods described by Fishman (1993). Pesticide samples were analyzed according to methods described by Zaugg and others (1995) and Lindley and others (1996) for schedule 2010 analytes, and Werner and others (1996) for schedule 2051 analytes. Censored data for schedule 2702 analyte concentrations are reported in terms of minimum reporting levels (MRLs); for schedule 2010 and 2051 concentrations are reported in terms of method detection limits (MDLs). The MRL is the minimum concentration that can be reliably reported for an analyte for a given analytical method (Timme, 1995), whereas the MDL is the minimum concentration detected and reported with a 99-percent confidence level as being greater than zero (Pritt, 1994).

Data from this study are stored in the USGS's National Water Information System (NWIS) database and were retrieved for analysis in this report on March 6, 1996. Owing to periodic updates to NWIS from the NWQL, data in NWIS are subject to change at a future date. In some cases, pesticide concentrations are reported as estimated; estimated concentrations are associated only with an increased uncertainty of analytical precision, and not with any increased uncertainty of analytical detection.

## Total Nitrogen Calculation

Total nitrogen concentrations were calculated as the sum of the total Kjeldahl nitrogen (KJDL, sum of the organic and ammonium nitrogen concentrations as N [nitrogen]) and the filtered nitrite plus nitrate concentrations as N (henceforth referred to as nitrate [$NO_3$-N] because 95 percent of the detected nitrite concentrations were less than 7.5 percent of the summed nitrite plus nitrate concentrations). A method modified from Bonn and others (1995) was used for the total nitrogen calculations. Five cases were considered: (1) values for both KJDL and $NO_3$-N were greater than the MRLs for each constituent (the MRL for KJDL was 0.2 mg/L [milligrams per liter], and the MRL for $NO_3$-N was 0.05 mg/L), (2) values for both KJDL and $NO_3$-N were less than their respective MRLs, (3) $NO_3$-N values less than its MRL, and KJDL values were greater than its MRL, (4) $NO_3$-N values were greater than its MRL and KJDL values were less than its MRL, and (5) when either $NO_3$-N or KJDL had not been analyzed (missing). For case (1), a simple sum was used, and for case (5), the total nitrogen value was not calculated. For the remaining cases, the relative magnitudes of the respective MRLs were considered. The various cases and the resulting frequencies of samples for each case are summarized in table 3.

## Quality-Control Methods and Results

Quality-control (QC) samples were used to quantify accuracy, precision, presence of laboratory contamination, and analytical bias (Fuhrer and others, 1995). The sources of variability and bias associated with collection and processing of the sample limit the interpretation of water-quality data. The NAWQA program recommends using a series of field-equipment blanks, splits, surrogates, and field-matrix-spike (FMS) samples to check the validity of data for pesticides and nutrients. QC samples were processed using the same equipment, personnel, procedures and sequences as used for the environmental samples. Complete descriptions of the different QC samples are described by Shelton (1994).

Field-equipment blank samples were prepared using solutions of inorganic- or organic-free water that did not contain detectable concentrations of the analytes of interest. Preparation of a field-equipment blank sample required that a volume of blank water be poured through all sampling equipment prior to collecting the environmental sample. The field blank was processed in the same manner as the environmental sample. Pesticide field equipment blanks are important in the analysis of organic compounds at low concentrations because of potential bias from contamination of sampling and processing equipment and storage containers.

Split samples were prepared by dividing the environmental sample into two or more equal volumes and treating each volume as a separate sample. These split samples are designed to determine precision (reproducibility) of values after sample collection.

A surrogate solution, as used in this study, contained a series of organic compounds of known concentration that was added to every environmental sample. The surrogate compounds were not expected to be present in the environment, yet were expected to behave similarly to selected target analytes found in the environment. Data from the three surrogates added to the SH2010 samples—a organophosphorus compound (diazi-

**Table 3.** Calculation of total nitrogen as N, Willamette Basin, Oregon, April 1993 through September 1995

[Values in milligrams per liter as N (nitrogen); $NO_3$-N, sum of the filtered nitrite-plus-nitrate concentrations as N; KJDL, total Kjeldahl nitrogen concentration as N; the minimum reporting level (MRL) for $NO_3$-N is 0.05 mg/L (milligrams per liter); the MRL for KJDL is 0.2 mg/L; - -, no condition specified; Missing, constituent not analyzed; nc, not computed; "filtered water" is an operational definition referring to the chemical analysis of that portion of a water-suspended sediment sample that passes through a nominal 0.45 micrometer filter (Fuhrer and others, 1995)]

| Case | Filtered $NO_3$-N | Total KJDL | Condition | Total nitrogen | Case frequency |
|---|---|---|---|---|---|
| 1 | Value ($NO_3$-N) | Value (KJDL) | - - | Value ($NO_3$-N) + Value (KJDL) | 180 |
| 2 | < 0.05 | < 0.2 | - - | < 0.25 | 2 |
| 3a | < 0.05 | Value (KJDL) | Value (KJDL) < 0.25 | < 0.25 | 0 |
| 3b | < 0.05 | Value (KJDL) | Value (KJDL) >= 0.25 | Value (KJDL) | 5 |
| 4a | Value ($NO_3$-N) | < 0.2 | Value ($NO_3$-N + 0.1) < 0.25 | < 0.25 | 15 |
| 4b | Value ($NO_3$-N) | < 0.2 | Value ($NO_3$-N + 0.1) >= 0.25 | Value ($NO_3$-N + 0.1) | 58 |
| 5 | Missing | Missing | - - | nc | 29 |

non-$d_{10}$), a triazine compound (terbuthylazine), and a organochlorine compound (*alpha*-HCH-$d_6$)—were used to assess the recoveries and precision of the analytical method, over time, for the targeted analytes.

An FMS, as used in this study, contained the series of organic compounds used in the analytical schedule that was added to a environmental split sample and processed and analyzed in tandem with the environmental split sample. FMS samples were used to assess extraction and elution recoveries from filtered-water matrices; they provided information for evaluating accuracy and precision of results for the target analytes in different environmental matrices (Shelton, 1994).

Review of the quality of the data was done routinely, and reruns were requested for results that appeared to be unreasonable. The decision to request a rerun was based on comparisons with previous data, statistical and graphical approaches, and, in the case where nutrient concentrations were large, also on checks of the anion/cation balance.

## Nutrient Blanks, Splits, and Spikes

Analysis of field-equipment-blank water samples showed only seven detections (table 4). All seven detections were at low concentrations and were generally near their respective MRLs. Relative differences between environmental split samples ranged from 0 to 29 percent (table 5). Fifty-seven percent of the samples showed no difference between the split samples. Low-level FMS samples also were analyzed for $NO_3$-N, total phosphorus as P (phosphorus) (TP), and soluble reactive phosphorus as P (SRP) in a USGS cooperative study of the Tualatin River Subbasin during a time period similar to that of the Willamette Basin NAWQA sampling program. Recoveries for the spike mixtures are summarized in figure 4A and 4B, and table 6. Spike recoveries for $NO_3$-N ranged from 96 to 106 percent; spike recoveries for TP ranged from 31 to 188 percent; and spike recoveries for SRP ranged from 56 to 104 percent. Median recoveries for $NO_3$-N, TP, and SRP were 100, 88, 86 percent, respectively.

## Pesticide Field Blanks and Splits

No pesticides were detected in the field blanks, with the exception of one low-level detection for EPTC of 0.004 μg/L (micrograms per liter). Relative differences for pesticide split samples ranged from 0 to 177 percent (median relative difference was 0 percent; table 7).

## Pesticide-Surrogate and Field-Matrix Spikes

Median recoveries for the 3 surrogates in the "split" samples were 100, 99, and 90 percent, respectively, for diazinon-$d_{10}$, terbuthylazine, and *alpha*-HCH-$d_6$. Recoveries for the three surrogates used in the SH2010 environmental samples are summarized in figure 5. All but a few of the values fell within the expected recovery range of 60 to 140 percent, with median recoveries of 100, 109, and 96 percent, respectively, for diazinon-$d_{10}$, terbuthylazine, and *alpha*-HCH-$d_6$ (fig. 5A). On two

**Table 4.** Concentrations of nutrients in field-equipment-blank water samples, Willamette Basin, Oregon, April 1993 through September 1995

[Values are reported in milligrams per liter; <, less than; - -, not analyzed; number in parentheses refers to map reference number in table 2 and figure 2; N, nitrogen; P, phosphorus; values of total nitrogen as N were computed; bold designation indicates analyses that were above the minium reporting level; "filtered water" is an operational definition referring to the chemical analysis of the portion of a water-suspended sediment sample that passes through a nominal 0.45 micrometer filter (Fuhrer and others, 1995)]

| | Station number, map reference number, and sampling date | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 14200400 (1) | | | 14201300 (2) | 14202000 (3) | | | | | | 14203750 (4) |
| **Analyte** | 02–16–94 | 05–12–94 | 08–08–95 | 10–04–93 | 08–31–93 | 08–31–93 | 04–12–94 | 05–25–94 | 08–10–94 | 01–26–95 | 09–02–93 |
| Total nitrogen as N | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 |
| Total Kjeldahl nitrogen as N | < .2 | < .2 | < .2 | < .2 | < .2 | < .2 | < .2 | < .2 | < .2 | < .2 | < .2 |
| Filtered nitrite plus nitrate as N | < .05 | < .05 | < .05 | < .05 | < .05 | < .05 | < .05 | < .05 | < .05 | < .05 | < .05 |
| Total phosphorus as P | **.01** | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | **.02** |
| Soluble reactive phosphorus as P | **.02** | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 |

| | Station number, map reference number, and sampling date | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 14203750 (4) | | | | | 14207500 (6) | | 14211720 (7) | 45024512254202 (28) | 450901122473202 (34) |
| **Analyte** | 11–09–93 | 12–15–93 | 01–13–94 | 03–17–94 | 06–16–94 | 03–08–95 | 05–26–95 | 09–26–95 | 04–27–93 | 08–17–94 |
| Total nitrogen as N | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | - - | - - | <0.25 |
| Total Kjeldahl nitrogen as N | < .2 | < .2 | < .2 | < .2 | < .2 | < .2 | < .2 | - - | - - | < .2 |
| Filtered nitrite plus nitrate as N | < .05 | < .05 | < .05 | **.064** | < .05 | < .05 | < .05 | <0.05 | < 0.05 | < .05 |
| Total phosphorus as P | < .01 | **.01** | < .01 | < .01 | < .01 | < .01 | < .01 | - - | - - | **.01** |
| Soluble reactive phosphorus as P | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | < .01 | **.01** |

**Table 5.** Concentrations of nutrients in split environmental water samples, Willamette Basin, Oregon, April 1993 through September 1995

[Values are reported in milligrams per liter; <, less than; - -, not analyzed; nc, not computed; number in parentheses refers to map reference number in table 2 and figure 2; Kjeldahl, organic plus ammonia nitrogen; N, nitrogen; P, phosphorus; "filtered water" is an operational definition referring to the chemical analysis of that portion of a water-suspended sediment sample that passes through a nominal 0.45 micrometer filter (Fuhrer and others, 1995); relative percent difference for two samples = $\frac{|R1-R2|}{\left(\frac{R1+R2}{2}\right)} \times 100$, where R1 = sample 1 result and R2 = sample 2 result]

| Analyte | Station number, map reference number, and sampling date | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 14201000<br>(26) | | | 14201300<br>(2) | | | | | | 14202000<br>(3) | | | | | | |
| | 04–26–93 | | | 08–02–94 | | | 08–18–94 | | | 08–31–93 | | | | 02-15-94 | | |
| | Sample 1 | Sample 2 | Relative percent difference | Sample 1 | Sample 2 | Relative percent difference | Sample 1 | Sample 2 | Relative percent difference | Sample 1 | Sample 2 | Sample 3 | Relative percent difference | Sample 1 | Sample 2 | Relative percent difference |
| Total nitrogen as N | - - | - - | - - | 4.1 | 4.1 | 0 | 3.6 | 3.8 | 5.4 | 1.9 | 1.9 | 1.9 | 0 | 2.4 | 2.7 | 12 |
| Total Kjeldahl nitrogen as N | - - | - - | - - | .5 | .5 | 0 | .4 | .5 | 22 | .4 | .4 | .4 | 0 | .3 | .3 | 0 |
| Filtered nitrite plus nitrate as N | 0.76 | 0.74 | 2.7 | 3.6 | 3.6 | 0 | 3.2 | 3.3 | 3.1 | 1.5 | 1.5 | 1.5 | 0 | 2.1 | 2.4 | 13 |
| Total phosphorus as P | - - | - - | - - | .43 | .42 | 2.4 | .42 | .39 | 7.4 | .17 | .20 | .17 | 0–16 | .11 | .11 | 0 |
| Soluble reactive phosphorus as P | .02 | .02 | 0 | .39 | .38 | 2.6 | .37 | .37 | 0 | .16 | .16 | .15 | 0–6.4 | .06 | .06 | 0 |

| Analyte | Station number, map reference number, and sampling date | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 14203750<br>(4) | | | 442223123153703<br>(12) | | | 450245122542202<br>(28) | | | 450901122473202<br>(34) | | | 451259122481902<br>(38) | | |
| | 09–02–93 | | | 05–04–94 | | | 04–27–93 | | | 04–28–93 | | | 04–29–93 | | |
| | Sample 1 | Sample 2 | Relative percent diffeence | Sample 1 | Sample 2 | Relative percent difference | Sample 1 | Sample 2 | Relative percent difference | Sample 1 | Sample 2 | Relative percent difference | Sample 1 | Sample 2 | Relative percent difference |
| Total nitrogen as N | <0.25 | 0.35 | nc | 1.05 | 0.95 | 10 | - - | - - | - - | - - | - - | - - | - - | - - | - - |
| Total Kjeldahl as nitrogen as N | <.2 | .2 | nc | .4 | .3 | 29 | - - | - - | - - | - - | - - | - - | - - | - - | - - |
| Filtered nitrite plus nitrate as N | .14 | .15 | 6.9 | .65 | .65 | 0 | 5.0 | 5.0 | 0 | 1.4 | 1.4 | 0 | 4.8 | 4.8 | 0 |
| Total phosphorus as P | .03 | .03 | 0 | .02 | .02 | 0 | - - | - - | - - | - - | - - | - - | - - | - - | - - |
| Soluble reactive phosphorus as P | .02 | .02 | 0 | <.01 | .01 | nc | .73 | .78 | 6.6 | .03 | .03 | 0 | .08 | .08 | 0 |

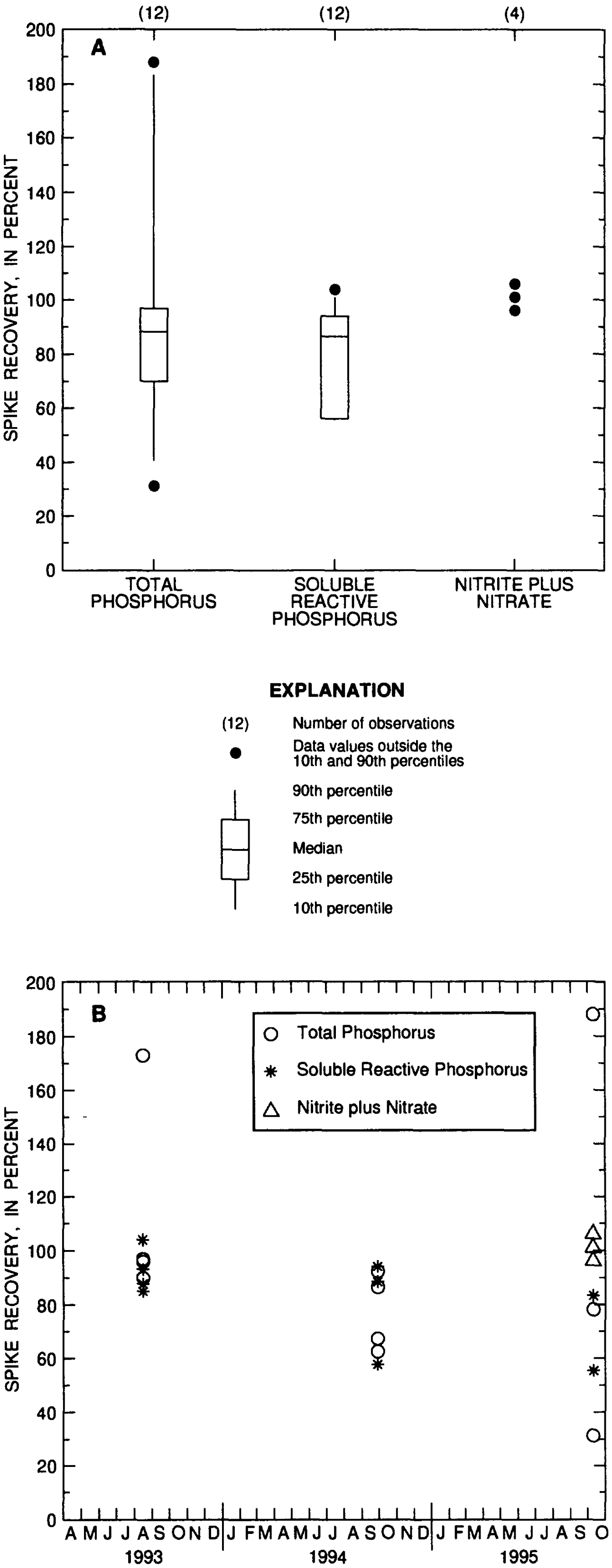

**Figure 4.** Spike recoveries for total phosphorus, soluble reactive phosphorus, and nitrite and nitrate by (A) constituent group and (B) sampling dates.

occasions, recoveries for the three surrogates were reported as 0 percent; it is possible that the surrogates were inadvertently omitted from these samples. Review of the surrogate recovery results for the last 2-1/2 years of field collection activities (fig. 5B) revealed no apparent periods where significant bias in the data occurred; however, some samples did show slightly greater diazinon-$d_{10}$ recovery variability (40–200 percent) than recoveries for the other two surrogates (60–150 percent).

A FMS mixture was available for 47 of 48 analytes in SH2010 (fig. 6A), but only for 29 of 41 analytes in SH2051 (fig. 6B). Acetochlor was not part of SH2010 until April 1994 and was therefore not included in the earlier FMS mixtures. Three analytes common to both schedules (carbaryl, carbofuran, and linuron) were included in both FMS mixtures.

About 87 percent of the SH2010 spike recoveries fell within the expected recovery range of 60–140 percent, with an overall median recovery of 94 percent (medians ranged from 0 [dimethoate; 7 samples] to 150 [carbofuran; 8 samples] percent, fig. 6A). However, only about 37 percent of the SH2051 spike recoveries fell within the expected range, with an overall median recovery of 53 percent (medians ranged from 5 [1-naphthol] to 120 [linuron] percent, fig. 6B). Only 7 of the 47 FMS SH2010 analytes had either low or highly variable spike recoveries: desethylatrazine, azinphos-methyl, carbaryl, carbofuran, dimethoate, and propargite. With the exception of propargite, these analytes also had either low recoveries or variable performance in all matrices and concentrations during preliminary testing of the analytical method (Zaugg and others, 1995). Dimethoate produced such low and variable recoveries that it was deleted from the method in November 1994; analytical results for desethylatrazine, azimphos-methyl, carbaryl, carbofuran, and terbacil have been qualified as estimated concentrations because of poor or variable performance (Zaugg and others, 1995).

Eighteen of 29 SH2051 analytes had FMS median recoveries below the lower of the expected recovery range (60 percent; fig. 6B). Six of these 18 analytes (1-naphthol, aldicarb, aldicarb sulfone, carbaryl, methiocarb, and oxamyl) have been designated for "qualitative reporting only" on the basis of poor overall recoveries and preci-

**Table 6.** Concentrations of nutrients in spiked environmental water samples, Tualatin River Subbasin, Oregon, August 1993 through October 1995

[Values are reported in milligrams per liter; <, less than; - -, not analyzed; samples were collected as part of a cooperative project; C, concentration; N, nitrogen; P, phosphorus; R, River; Cr, Creek; nr, near; Rd, road; "filtered water" is an operational definition referring to the chemical analysis of that portion of a water-suspended sediment sample that passes through a nominal 0.45 micrometer filter (Fuhrer and others, 1995); percent recovery = $\frac{Cspike-Cunspiked}{SpikeAmount} \times 100$, where Cspiked = concentration of spiked sample and Cunspiked = concentration of unspiked sample]

| Analyte | Station number and sampling date | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tualatin R at Dilley | | | | East Fork Dairy Cr nr Roy | | | | Rock Creek nr Hillsboro | | | | Tualatin R at Elsner Rd nr Sherwood | | | |
| | 08–16–93 | | | | 08–16–93 | | | | 08–16–93 | | | | 08–16–93 | | | |
| | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery |
| Filtered nitrite plus nitrate as N | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - |
| Total phosphorus as P | 0.011 | 0.107 | 0.1 | 96 | 0.046 | 0.143 | 0.1 | 97 | 0.2 | 0.373 | 0.1 | 173 | 0.104 | 0.194 | 0.1 | 90 |
| Soluble reactive phosphorus as P | .003 | .072 | .074 | 93 | .006 | .069 | .074 | 85 | .124 | .189 | .074 | 88 | .034 | .111 | .074 | 104 |

| Analyte | Station number and sampling date | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tualatin R at Springhill Rd | | | | Rock Cr nr Hillsboro | | | | Tualatin R at Elsner Rd nr Sherwood | | | | Fanno Cr at Durham | | | |
| | 09–28–94 | | | | 09–28–94 | | | | 09–28–94 | | | | 09–28–94 | | | |
| | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery |
| Filtered nitrite plus nitrate as N | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - | - - |
| Total phosphorus as P | 0.021 | 0.111 | 0.104 | 86 | 0.268 | 0.364 | 0.104 | 92 | 0.084 | 0.149 | 0.104 | 62 | 0.175 | 0.245 | 0.104 | 67 |
| Soluble reactive phosphorus as P | .002 | .051 | .052 | 94 | .144 | .193 | .052 | 94 | .02 | .066 | .052 | 88 | .082 | .112 | .052 | 58 |

| Analyte | Station number and sampling date | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tualatin R at Cherry Grove | | | | Rock Cr nr Hillsboro | | | | Tualatin R at Elsner Rd | | | | Fanno Cr at Durham | | | |
| | 10–11–95 | | | | 10–11–95 | | | | 10–11–95 | | | | 10–11–95 | | | |
| | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery | Native water | Spiked sample | Spike concentration | Percent recovery |
| Filtered nitrite plus nitrate as N | 0.32 | 0.53 | 0.208 | 101 | 0.29 | 0.51 | 0.208 | 106 | 1.7 | 1.9 | 0.208 | 96 | 0.50 | 0.72 | 0.208 | 106 |
| Total phosphorus as P | .1 | .12 | .064 | 31 | .36 | .41 | .064 | 78 | .08 | .13 | .064 | 78 | .36 | .48 | .064 | 188 |
| Soluble reactive phosphorus as P | < .01 | .03 | .036 | 83 | .13 | .15 | .036 | 56 | .05 | .07 | .036 | 56 | .05 | .07 | .036 | 56 |

**Table 7.** Concentrations of pesticide compounds in split filtered environmental water samples, Willamette Basin, Oregon, April 1993 through September 1995

[All values are reported in µg/L, micrograms per liter; <, less than; - -, not analyzed; nc, not computed; E, estimated concentration; **, not detected; DCPA, dimethyltetrachloroterephthalate; DDE, dichlorodiphenyldichloroethylene; EPTC, S-ethyl dipropylthiocarbamate; HCH, hexachlorocyclohexane; 2,4-D, (2,4-Dichlorophenoxy)acetic acid; number in parentheses refers to map reference number in table 2 and figure 2; "filtered water" is an operational definition referring to the chemical analysis of that portion of a water-suspended sediment sample that passes through a nominal 0.7 micrometer filter (Fuhrer and others, 1995); relative percent difference for two samples = $\frac{|R1-R2|}{\left(\frac{R1+R2}{2}\right)} \times 100$, where R1 = sample 1 result and R2 = sample 2 result]

| SH2010/2051 Analytes (see Appendixes 1 and 2 for method detection limits) | Station number, map reference number, and sampling date | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 14201300 (2) | | | | 14202000 (3) | | | | | | |
| | 08–02–94 | | | | 08–31–93 | | | | 02–15–94 | | |
| | Sample 1 | Sample 2 | Sample 3 | Relative percent difference | Sample 1 | Sample 2 | Sample 3 | Relative percent difference | Sample 1 | Sample 2 | Relative percent difference |
| Atrazine | 0.120 | 0.110 | - - | 9 | 0.040 | 0.041 | 0.042 | 2–5 | 0.034 | 0.035 | 3 |
| Azinphos-methyl | < .001 | < .001 | - - | nc | E .099 | E .063 | E .056 | E 12–55 | < .001 | < .001 | nc |
| Carbofuran | E .027 | E .085 | - - | E 104 | < .003 | < .003 | < .003 | nc | < .003 | < .003 | nc |
| Chlorpyrifos | .015 | .017 | - - | 12 | < .004 | < .004 | < .004 | nc | .004 | .010 | 86 |
| DCPA | < .002 | .002 | - - | nc | < .002 | < .002 | < .002 | nc | E .001 | E .001 | E 0 |
| *p,p'*-DDE | < .006 | < .006 | - - | nc | < .006 | < .006 | < .006 | nc | < .006 | < .006 | nc |
| Desethylatrazine | E .024 | E .018 | - - | E 29 | < .002 | < .002 | E .004 | nc | E .008 | E .014 | E 54 |
| Diazinon | .026 | .025 | - - | 4 | < .002 | < .002 | < .002 | nc | .003 | .004 | 29 |
| Dieldrin | < .001 | < .001 | - - | nc | < .001 | < .001 | < .001 | nc | < .001 | < .001 | nc |
| EPTC | .020 | .018 | - - | 10 | < .002 | < .002 | < .002 | nc | .003 | .003 | 0 |
| Fonofos | .005 | .003 | - - | 50 | < .003 | < .003 | < .003 | nc | < .003 | < .003 | nc |
| *gamma*-HCH (Lindane) | .094 | .090 | - - | 4 | < .004 | < .004 | < .004 | nc | < .004 | < .004 | nc |
| Metolachlor | .036 | .026 | - - | 32 | .028 | .029 | .029 | 0–4 | .059 | .062 | 5 |
| Napropamide | .009 | .010 | - - | 10 | < .003 | < .003 | < .003 | nc | .007 | .008 | 13 |
| Prometon | < .018 | < .018 | - - | nc | < .018 | < .018 | < .018 | nc | < .018 | < .018 | nc |
| Simazine | 1.3 | 1.3 | - - | 0 | < .005 | < .005 | .013 | nc | .051 | .052 | 2 |
| Terbacil | < .007 | < .007 | - - | nc | < .007 | < .007 | < .007 | nc | < .007 | < .007 | nc |
| Trifluralin | < .002 | < .002 | - - | nc | < .002 | < .002 | < .002 | nc | < .002 | < .002 | nc |
| Diazinon-$d_{10}$ surrogate (percent) | 112 | 110 | - - | 2 | 93 | 81 | 81 | 0–14 | 127 | 132 | 4 |
| Terbuthylazine surrogate (percent) | 137 | 108 | - - | 24 | 93 | 98 | 99 | 1–6 | 95 | 99 | 4 |
| *alpha*-HCH-$d_6$ surrogate (percent) | 128 | 96 | - - | 28 | 80 | 77 | 83 | 4–8 | 89 | 93 | 4 |
| 2,4-D | ** | ** | ** | nc | ** | ** | - - | nc | ** | ** | nc |
| Diuron | E 1.00 | E .68 | .060 | E 38–177 | - - | ** | - - | nc | ** | ** | nc |
| Trichlopyr | ** | ** | ** | nc | ** | ** | - - | nc | ** | ** | nc |

**Table 7.** Concentrations of pesticide compounds in split filtered environmental water samples, Willamette Basin, Oregon, April 1993 through September 1995—Continued

| SH2010/2051 Analytes (see Appendixes 1 and 2 for method detection limits) | Station number, map reference number, and sampling date | | | | | |
|---|---|---|---|---|---|---|
| | 442223123153703 (12) | | | 452823122240900 (48) | | |
| | 05–04–94 | | | 11–01–94 | | |
| | Sample 1 | Sample 2 | Relative percent difference | Sample 1 | Sample 2 | Relative percent difference |
| Atrazine | 0.110 | 0.110 | 0 | 0.047 | 0.047 | 0 |
| Azinphos-methyl | < .001 | < .001 | nc | < .001 | < .001 | nc |
| Carbofuran | < .003 | < .003 | nc | < .003 | < .003 | nc |
| Chlorpyrifos | < .004 | < .004 | nc | < .004 | < .004 | nc |
| DCPA | < .002 | < .002 | nc | < .002 | < .002 | nc |
| *p,p'*-DDE | < .006 | < .006 | nc | E .003 | E .002 | E 40 |
| Desethylatrazine | < .002 | < .002 | nc | E .005 | E .010 | E 67 |
| Diazinon | < .002 | < .002 | nc | E .008 | .007 | E 13 |
| Dieldrin | < .001 | < .001 | nc | .016 | .015 | 6 |
| EPTC | < .002 | < .002 | nc | < .002 | < .002 | nc |
| Fonofos | < .003 | < .003 | nc | < .003 | < .003 | nc |
| *gamma*-HCH (Lindane) | < .004 | < .004 | nc | E .005 | < .004 | nc |
| Metolachlor | < .002 | < .002 | nc | .190 | .191 | < 1 |
| Napropamide | < .003 | < .003 | nc | .097 | .099 | 2 |
| Prometon | < .018 | < .018 | nc | .009 | E .010 | E 10 |
| Simazine | < .005 | < .005 | nc | .078 | .085 | 9 |
| Terbacil | < .007 | < .007 | nc | E .010 | E .013 | E 26 |
| Trifluralin | < .002 | < .002 | nc | E .005 | .005 | E 0 |
| Diazinon-$d_{10}$ surrogate (percent) | 122 | 122 | 0 | 100 | 103 | 3 |
| Terbuthylazine surrogate (percent) | 114 | 115 | 1 | 97 | 105 | 8 |
| *alpha*-HCH-$d_6$ surrogate (percent) | 109 | 112 | 3 | 80 | 88 | 10 |
| 2,4-D | ** | ** | nc | ** | ** | nc |
| Diuron | .090 | .12 | 29 | ** | ** | nc |
| Trichlopyr | ** | ** | nc | .46 | .38 | 19 |

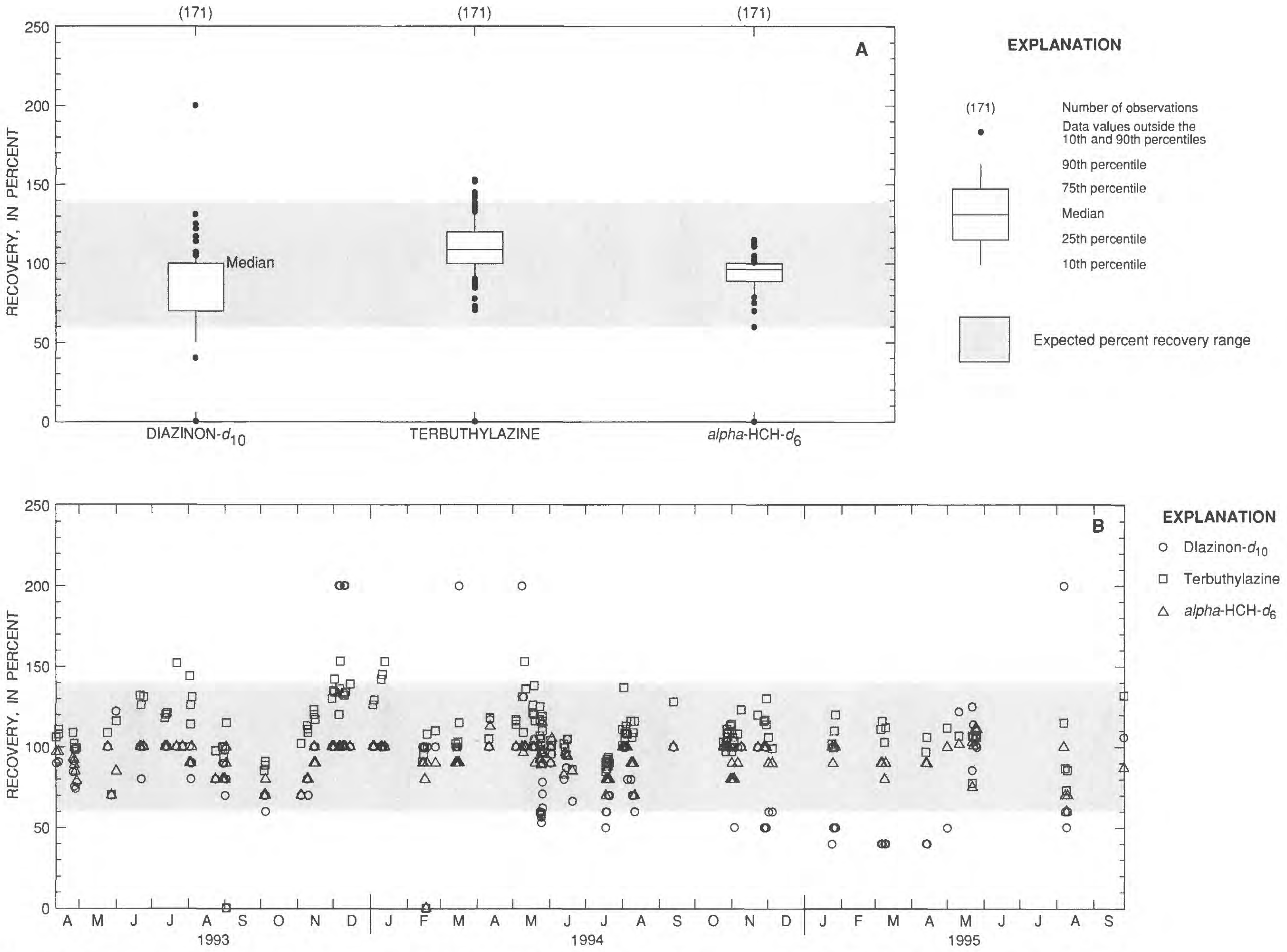

**Figure 5.** Recoveries for diazinon-$d_{10}$, terbuthylazine, and *alpha*-HCH-$d_6$ in Schedule 2010 by (A) surrogate group and (B) sampling dates.

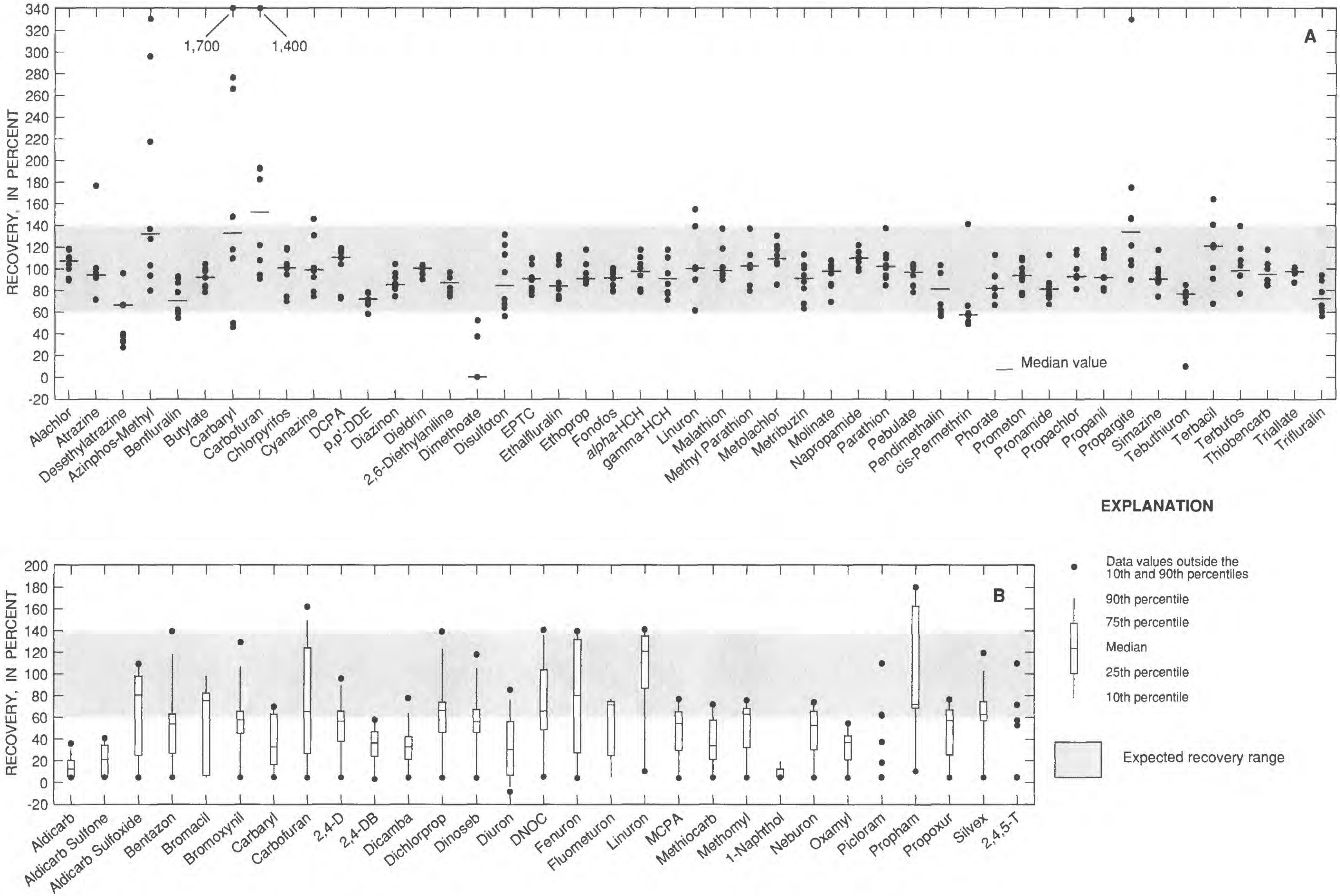

**Figure 6.** Spike recoveries for pesticides and degradation products analyzed in (A) Schedule 2010 and (B) Schedule 2051. (Boxplots were constructed if nine or more data points were available, otherwise individual data points were plotted.)

sion (NAWQA/NWQL Quality Assurance Committee, USGS, internal SH2050/2051 guidance memorandum, 1995). The analyte 4,6-Dinitro-o-cresol (DNOC), which also had been designated for "qualitative reporting only," had a higher median FMS recovery of 66 percent. Although 12 of the SH2051 analytes were not included in the FMS, the USGS laboratory control spikes (LCS), which included these analytes, demonstrated that 5 of these 12 (chloramben, chlorothalonil, dichlobenil, esfenvalerate, and 4-(4-chloro-o-tolyloxy)butyric acid [MCPB]) had median recoveries below 60 percent. Chlorothalonil, dichlobenil, esfenvalerate, and MCPB also have been designated for "qualitative reporting only" based on poor overall recoveries and precision (NAWQA/NWQL Quality Assurance Committee, USGS, internal SH2050/2051 guidance memorandum, 1995). Five compounds—chlorothalonil, dichlobenil, DNOC, esfenvalerate, and 1-napthol—demonstrated variable solid-phase extraction (SPE) or high-performance liquid chromatography (HPLC) performance, or both, and concentrations were indicated by the USGS NWQL as being estimated (Werner and others, 1996).

### Quality-Control Observations

#### Nutrients

On the basis of the nutrient QC results, it was concluded that nutrient concentrations in the environmental samples were of sufficiently high quality to meet the study's objectives, including detection of nutrient presence and (or) absence, determination of concentration distributions in time and space, and comparisons to water-quality guidelines and criteria. The larger variability in the low-level spike recoveries for TP affects the interpretability of only low-level TP concentrations (<0.01–0.05 mg/L) observed at the background (forested) sites.

#### Pesticides

On the basis of the pesticide QC results, the following guidelines were used to interpret pesticide results in the environmental samples:

- If a SH2010 or SH2051 analyte was detected in an environmental sample, there was a good chance that it was present; however, the converse was not necessarily true, particularly, for SH2051 analytes. Because of the consistently low FMS and LCS recoveries for most of the SH2051 analytes, a nondetect (censored) concentration was not interpreted as being below a particular method detection limit value, but rather as if there was insufficient information to determine if it was present or not. In addition, for the three analytes—carbaryl, carbofuran, and linuron—analyzed in both schedules, data interpretation was limited to only those analytical results from the SH2010 schedule because of the uncertainties of the SH2051 schedule.
- SH2010 surrogate and FMS results suggest that most analytes associated with the schedule (40 out of 47) yield quantitative information. SH2051 FMS and LCS results suggest that only about 18 of the 41 analytes associated with the schedule, those with median spike recoveries above 60 percent, yield quantitative information.
- Even though many analytes in both schedules probably yield quantitative information, because the expected acceptable recovery range is relatively wide (60 to 140 percent) SH2010 analyte concentrations may need to differ, at times, by as much as a factor of 3, and SH2051 analyte concentrations may need to vary by as much as a factor of 10 (due to poorer precision), before being interpreted as being from different populations.

## RESULTS AND DISCUSSION

### Hydrologic Sampling Conditions

Hydrologic conditions often affect the water quality of a stream. During the study period, average monthly precipitation amounts commonly were outside the interquartile range of the long-term (1961–90) monthly averages (fig. 7A). During water years 1993, 1994, and 1995, annual precipitation volumes at Salem (fig. 7A) were, respectively, 106 percent, 68.6 percent, and 123 percent of the average annual rainfall for the 30-year 1961–90 calendar year base period (39.16 inches), thus, showing the extent of the precipitation variability that occurred during this study.

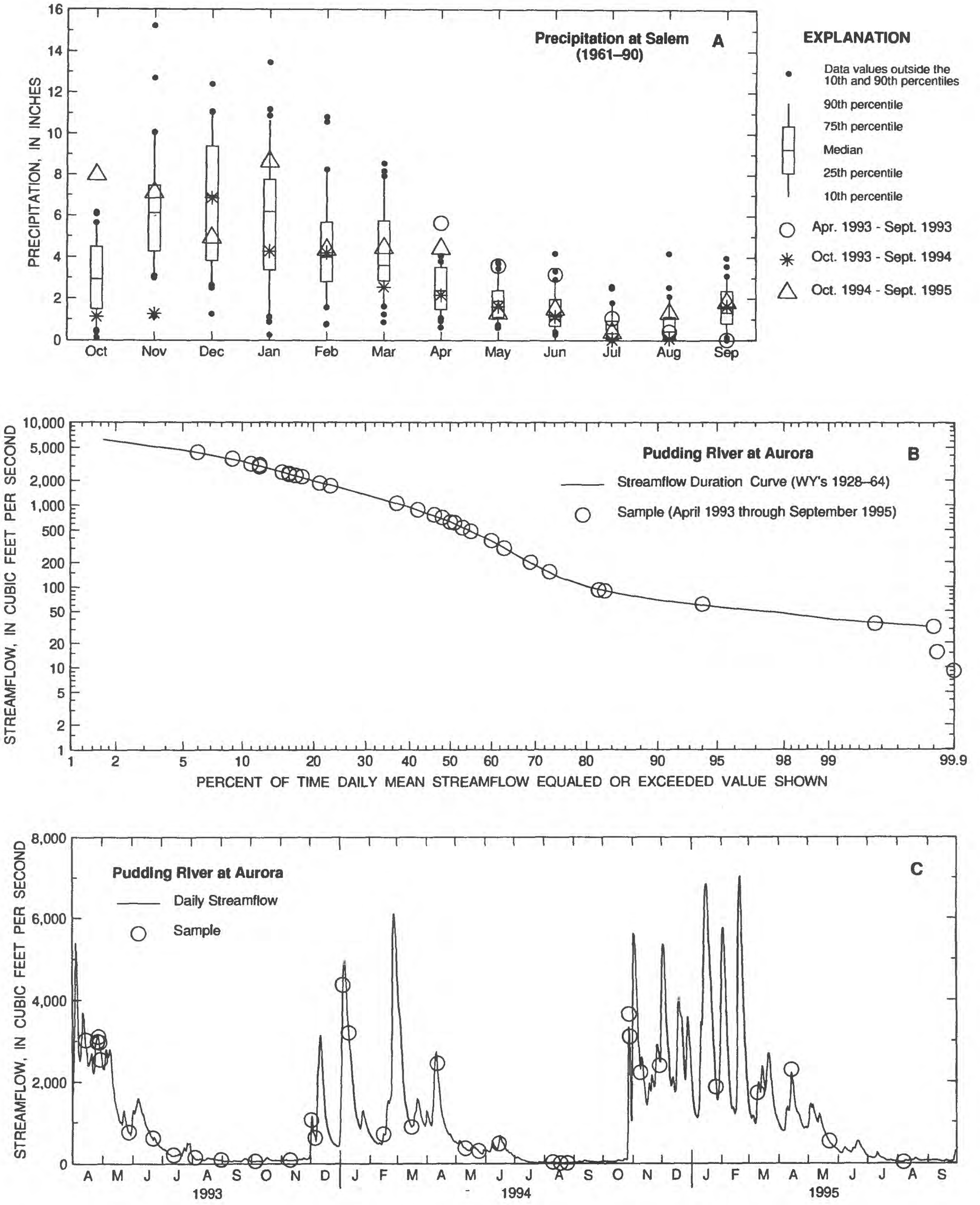

**Figure 7.** (A) Monthly precipitation at Salem, April 1993 through September 1995, compared with average monthly values for 1961–90, (B) instantaneous streamflows at time of sample collection, Pudding River at Aurora, April 1993 through September 1995, compared with the long-term flow-duration curve for water years 1928–64, (C) instantaneous streamflows at time of sample collection, Pudding River at Aurora, compared with daily mean streamflows at the same site, April 1993 through September 1995.

Monthly precipitation at Salem for April 1993 through September 1995 generally was as variable or more variable than variations shown by the 30-year monthly totals (fig.7A). In water year (WY) 1993, monthly precipitation exceeded the 90th percentiles of the 30-year monthly totals for April, May and June, and was lower than the 10th percentiles for September; thus, WY 1993 had a much wetter spring and drier late summer than most years in the 30-year base period. In WY 1994, monthly precipitation amounts generally were lower than the 30-year monthly averages; were lower than the 25th percentiles of the 30-year monthly values for October, November, March, July and August; and also were lower than the 10th percentiles for November. Thus, WY 1994 was generally a drier year and had a drier midsummer than most years in the 30-year base period. In WY 1995, monthly precipitation amounts were generally greater than the 30-year monthly averages and exceeded the 90th percentiles of the 30-year monthly totals for October and April. Thus, WY 1995 was generally a wetter year than most years in the 30-year base period.

Precipitation patterns for each year of the WY's 1993–95 period did not represent individually years typical of average conditions observed during WY's 1961–90. However, when the 2-1/2 years of precipitation were combined, the overall precipitation pattern during the study period was variable, and water-quality samples collected during this time appear to represent a wide range of hydrologic conditions similar to what would have been collected during WY's 1961–90. As an example, for the Pudding River fixed-station-network site, water-quality samples were collected over a broad range of flow conditions that represented moderately high to low-flow conditions (fig. 7B); however, not all peak flows during the study period were sampled (fig. 7C).

## Nutrients

More than 260 water samples were collected from 51 locations in the Willamette Basin and analyzed for KJDL, $NO_3$-N, TP, and SRP. From the nitrogen analytical results, 260 total nitrogen as N (TN) concentrations were calculated from the algorithms described in table 3. Individual nutrient species (TN, $NO_3$-N, TP, and SRP) were detected in 89 to 98 percent of the samples (table 8 and fig. 8A).

TN detections ranged in concentration from 0.25 to 24 mg/L; the upper 10 percent of the concentrations was above 7.3 mg/L (fig. 8B). $NO_3$-N detections ranged in concentration from 0.054 to 22 mg/L; the upper 10 percent of the concentrations was above 5.9 mg/L. Most of the upper 10 percent of the concentrations for both nitrogen species occurred at sites receiving predominantly agricultural runoff (a few sites were downstream from point-source discharges). About 3-1/2 percent of the $NO_3$-N concentrations exceeded the "maximum contaminant level" (MCL) of 10 mg/L for nitrate as nitrogen established by the U.S. Environmental Protection Agency (USEPA) for domestic drinking water (U.S. Environmental Protection Agency, 1996); 90 percent of the exceedances occurred in the agricultural subbasins.

Although the interpretation of ammonia nitrogen concentrations was beyond the scope of this report, its toxicity impacts were assessed by examining the amount of un-ionized ammonia present in the water samples. The un-ionized ammonia, not to be confused with ammonium ion, has been demonstrated to be the principal toxic form of ammonia to aquatic life (U.S. Environmental Protection Agency, 1986). The equilibrium concentration of un-ionized ammonia in a water sample depends on the concentration of the ammonium ion present and the pH and temperature of the water sample. During this study, ammonium ion concentrations ranged from less than (<) 0.01 to 2.1 mg/L as N; whereas, water temperatures and pH ranged from 2.4 to 28 degrees Celsius and 6.5 to 9.1 pH units, respectively. Only one sample, collected at a tributary to Zollner Creek at Marquam Road (table 2, map reference number 41), had a concentration that exceeded the 4-day average concentration of un-ionized ammonia established for the protection of aquatic organisms (the criterion exceeded was for a stream where salmonid and other cold water fish species are absent; U.S. Environmental Protection Agency, 1986).

TP detections varied in concentration from 0.01 to 7.0 mg/L; the upper 10 percent of the concentrations was above 0.36 mg/L (fig. 8B). SRP detections ranged in concentration from 0.01 to 5.8 mg/L; the upper 10 percent of the concentra-

**Table 8.** Statistical summary of detections for nutrients and pesticides at all sites sampled in the Willamette Basin, Oregon, April 1993 through September 1995

[USEPA STORET number, U.S. Environmental Protection Agency's Storage and Retrieval system number; MRL, minimum reporting level (nutrients); MDL, method detection limit (pesticides); mg/L, milligrams per liter; µg/L, micrograms per liter; N, nitrogen; P, phosphorus; E, estimated concentration, EPTC, S-ethyl dipropylthiocarbamate; DCPA, dimethyltetrachloroterephthalate; 2,4-D, (2,4-dichlorophenoxy)acetic acid; HCH, hexachlorocyclohexane; DDE, dichlorodiphenyldichloroethylene; MCPA, (4-chloro-2-methylphenoxy) acetic acid; a numerical value is reported for measurements less than the MDL if a peak is observed at the correct retention time and the qualifying information from the spectra conclusively identifies the analyte, although National Water Quality Laboratory indicates results with an "E" remark code (Pritt, 1994); "filtered water" is an operational definition referring to the chemical analysis of the portion of a water-suspended sediment sample that passes through a nominal 0.45 micrometer (nutrients) or a 0.7 micrometer filter (pesticides) (Fuhrer and others, 1995)]

| | | | | | | Concentrations | | |
|---|---|---|---|---|---|---|---|---|
| **USEPA STORET number** | **Parameter name** | **Number of samples** | **Number of detections** | **Percent detections** | **MRL/ MDL** | **Minimum** | **Median** | **Maximum** |
| | **Nutrients** | | | | | | **mg/L** | |
| 00600 | Total nitrogen as N | 260 | 243 | 93.5 | 0.25 | 0.25 | 1.5 | 24 |
| 00625 | Total Kjeldahl nitrogen as N | 259 | 184 | 71.0 | .20 | .20 | .50 | 4.1 |
| 00631 | Filtered nitrite plus nitrate as N | 289 | 282 | 97.6 | .05 | .054 | 1.1 | 22 |
| 00665 | Total phosphorus as P | 263 | 249 | 94.7 | .01 | .01 | .09 | 7.0 |
| 00671 | Soluble reactive phosphorus as P | 284 | 253 | 89.1 | .01 | .01 | .05 | 5.8 |
| | **Filtered pesticides** | | | | | | **µg/L** | |
| 39632 | Atrazine | 195 | 183 | 93.8 | .001 | .002 | .072 | 4.5 |
| 04035 | Simazine | 195 | 164 | 84.1 | .005 | E .004 | .077 | 5.8 |
| 39415 | Metolachlor | 192 | 152 | 79.2 | .002 | .002 | .022 | 3.3 |
| 04040 | Desethylatrazine (E) | 171 | 124 | 72.5 | .002 | E .001 | .011 | .27 |
| 49300 | Diuron | 141 | 83 | 58.9 | .020 | .050 | .54 | 14 |
| 39572 | Diazinon | 193 | 105 | 54.4 | .002 | .002 | .016 | 1.2 |
| 82684 | Napropamide | 171 | 64 | 37.4 | .003 | .004 | .029 | 1.7 |
| 82668 | EPTC | 192 | 67 | 34.9 | .002 | E .001 | .010 | 1.0 |
| 82682 | DCPA | 171 | 59 | 34.5 | .002 | E .001 | .004 | .061 |
| 38933 | Chlorpyrifos | 193 | 65 | 33.7 | .004 | E .002 | .011 | .40 |
| 82674 | Carbofuran (E) | 171 | 51 | 29.8 | .003 | .009 | .083 | 9.0 |
| 82665 | Terbacil | 168 | 50 | 29.8 | .007 | E .006 | .020 | .11 |
| 82672 | Ethoprop | 171 | 49 | 28.7 | .003 | E .002 | .014 | 2.0 |
| 04037 | Prometon | 171 | 46 | 26.9 | .018 | E .003 | .024 | .076 |
| 82680 | Carbaryl (E) | 192 | 46 | 24.0 | .003 | E .002 | .015 | 2.0 |
| 04095 | Fonofos | 193 | 45 | 23.3 | .003 | E .002 | .009 | .10 |
| 82670 | Tebuthiuron | 171 | 36 | 21.0 | .010 | E .003 | .019 | .14 |
| 82676 | Pronamide | 171 | 30 | 17.5 | .003 | .004 | .009 | .065 |
| 82661 | Trifluralin | 171 | 30 | 17.5 | .002 | E .001 | .006 | .036 |
| 82630 | Metribuzin | 192 | 33 | 17.2 | .004 | .006 | .029 | .15 |
| 39732 | 2,4-D | 145 | 19 | 13.1 | .035 | E .020 | .21 | .79 |
| 49309 | Carbofuran | 141 | 14 | 9.9 | .028 | .050 | .24 | 1.9 |
| 49235 | Triclopyr | 143 | 12 | 8.4 | .050 | E .020 | .25 | .72 |
| 39341 | *gamma*-HCH (Lindane) | 172 | 13 | 7.6 | .004 | .004 | .021 | .094 |
| 39532 | Malathion | 172 | 12 | 7.0 | .005 | .007 | .014 | .24 |
| 46342 | Alachlor | 192 | 13 | 6.8 | .002 | .002 | .011 | .36 |
| 82683 | Pendimethalin | 192 | 13 | 6.8 | .004 | .005 | .018 | .13 |
| 39381 | Dieldrin | 172 | 10 | 5.8 | .001 | .007 | .012 | .021 |
| 49303 | Dichlobenil (E) | 141 | 8 | 5.7 | .020 | E .010 | .060 | .42 |
| 49301 | Dinoseb | 143 | 8 | 5.6 | .035 | .060 | .12 | 1.0 |

**Table 8.** Statistical summary of detections for nutrients and pesticides at all sites sampled in the Willamette Basin, Oregon, April 1993 through September 1995—Continued

|  |  |  |  |  |  | Concentrations |  |  |
|---|---|---|---|---|---|---|---|---|
| USEPA STORET number | Parameter name | Number of samples | Number of detections | Percent detections | MRL/ MDL | Minimum | Median | Maximum |
|  | **Filtered pesticides—Continued** |  |  |  |  |  |  | µg/L |
| 38711 | Bentazon | 143 | 7 | 4.9 | 0.014 | E 0.010 | 0.26 | 1.2 |
| 04024 | Propachlor | 171 | 8 | 4.7 | .007 | E .002 | .006 | .013 |
| 34653 | *p,p'*-DDE | 171 | 8 | 4.7 | .006 | E .001 | .003 | .004 |
| 82662 | Dimethoate (E) | 68 | 3 | 4.4 | .004 | .033 | .086 | .35 |
| 49310 | Carbaryl | 141 | 4 | 2.8 | .008 | .050 | .065 | .25 |
| 38482 | MCPA | 143 | 4 | 2.8 | .050 | E .030 | .30 | .63 |
| 38442 | Dicamba | 143 | 3 | 2.1 | .035 | .12 | .22 | .29 |
| 04029 | Bromacil | 143 | 3 | 2.1 | .035 | .17 | .20 | .20 |
| 49292 | Oryzalin | 141 | 3 | 2.1 | .019 | .17 | .23 | 1.8 |
| 49293 | Norflurazon | 141 | 3 | 2.1 | .024 | E .010 | .020 | .45 |
| 82686 | Azinphos-Methyl (E) | 168 | 3 | 1.8 | .001 | .099 | .17 | .18 |
| 82678 | Triallate | 171 | 3 | 1.8 | .001 | .004 | .005 | .008 |
| 04041 | Cyanazine | 171 | 3 | 1.8 | .004 | .007 | .021 | .024 |
| 49311 | Bromoxynil | 143 | 2 | 1.4 | .035 | E .030 | .070 | .11 |
| 82685 | Propargite | 171 | 2 | 1.2 | .013 | E .007 | .031 | .054 |
| 38501 | Methiocarb | 141 | 1 | .7 | .026 | .10 | .10 | .10 |
| 38866 | Oxamyl | 141 | 1 | .7 | .018 | .070 | .070 | .070 |
| 04028 | Butylate | 171 | 1 | .6 | .002 | .004 | .004 | .004 |
| 82666 | Linuron | 171 | 1 | .6 | .002 | .011 | .011 | .011 |
| 82669 | Pebulate | 171 | 1 | .6 | .004 | .007 | .007 | .007 |
| 82679 | Propanil | 171 | 1 | .6 | .004 | E .003 | E .003 | E .003 |
| 82687 | *cis*-Permethrin | 171 | 1 | .6 | .005 | .019 | .019 | .019 |
|  | **Surrogate recoveries** |  |  |  |  |  | Percent |  |
| 91063 | Diazinon-$d_{10}$ | 171 | 170 | 99.4 | .1 | 37 | 100 | 200 |
| 91064 | Terbuthylazine | 171 | 170 | 99.4 | .1 | 70 | 109 | 153 |
| 91065 | *alpha*-HCH-$d_6$ | 171 | 170 | 99.4 | .1 | 60 | 96 | 128 |

tions was above 0.22 mg/L (fig. 8B). Most of the upper 10 percent of the concentrations for both TP and SRP also occurred at sites receiving predominantly agricultural runoff (a few sites were downstream from point-source discharges). About 47 percent of the TP concentrations equaled or exceeded the 0.10 mg/L desired limit for TP considered necessary for the prevention of nuisance plant growth in streams or other flowing water that does not discharge directly to lakes or impoundments (Mackenthun, 1973).

About 70 percent of the nutrient samples and associated detections occurred at the seven sites of the fixed-station network. Individual nutrient species at the fixed-station sites were detected in 92 to 99 percent of the samples analyzed. Concentrations were variable among sites (fig. 9). Zollner Creek near Mount Angel, located in the Pudding River Subbasin, is an indicator site for agricultural activities and generally had the largest nutrient concentrations (fig. 9). The largest concentrations for TN (24 mg/L) and $NO_3$-N (22 mg/L) observed at Zollner Creek near Mount Angel also were the largest concentration observed for all samples analyzed during this study. In addition, the largest concentrations for TP (0.81 mg/L) and SRP (0.39 mg/L) observed at the Mount Angel site ranked in the upper 95th percentile for all sample detections. The two forested background sites, Little Abiqua Creek near Scotts Mills (Pudding River Subbasin) and Gales Creek near Glenwood (Tualatin River Subbasin), generally had the lowest observed

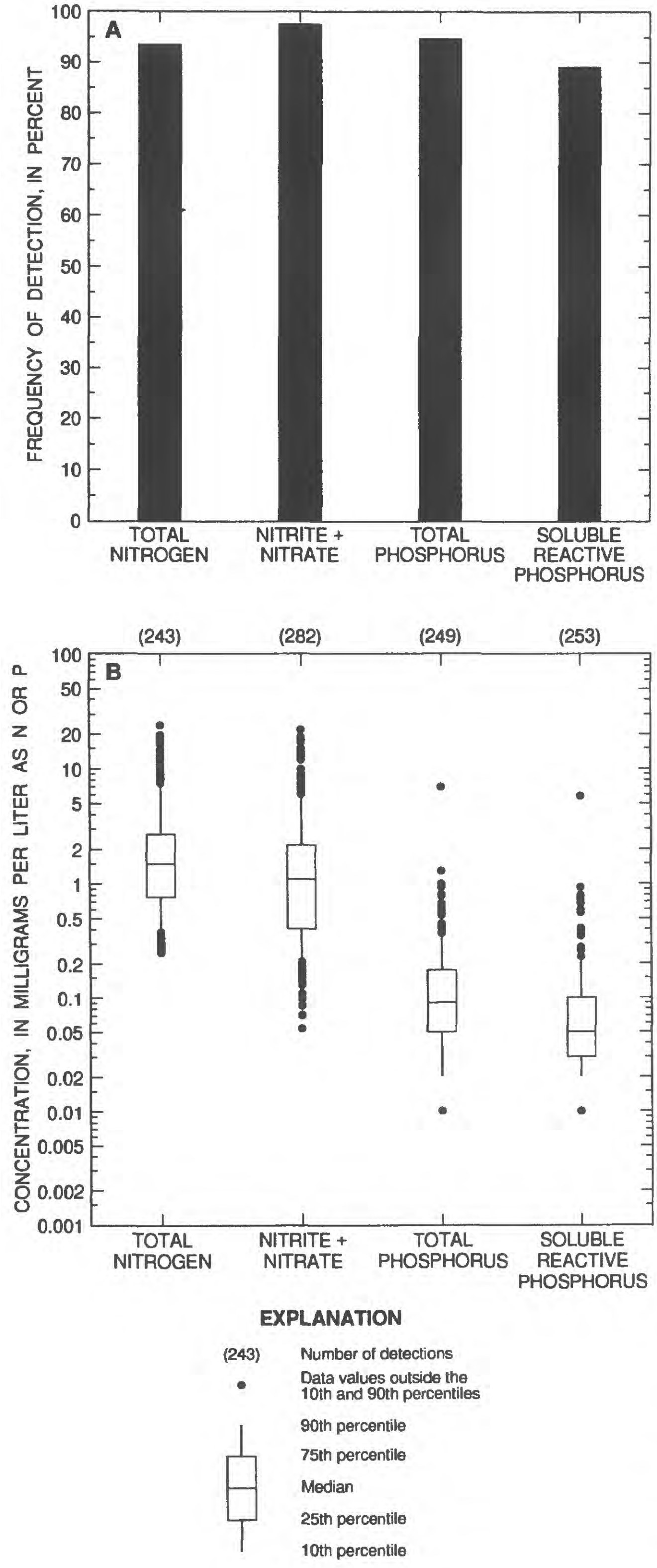

**Figure 8.** (A) Frequencies of detection and (B) statistical distribution of concentrations for total nitrogen, nitrite plus nitrate, total phosphorus, and soluble reactive phosphorus, Willamette Basin, April 1993 through September 1995.

nutrient concentrations. Samples from two of the integrator sites, Pudding River at Aurora and Tualatin River at West Linn, had similar TN and NO$_3$-N concentration distributions, and generally had concentrations larger than those observed at the urban indicator site (Fanno Creek at Durham) and the largest integrator site (Willamette River at Portland); however, samples from these four sites generally had similar TP and SRP concentration distributions.

Analysis of variance (ANOVA) was performed on the rank-transformed nutrient concentrations of the fixed-station sites to determine, using the Tukey's Honest Significant Difference test (Tukey's test), which median-ranked concentrations differed among sites ($p < 0.05$). Median TN, NO$_3$-N, TP, and SRP concentrations at the predominantly agricultural site (Zollner Creek) ranked significantly higher than at all other sites, including the two forested sites (Little Abiqua and Gales Creeks; fig. 9). Nutrient concentrations at the two forested sites ranked significantly lower than at all other sites, with the exception of NO$_3$-N concentrations at Little Abiqua Creek which had a similar ranking to NO$_3$-N concentrations at the Willamette River site (fig. 9).

Nutrient samples were collected over a 2-1/2 year period (April 1993through September 1995) at the seven fixed-station sites. Examination of the seasonal variability of TN, NO$_3$-N, TP, and SRP concentrations at these sites revealed seasonal patterns (figs. 10 and 11). Seasonal nutrient variability appeared to relate to surface- and (or) subsurface-water runoff from winter and spring rains at all sites, and at the Pudding River at Aurora site also to point-source nutrient discharges. Similar seasonal variations were documented by Bonn and others (1995) in an analysis of historical water-quality data for the Willamette Basin.

November through December storms generally coincided with the largest TN and NO$_3$-N concentrations at the Pudding River site (figs. 12A and B). Storms that followed later in the winter and spring months also caused elevated nitrogen concentrations; however, concentrations were smaller than what had been observed during the November-December storms, and values decreased with time. The decrease in concentrations with time suggests that the first series of fall storms may flush to the river larger nitrogen containing matter

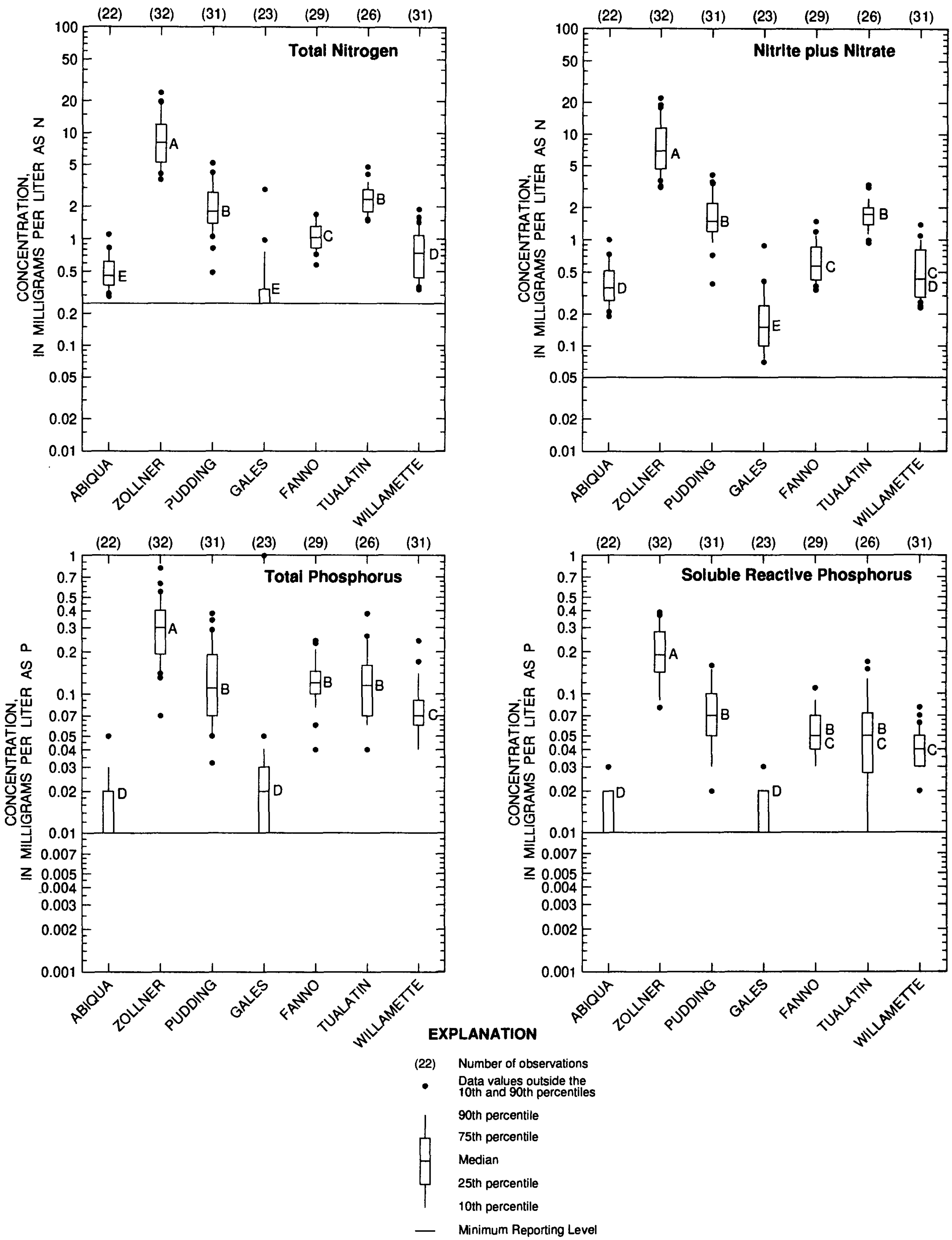

**Figure 9.** Statistical distributions of total nitrogen, nitrite plus nitrate, total phosphorus, and soluble reactive phosphorus concentrations for fixed-station sites in subbasins of the Willamette Basin, April 1993 through September 1995 (see table 2 for site names). (Groups derived from Tukey test are represented by letters A through E; basins in group A have the highest mean concentration rank, whereas basins in groups B through E have successively lower mean ranks. Basins that have letters in common do not differ significantly from one another.)

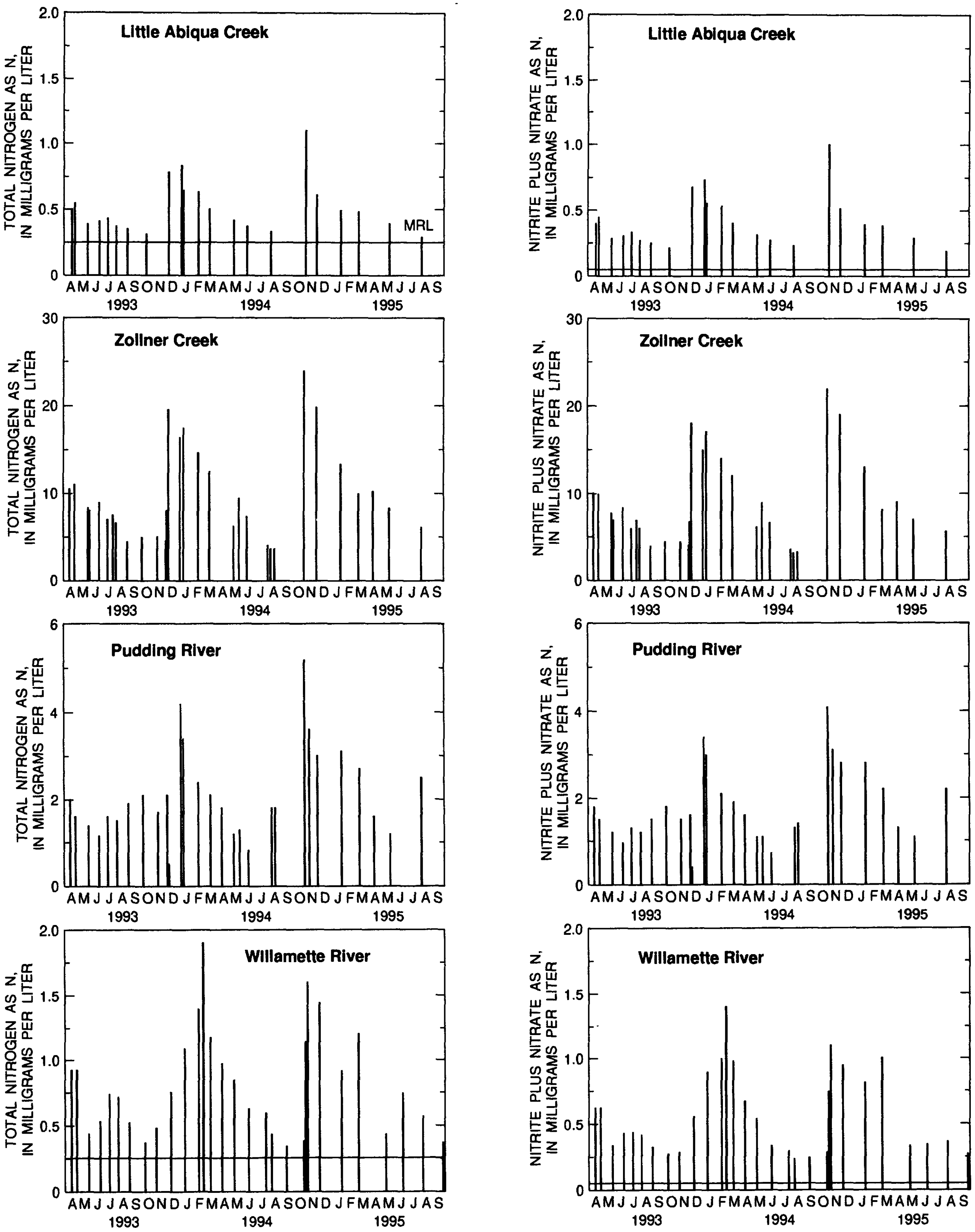

**Figure 10.** Seasonal variability of total nitrogen and nitrite plus nitrate at selected fixed-stations sites, April 1993 through September 1995. (MRL is the minimum reporting level; note when comparing values between sites that different ordinate scales are used.)

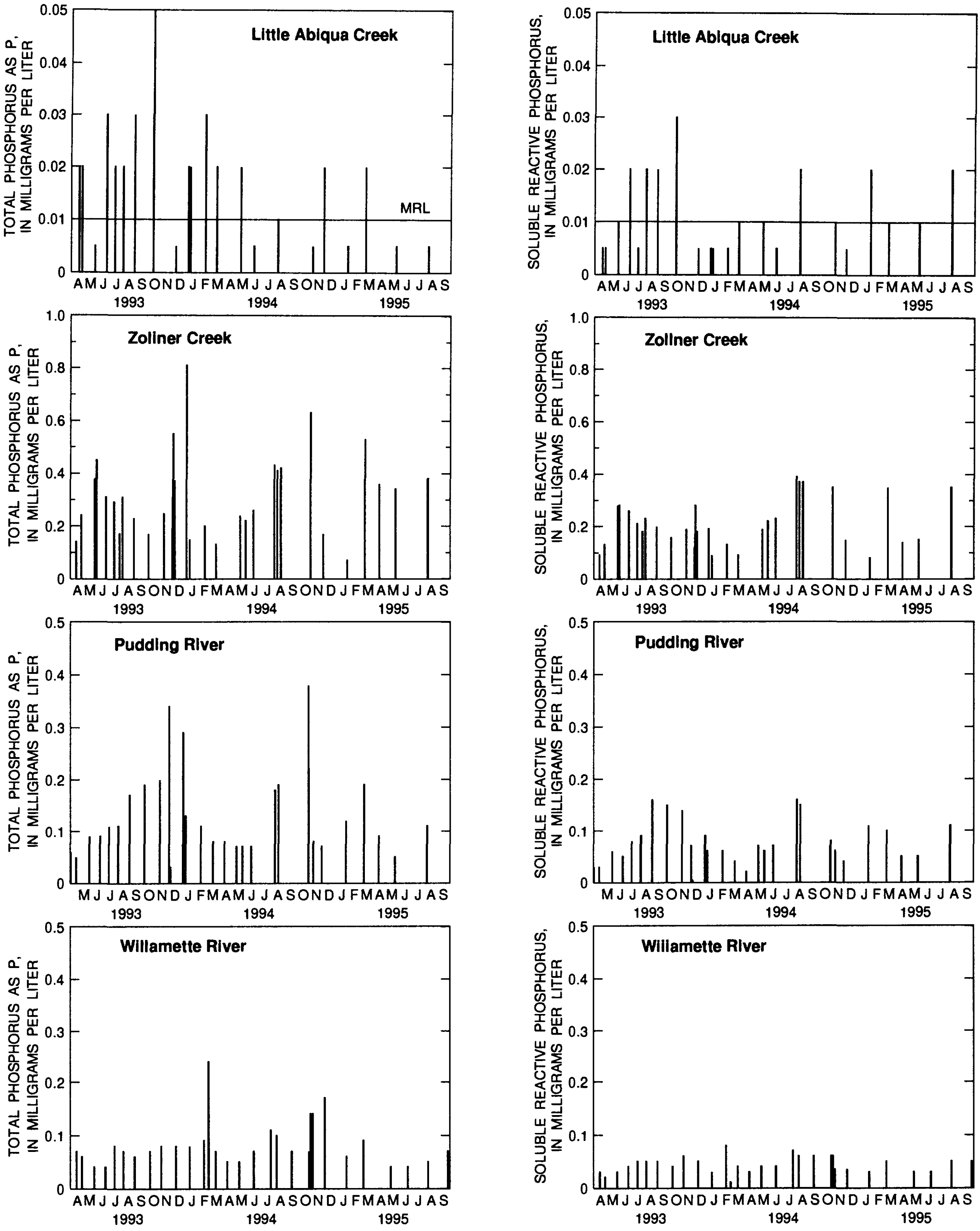

**Figure 11**. Seasonal variability of total phosphorus and soluble reactive phosphorus at selected fixed-stations sites, April 1993 through September 1995. (Censored data for Little Abiqua Creek have been plotted at one-half of minimum reporting levels (MRL); note when comparing values between sites that different ordinate scales are used.)

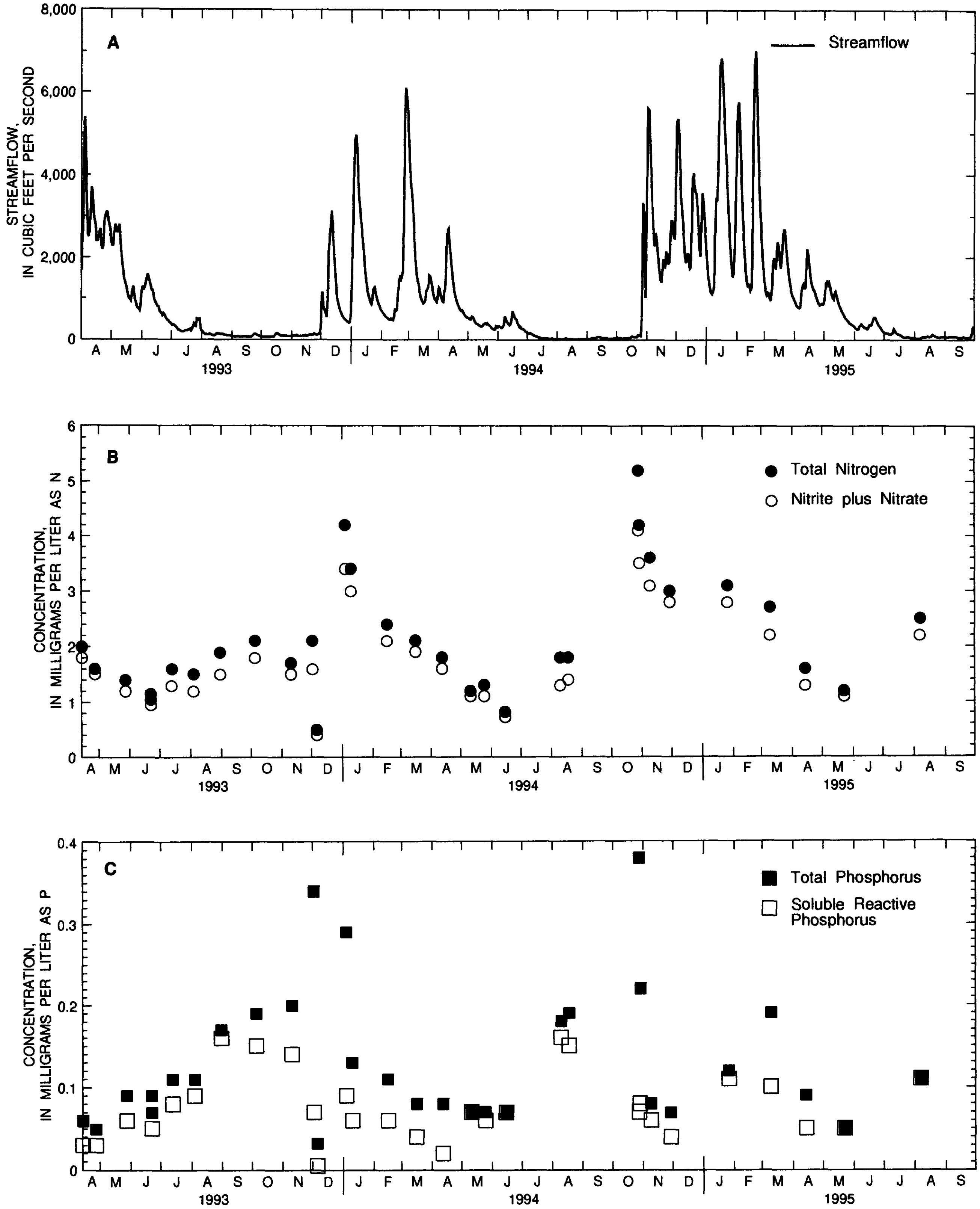

**Figure 12**. Seasonal variability of (A) streamflow, (B) total nitrogen and nitrite plus nitrate, and (C) total phosphorus and soluble reactive phosphorus concentrations, Pudding River at Aurora, Oregon, April 1993 through September 1995.

that build up on the landscape during summer, thus accounting for the large TN and $NO_3$-N concentrations first observed in autumn. Each succeeding storm would have less of a reservoir of nitrogen containing matter to flush, thus leading to successively smaller nitrogen concentrations in the streams with time.

TN and $NO_3$-N concentrations generally decreased during the summer and autumn low-flow period at the fixed-station sites (fig. 10), with the exception of the Pudding River at Aurora (fig. 12B). At the Pudding River site, TN and $NO_3$-N concentrations typically rose by 25 to 50 percent during the July, August, and early September period relative to concentrations observed during earlier months (May and June). Irrigation return flow and ground-water seepage were generally ruled out as causes because these increases were not observed at Zollner Creek, which receives large inputs from drainage tiles. The increase in the concentration of these nitrogen species during the summer and fall low-flow period may have been due to a combination of the discharge of nutrients from a sewage treatment plant (STP) located upstream and the smaller dilution of this discharge during the summer low-flow period than during the rest of the year (Bonn and others, 1995).

The seasonal variability of TN was related to the variability of $NO_3$-N because $NO_3$-N accounted for a major proportion of the TN concentration. The median ratio of all $NO_3$-N concentrations to TN concentrations for the seven fixed-station sites was 0.78 (median ratios for individual sites ranged from 0.58 at Fanno Creek to 0.91 at Zollner Creek).

Seasonal variability of SRP did not always follow the variability of TP, because SRP represented a variable part of the TP depending on the time of year. The median ratio of SRP concentrations to TP concentrations was 0.60 (median ratios for individual sites ranged from 0.43 at Tualatin River to 1.0 at Gales Creek). The largest concentrations of TP seasonally occurred during winter high-flow months (November through January) of each year (fig. 11); however, the relative SRP fraction of TP was less during the winter (0.44, median value for all fixed-station sites) than during summer. The larger concentrations of TP during the winter coupled with the smaller SRP fraction suggest that much of the TP was associated with overland runoff of particulate phosphorus attached to soil particles and resuspension of instream bottom sediment. Although elevated SRP concentrations also were observed during the winter high-flow period, the largest SRP concentrations did not always occur during that same timeframe. For the Zollner Creek and Pudding River sites, the largest SRP concentrations occurred generally during the July through September low-flow period (figs. 10–12). Sources of SRP during this time period for these sites could have been ground-water discharge and, in the case of the Pudding River, also from discharge of nutrients from the upstream STP. These inputs, coupled with a lack of dilution, could account for the elevated SRP concentrations observed during the low-flow period. Elevated TP concentrations also were observed at the Zollner Creek and Pudding River sites during the July through September low-flow periods.

## Pesticides in Filtered Water

Approximately 195 water samples were collected from 51 locations in the Willamette Basin and were analyzed for 86 pesticides and their degradation products (referred to as "pesticides" for the rest of this report). Fifty pesticides—34 herbicides and 16 insecticides—were detected during the 2-1/2 year study; a summary of the detected pesticides and their concentrations is included in table 8. Forty-nine of the 50 pesticides were detected at agricultural sites, 2 at forested sites, 25 at urban sites, and 29 at mixed-use sites. Of the 11 samples collected for analysis of pesticides at 6 sites designated as forested, very few pesticide detections occurred: 1 low-level occurrence of atrazine and desethylatrazine (0.004 µg/L) at Little Abiqua Creek near Scotts Mills and another low-level occurrence of atrazine (0.002 µg/L) at Soap Creek near Corvallis. The top 25 most frequently detected pesticides and the observed concentrations are listed on figure 13, in descending order of occurrence.

From 72 to 94 percent of water samples had detections of atrazine, simazine, metolachlor, and desethylatrazine ranging in concentration from 0.001 to 5.8 µg/L (fig. 13). These results are consistent with those observed by Anderson and others (1996) for samples collected in the Willamette

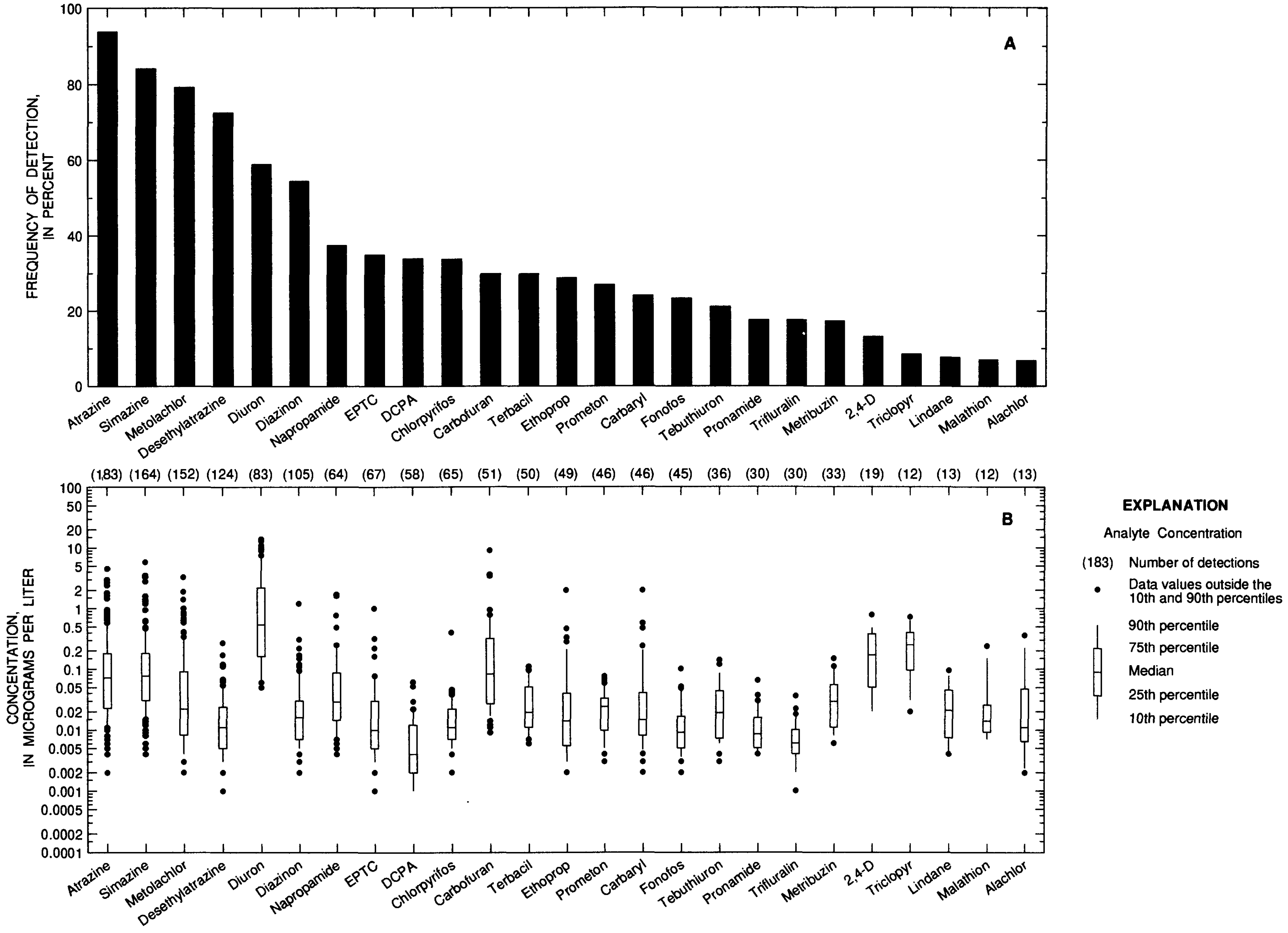

**Figure 13.** (A) Frequencies of detection and (B) statistical distributions of detections for the top 25 most frequently detected pesticides and degradation products for all sites sampled in the Willamette Basin, April 1993 through September 1995.

Basin during 1994. Further, those pesticides were among the top four most frequently detected compounds in samples collected from 20 of the Nation's major watersheds during the first set of the NAWQA water-quality assessments during 1991–95. Diuron and diazinon were detected in 54 to 59 percent of samples in concentrations ranging from 0.002 to 14 µg/L. Detections of napropamide, EPTC, DCPA, and chlorpyrifos were observed in about one-third (34–37 percent) of the samples, in concentrations ranging from an estimated 0.001 to 1.7 µg/L.

Water-quality criteria (see glossary for definition) for the protection of freshwater aquatic life from chronic toxicity (Nowell and Resek, 1994; Gilliom and others, in press) were exceeded for only a few of the 86 pesticides analyzed during this study: 4 of 183 detections for atrazine (greater than 2.0 µg/L), all 3 detections of azinphos-methyl (greater than 0.01 µg/L), 17 of 46 detections for carbaryl (greater than 0.02 µg/L), 3 of 51 detections for carbofuran (greater than 1.75 µg/L), 4 of 65 detections for chlorpyrifos (greater than 0.041 µg/L), 6 of 8 detections for *p,p'*-DDE (greater than 0.001 µg/L for DDT), 66 of 105 detections for diazinon (greater than 0.009 µg/L), all 10 detections for dieldrin (greater than 0.0019 µg/L), 24 of 83 detections for diuron (greater than 1.6 µg/L), 1 of 13 detections for *gamma*-HCH (lindane; greater than 0.08 µg/L), and 1 of 12 detections for malathion (greater than 0.1 µg/L). Most exceedances occurred in streams receiving either agricultural or urban runoff; however, the largest concentrations were observed at predominantly agricultural sites (Zollner Creek near Mount Angel, map reference number 2, and Johnson Creek at Palmblad Road near Gresham, map reference number 48). One chlorpyrifos concentration from a predominantly agricultural site was high (0.4 µg/L) enough to exceed the USEPA freshwater acute criterion (0.083 µg/L) for the protection of aquatic life (Zollner Creek near Mount Angel, map reference number 2). In addition, atrazine and simazine concentrations (4.5 and 5.8 µg/L, respectively) from a predominantly agricultural site (Zollner Creek near Mount Angel, map reference number 2) exceeded maximum contaminant levels (MCLs) established by the USEPA for drinking water. The USEPA MCLs for atrazine and simazine are 3.0 and 4.5 µg/L, respectively (U.S. Environmental Protection Agency, 1996).

About 60 percent of the pesticide samples collected during this study were from four of the seven sites associated with the fixed-station network (Zollner Creek near Mount Angel, Pudding River at Aurora, Fanno Creek at Durham and Willamette River at Portland). Because of cost constraints, only these four sites were selected for monthly and storm-related pesticide monitoring; pesticide samples were collected at the other three fixed-station sites only during periods of high- and low-flow conditions. Forty-three (29 herbicides and 14 insecticides) of the 46 pesticides detected at these 4 sites were observed at the Zollner Creek site; 34 pesticides (25 herbicides and 9 insecticides) were observed at the Pudding River site, 23 pesticides (16 herbicides and 7 insecticides) were detected at the Fanno Creek at Durham site and 23 pesticides (17 herbicides and 6 insecticides) were detected at the Willamette River at Portland site. Of all the pesticides detected, only prometon, tebuthiuron, and dichlobenil were detected most frequently in Fanno Creek, which is in a predominantly urban subbasin. Prometon, tebuthiuron, and dichlobenil are herbicides which generally are applied to noncropland areas, rangelands, right-of-ways, and industrial sites. Frequency of detections and resulting concentrations of the six most frequently detected pesticides in the basin (atrazine, simazine, metolachlor, diuron, diazinon, and desethylatrazine) were observed to vary among sites (fig. 14). Median concentrations of these pesticides were significantly ($p<0.05$) larger at the Zollner Creek site, 99 percent agricultural land use, (fig. 14) than at the other three sites, with the exception of diazinon concentrations at Zollner Creek, which were similarly to those at the predominantly urban site (Fanno Creek; fig. 14).

The Zollner Creek Subbasin is an agricultural subbasin of the Pudding River. During this study, 32 water samples were collected at the most downstream site in the Zollner Creek Subbasin (Zollner Creek near Mount Angel) and analyzed for pesticides. Samples collected at the Zollner Creek near Mount Angel site had the greatest number of different pesticides detected (43) of any site sampled in the Willamette Basin. The largest concentrations for 27 of the 50 different pesticides detected in the Willamette Basin occurred at the Zollner Creek near Mount Angel site; 3 additional pesticides detected at this site were at concentrations

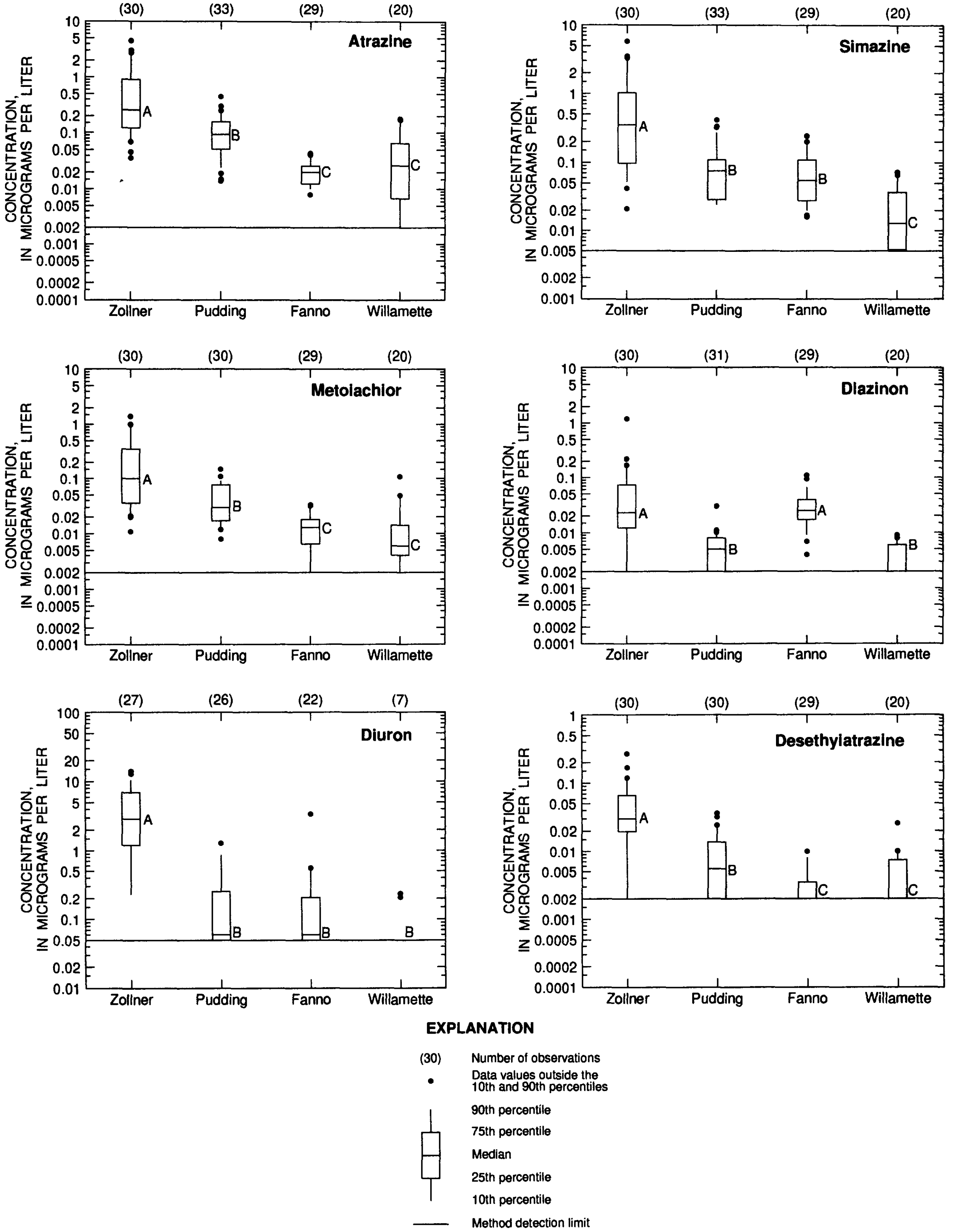

**Figure 14.** Statistical distribution of concentrations for atrazine, simazine, metolachlor, diazinon, diuron, and desethylatrazine for four fixed-station sites in subbasins of the Willamette Basin, April 1993 through September 1995 (see table 2 for site names). (Groups derived from Tukey test are represented by letters A through C; basins in group A have the highest mean concentration rank, whereas basins in groups B and C have successively lower mean ranks.)

that ranked in the upper 95th percentile of all samples analyzed.

Examination of seasonal variability of the six most frequently detected pesticides at the four fixed-station sites indicated that many of the patterns were too complex to be explained; however, some patterns appeared to reflect seasonal streamflow variability and, quite possibly, the effects of different land-use activities. An example of the complexity of the seasonal patterns is shown on figure 15, where atrazine, diazinon, and diuron concentrations are compared for Zollner Creek (an agricultural site) and Fanno Creek (an urban site). Winter high flows of 1993 and 1994 (reflecting overland runoff conditions) generally were associated with some rise in pesticide concentrations, except for diazinon concentrations at Zollner Creek for both years and atrazine concentrations at Fanno Creek during winter of 1994. In addition, a water sample collected at Zollner Creek during a small summer storm in July 1993 (such storms cause less overland runoff and soil flushing than occurs during winter conditions) showed elevated analyte concentrations for several pesticides, including atrazine (small rise), diazinon, and diuron. Rains following the application of pesticides and nutrients in the spring of each year (mid-March through early June) in Zollner Creek resulted, in many cases, in some of the largest pesticide concentrations for the six most frequently detected pesticides observed in the basin. Spring rains also caused elevated pesticide concentrations in Fanno Creek; however, the increases generally were not as large as those observed in Zollner Creek, with the exception of the elevated diuron concentration observed in the spring of 1995.

## Synoptic Investigations

### Pudding and Molalla River Subbasin High-Flow Study

Samples were collected during a moderate-sized storm on April 26–29, 1993, in the Pudding and Molalla River Subbasins to assess impacts of springtime runoff following agricultural applications of fertilizers and pesticides. Daily mean streamflow at the Pudding River at Aurora site was about 3,000 cubic feet per second; this runoff corresponds to an April streamflow that is exceeded only about 10 percent of the time on the basis of data from WY's 1928–64 (Moffatt and others, 1990). Twenty sites (including the three fixed-station sites located in the Pudding River Subbasin; fig. 2 and table 2) were sampled synoptically for several water-quality constituents, including $NO_3$-N, SRP, and 10 different pesticides (alachlor, atrazine, carbaryl, chlorpyrifos, diazinon, EPTC, fonofos, metolachlor, pendimethalin, and simazine; analyses performed by Kathryn M. Kuivila, USGS, Sacramento, California using analytical techniques outlined by Crepeau and others, 1994). Although water samples were not collected in a Lagrangian fashion, sampling generally was done at the most upstream sites in the subbasins on the first day and at the most downstream sites in the subbasins on the last day.

$NO_3$-N concentrations ranged from less than (<) 0.05 to 10.0 mg/L (median value, 2.0 mg/L), whereas SRP concentrations ranged from <0.01 to 0.73 mg/L (median value, 0.03 mg/L) (fig. 16). Atrazine and simazine were the two most frequently detected pesticides with detections in 95 and 82 percent of the samples, respectively. Atrazine concentrations ranged from <0.001 to 3.0 μg/L (median value, 0.160 μg/L) and simazine concentrations ranged from <0.005 to 1.4 μg/L (median value, 0.081 μg/L) (fig. 16).

The number, types, and concentrations of nutrients and pesticides detected generally related to the percentage of a subbasin's area in agriculture (fig. 17). Spearman correlation coefficients for $NO_3$-N, SRP, atrazine, and simazine versus percent of drainage area in agricultural land use ranged from 0.71 to 0.91 ($p < 0.05$) (fig. 17). All 10 pesticides analyzed were detected at Zollner Creek near Mount Angel, which has 99 percent of its area in agriculture; 8 pesticides were detected at Little Pudding River at Sunnyview Road, which has 89 percent of its area in agriculture; and 6 pesticides were detected at Lake Labish Ditch, which has 87 percent of its area in agriculture. Samples from the Zollner Creek near Mount Angel site had the largest concentrations observed for simazine (1.4 μg/L), atrazine (3.0 μg/L), diazinon (0.015 μg/L), alachlor (0.011 μg/L), and carbaryl (0.006 μg/L); samples from the Little Pudding River at Sunnyview Road site had the largest concentrations observed for chlorpyrifos (0.020 μg/L) and EPTC (0.011 μg/L); and samples from the Lake Labish

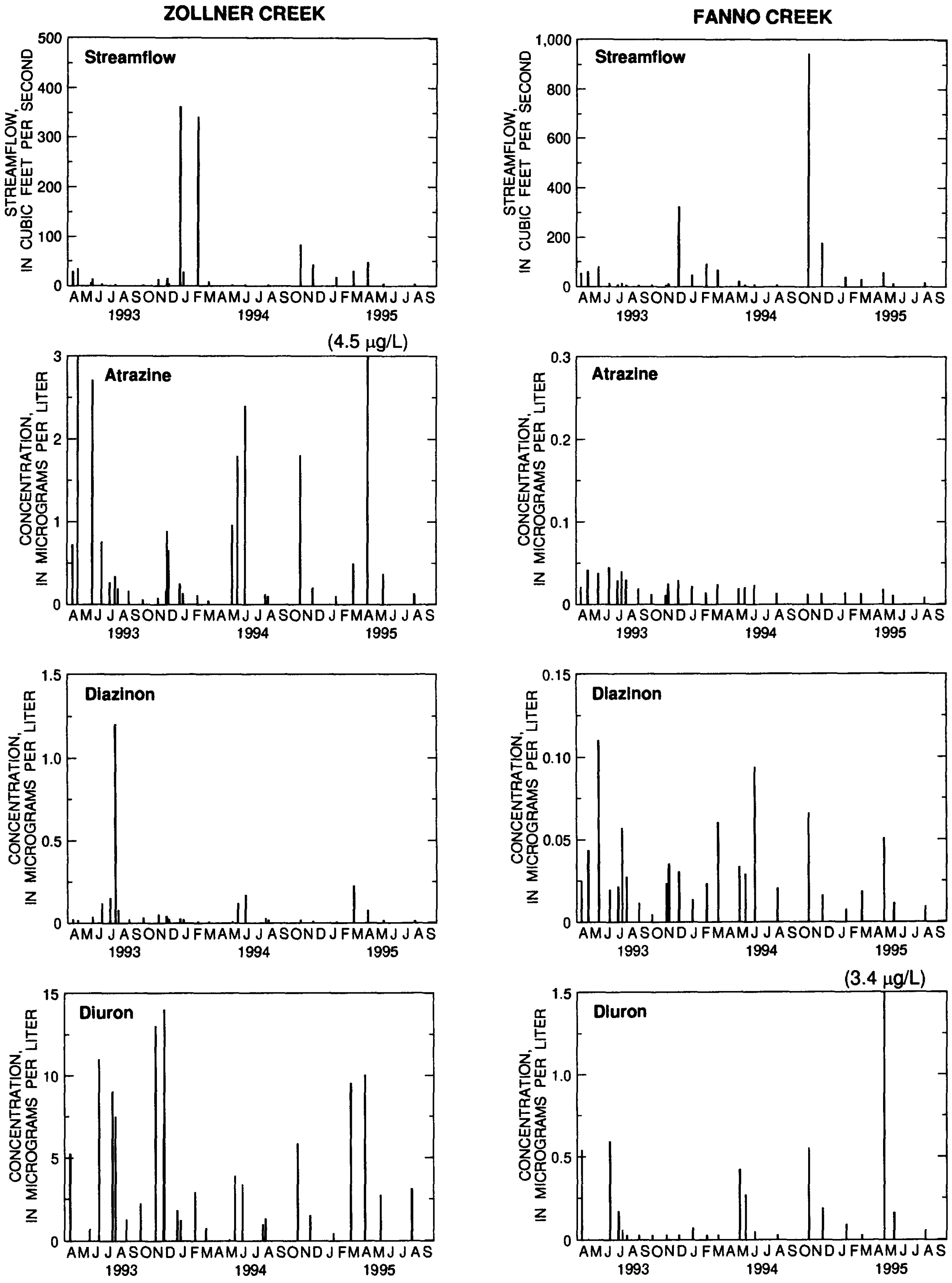

**Figure 15.** Seasonal variability of instantaneous streamflow, and concentrations of atrazine, diazinon, and diuron at Zollner Creek near Mount Angel and at Fanno Creek at Durham, April 1993 through September 1995. (Note when comparing values between Zollner Creek and Fanno Creek that different ordinate scales are used; µg/L, micrograms per liter.)

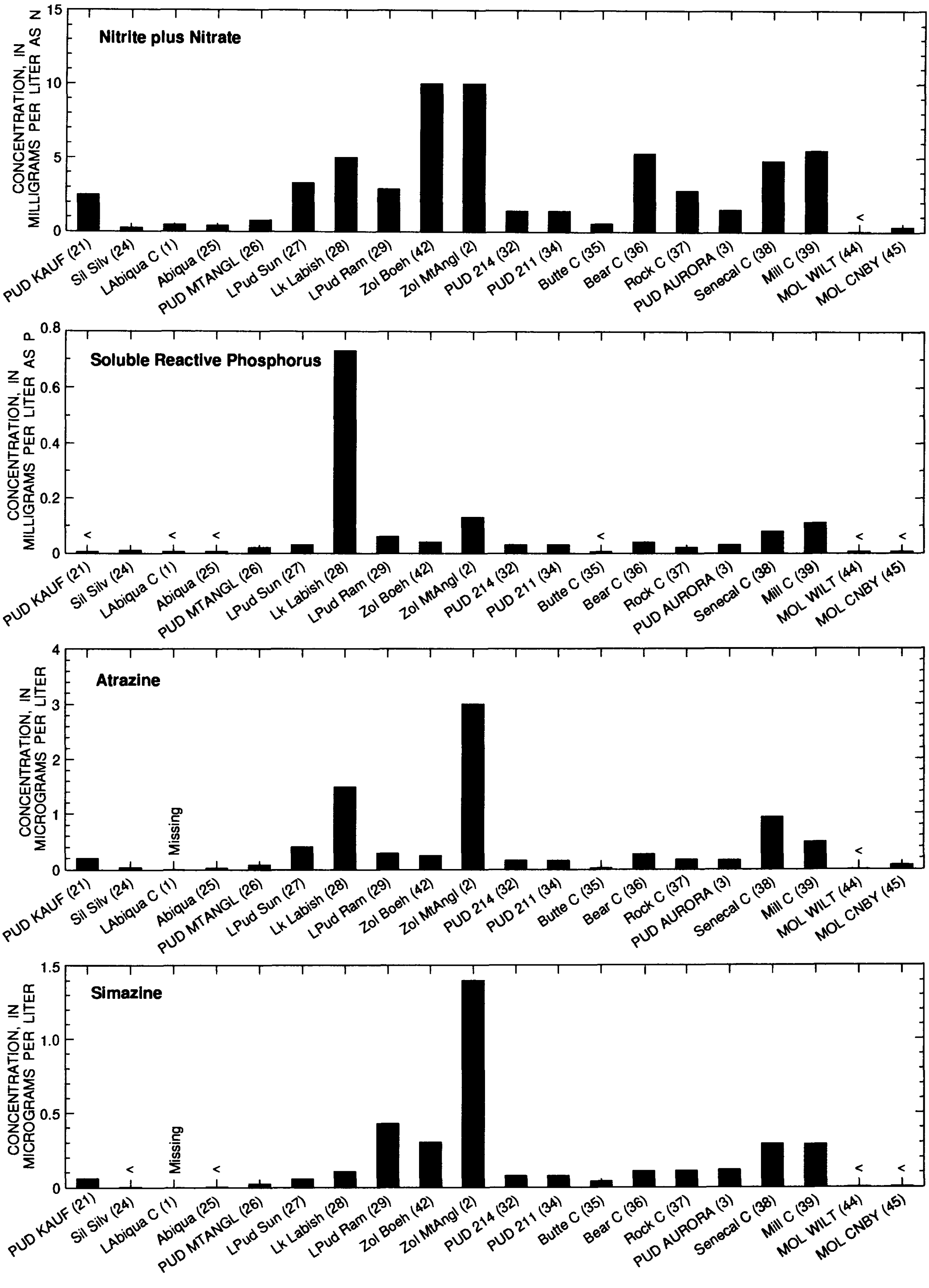

**Figure 16.** Concentrations for nitrite plus nitrate, soluble reactive phosphorus, atrazine, and simazine for sites sampled in the Pudding and Molalla River Subbasins, April 26–29, 1993. (Numbers in parenthesis refer to site locations in figure 2 and table 2; less than symbol (<) used to designate censored concentrations; sampling sites which are uppercased are main-stem sites in the Pudding and Molalla Rivers.)

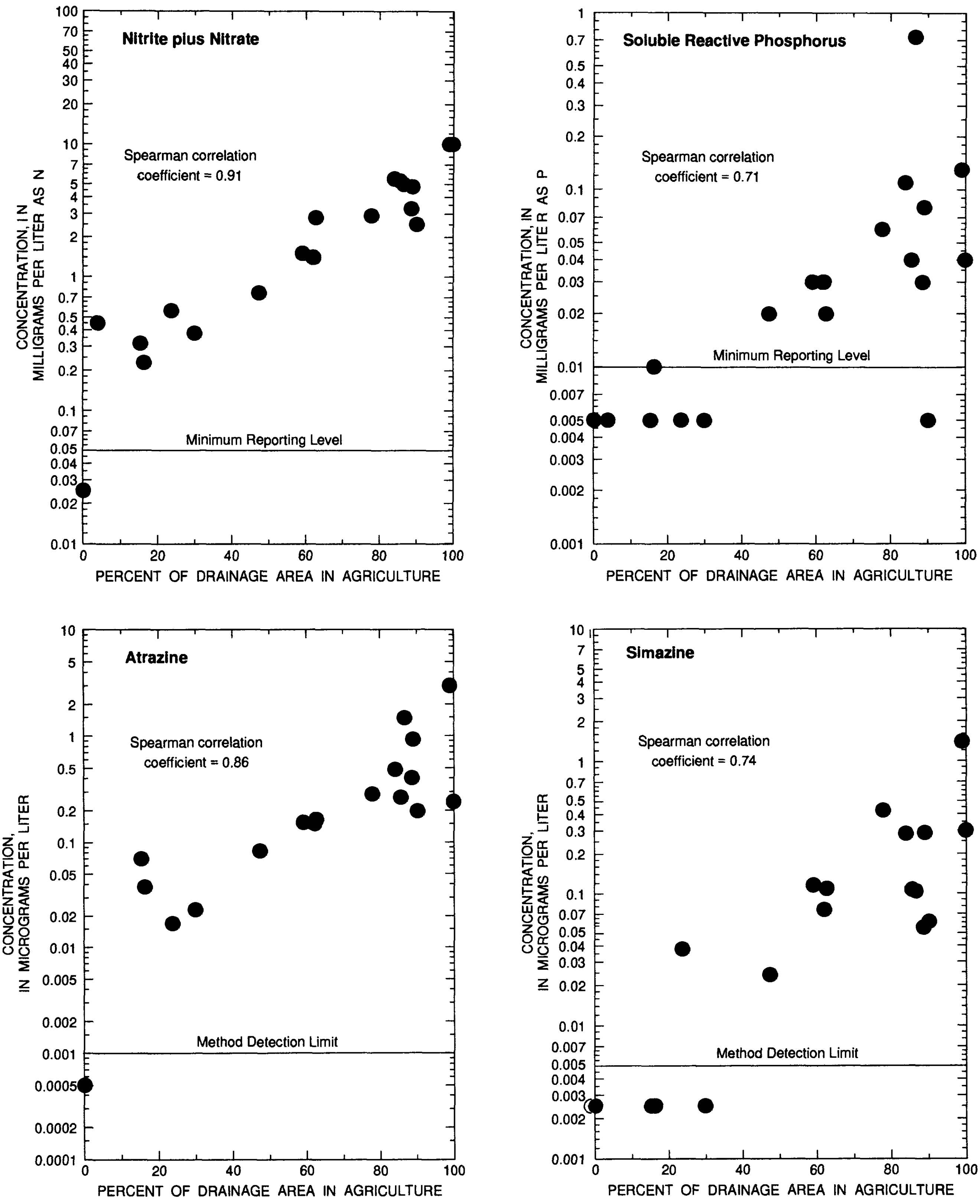

**Figure 17.** Relation between percent of drainage area in agriculture and concentrations of nitrite plus nitrate, soluble reactive phosphorus, atrazine, and simazine at sites sampled in the Pudding and Molalla River Subbasins, April 26–29, 1993. (Censored concentrations have been plotted at one-half their minimum reporting levels or method detection limits.)

Ditch site had the largest concentrations of fonofos (0.016 µg/L), metolachlor (0.144 µg/L), and pendimethalin (0.044 µg/L). The largest nutrient concentrations also occurred at these sites—a sample from Zollner Creek had the largest $NO_3$-N concentration (10 mg/L), and one from Lake Labish Ditch had the largest SRP concentration (0.73 mg/L). No nutrients or pesticides were detected at the Molalla River near Wilhoit site, which has a 100-percent forested drainage area.

### Pudding River Subbasin Low-Flow Study

A low-flow surface-water synoptic study was conducted during August 15–18, 1994, in the Pudding River Subbasin to characterize the effects of ground-water, irrigation-return flow, and point-source nutrient contributions to the subbasin. Daily mean streamflow at the Pudding River at Aurora site was about 9.0 cubic feet per second, which corresponds to an August streamflow that is exceeded more than 95 percent of the time on the basis of data for WY's 1928–64 (Moffatt and others, 1990). Eighteen sites (fig. 2 and table 2) were synoptically sampled in the subbasin for several water-quality constituents, including $NO_3$-N and SRP.

$NO_3$-N concentrations ranged from <0.05 to 15 mg/L (median value, 1.1 mg/L), and SRP concentrations ranged from <0.01 to 5.8 mg/L (median value, 0.14 mg/L) (fig. 18). During this low-flow study, the point-source effluent discharge from the STP at Woodburn to the main-stem Pudding River had the largest measured concentrations of $NO_3$-N (15 mg/L) and SRP (5.8 mg/L). Although the flow from the STP amounted to only about 13 percent (2.05 cubic feet per second) of the total flow at the Pudding River site at Highway 211 located downstream from the STP's discharge (RM 22.4; 15.5 cubic feet per second), $NO_3$-N and SRP concentrations increased by over 200 and 500 percent, respectively, from concentrations observed for the Pudding River site at Highway 214 (RM 26.9) located upstream of the STP's discharge.

The Bear Creek site, with 86 percent of its subbasin's area in agriculture, had the largest instream $NO_3$-N concentration (12.0 mg/L). $NO_3$-N concentrations at Lake Labish Ditch and Zollner Creek near Mount Angel were the next two largest instream values (4.5 and 3.2 mg/L, respectively). The Little Pudding River near Rambler Drive site, with 78 percent of its subbasin area in agriculture, had the largest tributary SRP concentration (0.67 mg/L). The SRP concentration at the Pudding River at Highway 211 site was the next largest concentration, at 0.63 mg/L.

The North Fork Silver Creek at Van Handle Road site, with 100 percent of its drainage area forested, had among the smallest observed $NO_3$-N and SRP concentrations (0.071 and <0.01 mg/L, respectively).

### Zollner Creek Subbasin High-Flow Study

To study the water-quality effects of the intensive agricultural activity in the Zollner Creek Subbasin, a high-flow study was conducted during April 26–27, 1993 at two sites: Zollner Creek near Mount Angel and Zollner Creek at Boehmer Road (fig. 2 and table 2). The Mount Angel site on Zollner Creek is located about 0.4 miles upstream from its confluence with the Pudding River, and the Boehmer Road site is located about 5 miles farther upstream. During the high-flow study, the mean daily flow at the Mount Angel site was 35 cubic feet per second, which corresponds to a daily mean streamflow that was not exceeded more than 12 percent of the time over the 2-1/2 years of daily streamflow record at that site. Water-quality constituents analyzed included $NO_3$-N, SRP, and the same 10 pesticides that had been selected for analysis during the Pudding and Molalla River Subbasin high-flow study.

Streamflow at the Mount Angel site was more than three times that observed at the Boehmer Road site, whereas $NO_3$-N concentrations at both sites were identical at 10 mg/L (fig. 19). For the Willamette Basin, a $NO_3$-N concentration of 10 mg/L is relatively high and ranked in the upper 95th percentile of all sample detections. The elevated $NO_3$-N concentrations at the Zollner Creek sites reflected the high level of agricultural activity in the subbasin, with the Boehmer Road site having about 100 percent of its drainage area in agriculture and the Mount Angel site having about 99 percent of its drainage area in agriculture. The SRP concentration at the Mount Angel site was about three times that observed at the Boehmer Road site, but observed concentrations at both sites were not elevated relative to other SRP concentrations detected in the Willamette Basin.

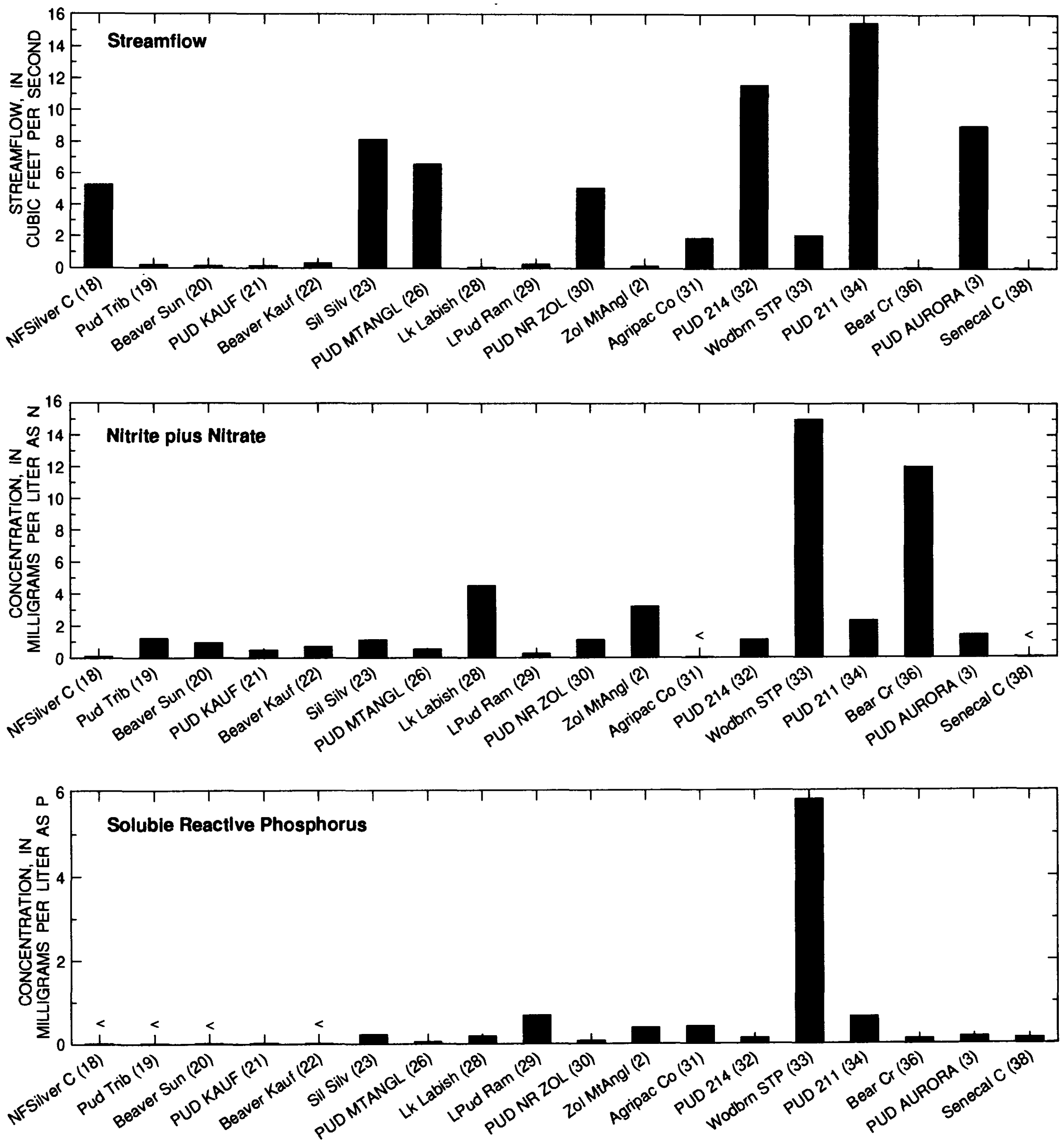

**Figure 18.** Streamflow and concentrations of nitrite plus nitrate and soluble reactive phosphorus for sites sampled in the Pudding River Subbasin, August 15–18, 1994. (Numbers in parenthesis refer to site locations in figure 2 and table 2; less than symbol (<) used to designate censored concentrations; sampling site names that are uppercased are main-stem sites in the Pudding River.)

The 10 pesticides analyzed were detected at the Zollner Creek near Mount Angel site, whereas only 4 of the 10 pesticides (alachlor, atrazine, metolachlor, and simazine) were detected at the Zollner Creek at Boehmer Road site. Observed concentrations for atrazine (3.0 µg/L) and simazine (1.4 µg/L) at the Mount Angel site ranked in the upper 99th- and 95th percentile, respectively, for all sample detections in the Willamette Basin. Concentrations of alachlor, atrazine, metolachlor, and simazine at the Mount Angel site ranged from about 120 percent (alachlor) to more than 1,200 percent (atrazine) of the concentrations observed at the Boehmer Road site. The 120 percent increase in the downstream concentration of alachlor corresponded to an increase in concentra-

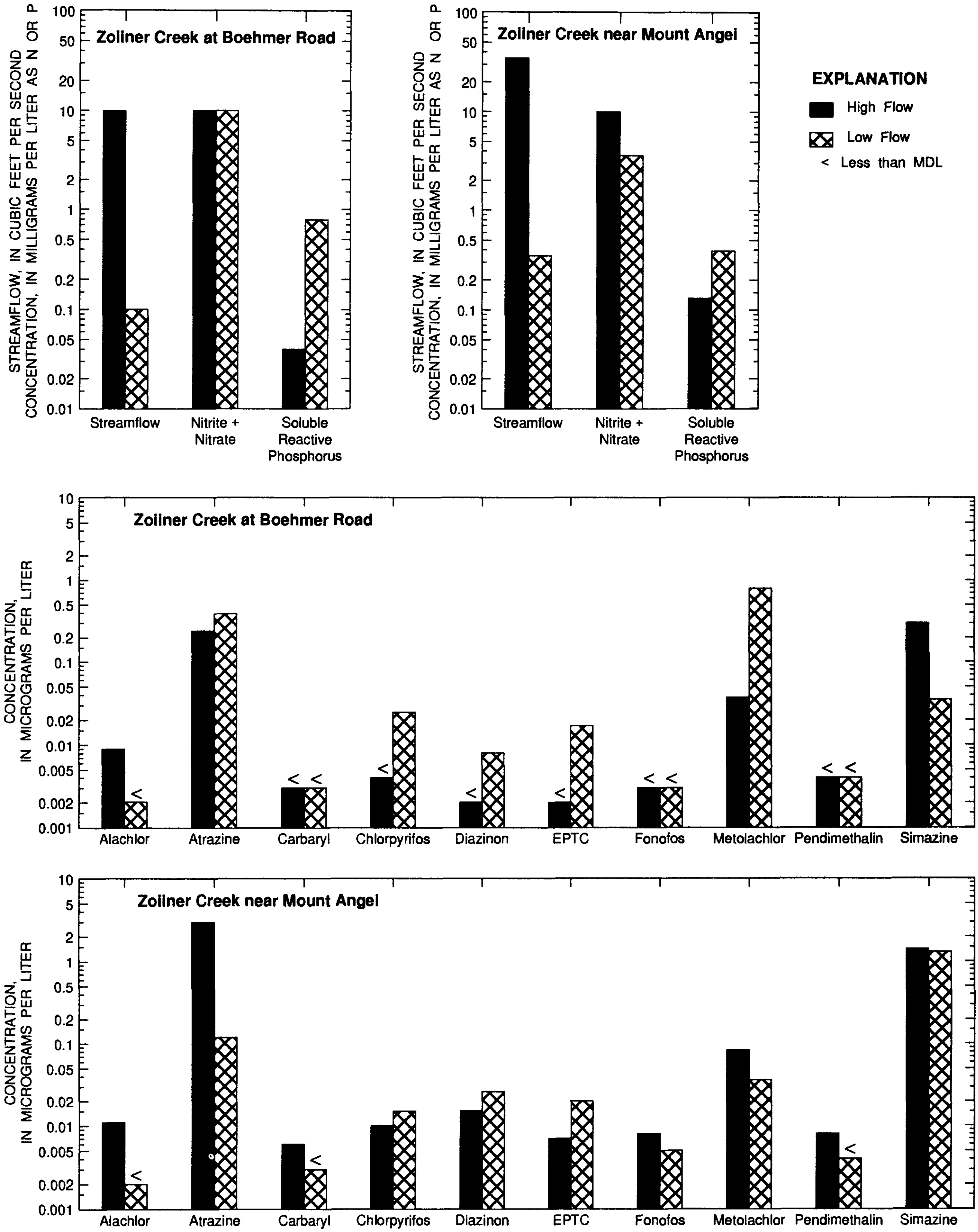

**Figure 19.** Streamflow and nutrient and pesticide concentrations at Zollner Creek at Boehmer Road and Zollner Creek near Mount Angel, April 26–27, 1993 (high flow) and August 2–4, 1994 (low flow). (Less than symbol "<" used to designate censored concentrations reported at their minimum reporting level or method detection limit [MDL].)

tion of 0.002 µg/L (from 0.009 to 0.011 µg/L), which is not a significant increase when considering the precision of the analytical method. Because the two sites in the Zollner Creek Subbasin were not sampled in a totally Lagrangian manner, it is difficult to assess whether the increased pesticide detections observed at the Mount Angel site were due to differences in agricultural practices between the two drainage areas or were an artifact of when the samples were collected.

### Zollner Creek Subbasin Low-Flow Study

A low-flow surface-water synoptic study was conducted in the Zollner Creek Subbasin during August 2–4, 1994 to characterize ground-water and irrigation return flow contributions of nutrients and pesticides to stream water quality. The mean daily streamflow at the Zollner Creek near Mount Angel site was 0.32 cubic feet per second, which corresponds to a daily mean streamflow that was exceeded more than 92 percent of the time for the 2-1/2 years of daily streamflow record at this site. Water samples were collected at five sites in the subbasin (fig. 2) of which only two were sites sampled during the high-flow Zollner Creek Subbasin study. The water samples were analyzed for 8 nutrient constituents (Appendix 3) and 86 pesticides (Appendixes 1 and 2). Because a primary objective of the Zollner Creek study was to compare analytical results between the high and low flows, data interpretation included here was limited to the constituents and sites sampled during both time periods.

Streamflow at the Mount Angel site on Zollner Creek was more than 3-1/2 times the flow observed at the Boehmer Road site on Zollner Creek in August. In contrast, $NO_3$-N and SRP concentrations at the Mount Angel site were roughly one-third and one-half, respectively, of the concentrations observed at the Boehmer Road site (fig. 19). The $NO_3$-N concentration at the Boehmer Road site was identical to the concentration observed during the high-flow synoptic (10 mg/L), whereas SRP concentrations at the Boehmer Road site (0.79 mg/L) and the Mount Angel site (0.39 mg/L) were much larger than what had been observed during the high-flow study (fig. 19). The elevated SRP concentrations at the Boehmer Road and the Mount Angel sites were in the upper 99th- and 95th percentile, respectively, for all sample detections in the Willamette Basin. The larger nutrient concentrations observed at the upstream site were contrary to what was observed during the high-flow study, in which the $NO_3$-N and SRP concentrations either remained the same or increased in concentration in a downstream direction. Possible reasons why nutrient concentrations did not increase in a downstream direction during the low-flow study were a combination of (1) the sampling not being performed in a Lagrangian manner, thus resulting in the same parcel of water at the upstream site not being sampled at the downstream site, (2) some of the nutrient constituents being biologically taken up as water flowed between the two sites, and (3) the downstream nutrient concentrations being diluted because of the increased subsurface flow between the two sites.

Seven of the 10 pesticides analyzed during the high-flow study were detected during the low-flow study; 6 of the pesticides were detected at both sites (atrazine, chlorpyrifos, diazinon, EPTC, metolachlor, and simazine) (fig. 19). Fonofos was detected only at the Mount Angel site. Observed concentrations for metolachlor at the Boehmer Road site (0.79 µg/L) and simazine at the Mount Angel site (1.3 µg/L) ranked in the upper 95th percentile for all sample detections in the Willamette Basin. Two pesticides (diazinon and simazine) increased in concentration in a downstream direction, and two pesticides (atrazine, and metolachlor) decreased in concentration in a down-stream direction. Concentrations for the three other pesticides (fonofos, EPTC, and chlorpyrifos), although showing some increases or decreases in concentration in a downstream manner from <0.003 to 0.005 µg/L, from 0.017 to 0.020 µg/L, and from 0.025 to 0.015 µg/L, respectively, were considered to have not changed when taking into consideration the precision of the analytical method.

Insufficient information is available to determine why certain pesticides either increased or decreased in concentration in a downstream direction. However, possible reasons why certain pesticides increased in concentration downstream include (1) sampling was non-Lagrangian, and (2) additional pesticides were contributed from ground-water or irrigation-return flows. Possible reasons why certain pesticides concentrations decreased downstream include (1) sampling was non-Lagrangian, (2) pesticide degradation as water flowed between the two sites, and (3) dilution of downstream pesticide concentrations by increased streamflow.

### Southern Willamette Basin Late-Spring Study

A series of late-spring water samples were collected from mid-May through early June 1994 in the Long Tom, Muddy, and the Calapooia River Subbasins to characterize the quality of runoff immediately following application of fertilizers and pesticides to agricultural areas. All three subbasins are located in the southern part of the Willamette Basin, with the Long Tom River Subbasin (downstream of Fern Ridge Reservoir), the Muddy Creek Subbasin, and the Calapooia River Subbasin having 58, 71, and 47 percent, respectively, of their drainage areas in agricultural development. Instantaneous streamflow of the Calapooia River at Albany site was 152 cubic feet per second on May 26, 1994, which corresponds to a May daily mean streamflow that has been exceeded more than 95 percent of the time on the basis of data for WY's 1940–81 (Moffatt and others, 1990). Thus, sampling conditions for this study were more typical of baseflow conditions for May than of high-flow conditions. Nine sites in subbasins having varying land uses were sampled in the three subbasins: five sites were located in the Long Tom River Subbasin; three sites were located in the Muddy Creek Subbasin; and one site was located in the Calapooia River Subbasin (see table 2 for listing of the sites sampled and summary of subbasin land use, and fig. 2 for site locations). Although sampling was not done in a Lagrangian fashion, a comparison was made of nutrient and pesticide concentrations among sites.

In the Long Tom Subbasin, the Flat Creek at Noraton Road site, which has about 87 percent of its drainage area in agriculture, had the largest observed concentrations for TN (6.2 mg/L), $NO_3$-N (5.4 mg/l), TP (0.14 mg/L), and SRP (0.08 mg/L) of all the southern sites sampled (figs. 2 and 20). However, none of the nutrient concentrations were considered elevated when compared with other sample concentrations in the Willamette Basin. The most downstream locations in each subbasin generally had the next largest nutrient concentrations for each subbasin, with TN values ranging from 0.81 to 1.90 mg/L, $NO_3$-N values ranging from 0.71 to 1.60 mg/L, TP values ranging from 0.02 to 0.08 mg/L, and SRP values ranging from 0.01 to 0.07 mg/L (fig. 20). TN, $NO_3$-N, and TP concentrations were not detected in a sample collected at the Ferguson Creek at Ferguson Road site which has 100 percent of its drainage area in forest, although a low-level SRP concentration of 0.01 mg/L was detected.

Of the 86 pesticides analyzed, only 14 pesticides were detected, in concentrations ranging from 0.002 to 2.0 µg/L (fig. 21). From 60 to 90 percent of the samples had detections of atrazine, desethylatrazine, and simazine, and about 40 percent of the samples had detections of EPTC, metolachlor, pronamide, and terbacil (fig. 21). Flat Creek and Muddy Creek near Peoria sites had the greatest number of different pesticides observed with 11 detections. No pesticides were detected at the forested Ferguson Creek at Ferguson Road site (fig. 22). The largest concentrations for all 14 pesticides were observed at only three sites: Flat Creek, with 87 percent of its drainage area in agriculture, had the largest concentrations for diazinon (0.17 µg/L), EPTC (0.077 µg/L), fonofos (0.006 µg/L), pronamide (0.019 µg/L), and tebuthiuron (0.022 µg/L); Long Tom River at Bundy Bridge, with 58 percent of its drainage area below Fern Ridge Reservoir in agriculture, had the largest concentrations for carbaryl (2.0 µg/L) and terbacil (0.073 µg/L); and Muddy Creek near Peoria, with 71 percent of its drainage area in agriculture, had the largest concentrations for atrazine (0.43 µg/L), bromacil (0.20 µg/L), 2,4-D (0.21 µg/L), desethylatrazine (0.034 µg/L), diuron (0.52 µg/L), metolachlor (0.005 µg/L), and simazine (0.63 µg/L). Although relatively few pesticides were detected during this late-spring sampling when compared to the 50 different pesticides detected basinwide, the largest observed concentrations of simazine and EPTC ranked in the upper 90th percentile of all sample detections, the largest observed concentration of diazinon ranked in the upper 95th percentile of all sample detections, and the largest observed concentrations of bromacil and carbaryl were the largest recorded values for all sample detections in the Willamette Basin.

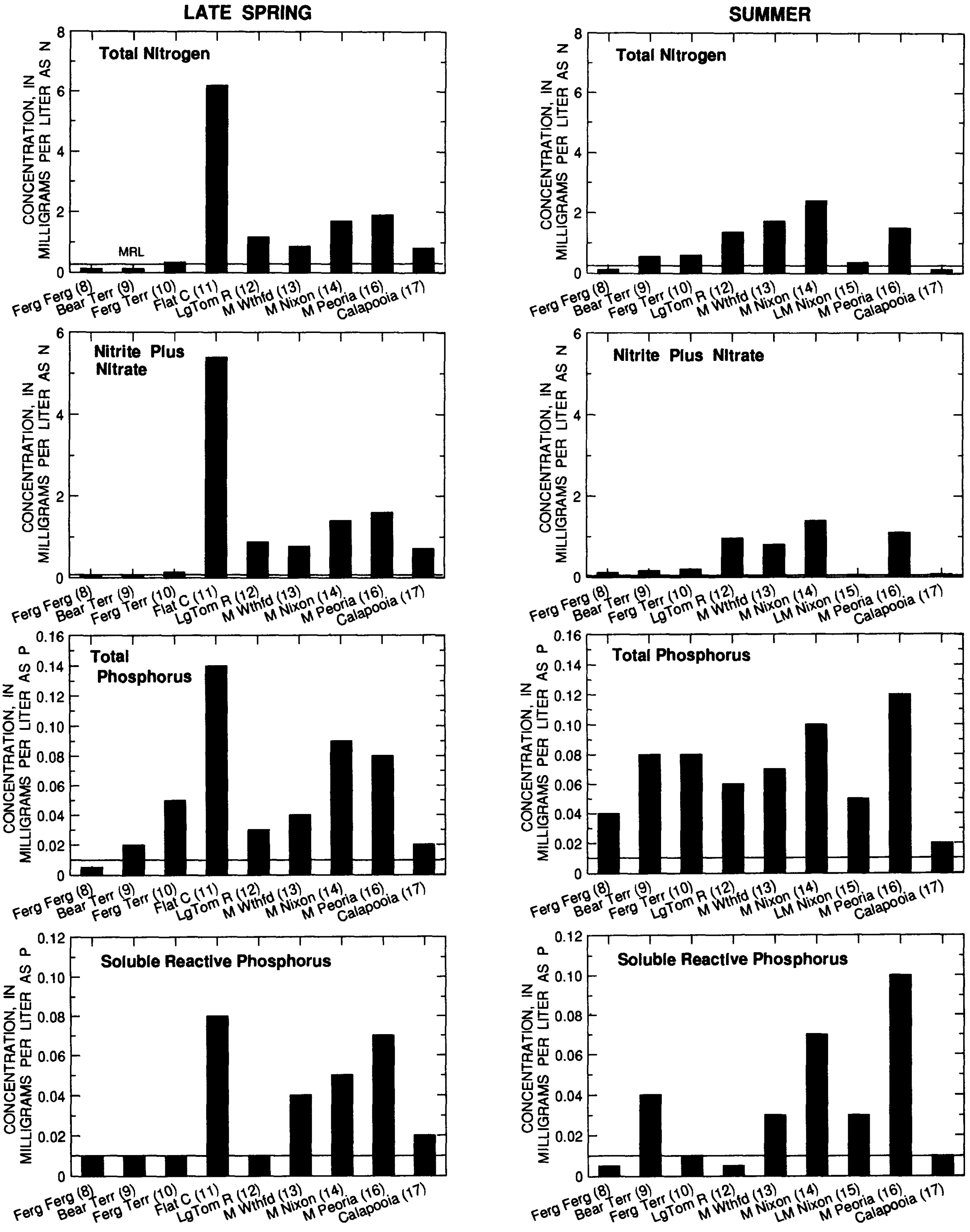

**Figure 20.** Concentrations of total nitrogen, nitrite plus nitrate, total phosphorus, and soluble reactive phosphorus at sites sampled in the southern Willamette Basin during mid-May through early June 1994 (late spring) and July 18–21, 1994 (summer). (Numbers in parenthesis refer to site locations in figure 2 and table 2; censored concentrations are reported at one-half of their minimum reporting level [MRL].)

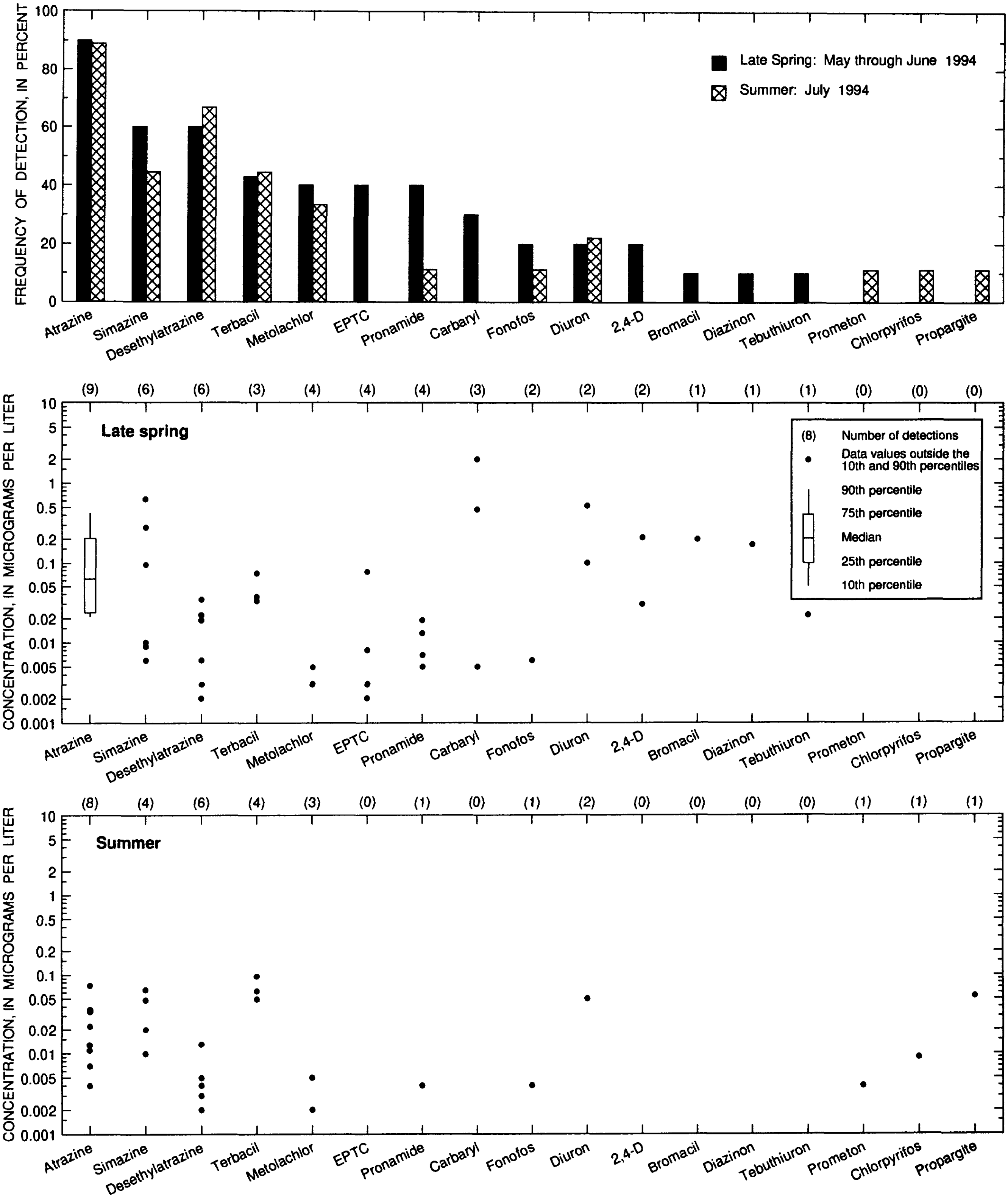

**Figure 21.** Frequencies of detection and concentrations of pesticides and degradation products at sites sampled in the southern Willamette Basin during mid-May through early June 1994 (late spring) and July 18–21, 1994 (summer). (Boxplots were constructed if nine or more data points were available, otherwise individual data points were plotted.)

### Southern Willamette Basin Summer Study

A summer surface-water synoptic study was conducted from July 18–21, 1994, in the Long Tom River, Muddy Creek, and Calapooia River Subbasins to characterize ground-water and irrigation-return flow contributions of nutrients and pesticides to stream-water quality. Instantaneous streamflow at the Calapooia River at Albany site on July 21, 1994 was 113 cubic feet per second, which corresponds to a July daily mean streamflow that is higher than normal for that time of the year, on the basis of data from WYs 1940–81 (Moffatt and others, 1990). Nine sites were sampled in the three subbasins: Four sites were located in the Long Tom River Subbasin; four sites were located in the Muddy Creek Subbasin, and one site was located in the Calapooia River Subbasin (see table 2 for listing of the sites sampled and summary of subbasin land use). Flat Creek at Noraton Road (map reference number 11), which had been sampled during the late-spring study, did not have flowing water in July, so an additional site in the Muddy Creek Subbasin (Little Muddy Creek at Nixon Road; map reference number 15) was sampled in its place.

Two sites in the Muddy Creek Subbasin—Muddy Creek at Nixon Road (59 percent of its drainage area in agriculture; map reference number 14) and Muddy Creek near Peoria (71 percent of its drainage area in agriculture; map reference number 16)—had the largest observed nutrient concentrations during the summer study (fig. 20). Muddy Creek at Nixon Road site had the largest TN (2.4 mg/L) and $NO_3$-N (1.4 mg/L) concentrations, and the Muddy Creek near Peoria site had the largest TP (0.12 mg/L) and SRP (0.10 mg/L) concentrations. These high TN and $NO_3$-N concentrations were only about one-third and one-fourth, respectively, of the largest concentrations observed during the spring study; however, the largest TP and SRP concentrations observed in both studies were comparable, when analytical precision of the methods are considered. Overall, nutrient concentrations at the predominantly forested Ferguson Creek at Ferguson Road site ranked near the lowest for all nutrient samples collected during the southern summer study—TN and SRP concentrations were below their MRLs, TP concentration was second lowest at 0.04 µg/L, and $NO_3$-N concentration was third lowest at 0.11 µg/L.

Eleven pesticides—atrazine, chlorpyrifos, desethylatrazine, diuron, fonofos, metolachlor, prometon, pronamide, propargite, simazine, and terbacil—were detected during the summer study, in concentrations ranging from 0.002 to 0.096 µg/L (fig. 21). Six of the pesticides detected during the spring study (carbaryl, bromacil, 2,4-D, diazinon, EPTC, and tebuthiuron) were not detected during the summer study, whereas three additional pesticides were detected (chlorpyrifos, prometon, and propargite; fig. 21). About 89 and 67 percent of the samples had detections for atrazine and desethylatrazine, respectively; 44 percent of the samples had detections for simazine and terbacil; and 33 percent of the samples had detections for metolachlor. These same five pesticides (atrazine, desethylatrazine, metolachlor, simazine, and terbacil) also were detected during the late-spring study.

The Long Tom River at Bundy Bridge (map reference number 12) and the Muddy Creek near Peoria sites had the greatest number of different pesticides observed with seven detections. None of the 11 pesticides were detected at the forested site, Ferguson Creek at Ferguson Road (map reference number 8). The largest concentrations for the 11 pesticides were detected at only 3 sites (fig. 22): The Long Tom River at Bundy Bridge site had the largest concentrations of atrazine (0.074 µg/L), chlorpyrifos (0.009 µg/L), metolachlor (0.005 µg/L), and prometon (0.004 µg/L); the Muddy Creek at Weatherford Lane site (map reference number 13) had the largest concentrations of fonofos (0.004 µg/L) and propargite (0.054 µg/L); and the Muddy Creek near Peoria site had the largest concentrations of diuron (0.05 µg/L), desethylatrazine (0.013 µg/L), pronamide (0.004 µg/L), simazine (0.065 µg/L), and terbacil (0.096 µg/L). The Long Tom River at Bundy Bridge and the Muddy Creek near Peoria sites had a relatively large number of elevated concentrations during both studies.

The largest concentrations for eight pesticides detected in the late spring and summer studies (atrazine, simazine, desethylatrazine, terbacil, metolachlor, pronamide, fonofos, and diuron) were generally lower during the summer rather than during the late-spring study (fig. 21). Comparison of pesticide results for atrazine, simazine, desethylatrazine, and metolachlor by site are shown in fig. 22. The largest terbacil concentration observed during the summer study ranked in the upper 90th percentile of all Willamette Basin sam-

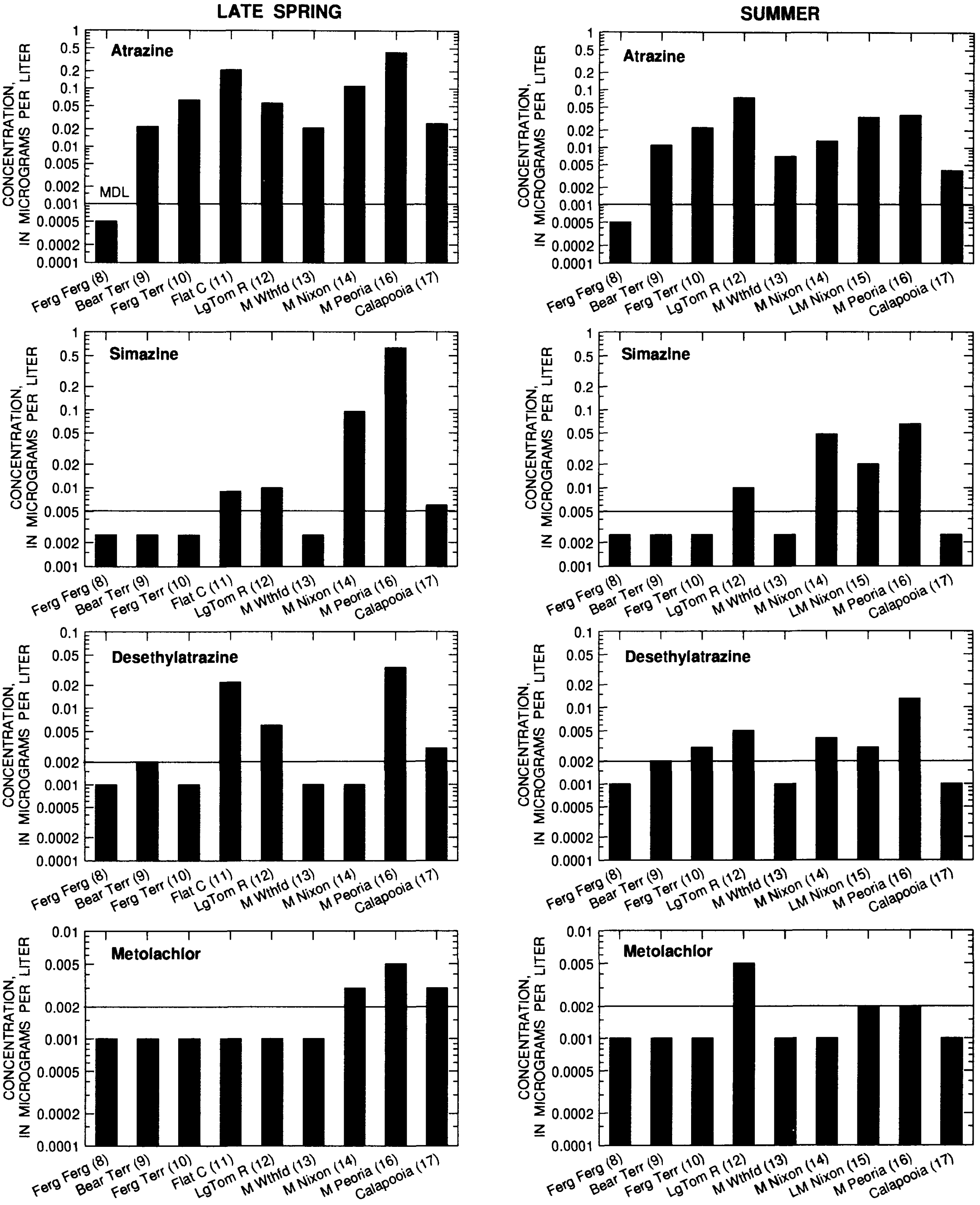

**Figure 22.** Concentrations of atrazine, simazine, desethylatrazine, and metolachlor at sites sampled in the southern Willamette Basin during mid-May through early June (late spring) 1994 and July 18–21, 1994 (summer). (Numbers in parenthesis refer to site locations described in figure 2 and table 2; censored concentrations are reported at one-half of their method detection limits.)

ple detections, and the detected propargite concentration (Muddy Creek at Weatherford Road, 0.054 µg/L) was the largest recorded value for all samples collected in the basin.

### Northern and Southern Willamette Basin Comparison Study

From May through November 1994, water samples were collected near the outflow of three predominantly agricultural subbasins in the southern Willamette Basin (Long Tom River at Bundy Bridge [four samples], Muddy Creek near Peoria [eight samples], and Calapooia River at Albany [four samples]). These nutrient and pesticide concentrations in the southern basin were compared with those in the northern basin, represented by three predominantly agricultural subbasins (Pudding River at Aurora [nine samples]), Champoeg Creek below Mission Creek near Butteville [two samples; Harrison and others, 1995] and Johnson Creek at Palmblad Road near Gresham [six samples; Harrison and others, 1995]).

Instantaneous streamflow for the nine water samples collected at Pudding River at Aurora ranged during this comparison study from about 9 to 3,650 cubic feet per second (median streamflow was 482 cubic feet per second) and covered much of the streamflow variability experienced during the April 1993 to September 1995 sampling period (fig. 23), but did not, however, cover the full range of environmental conditions seen during the 2-1/2 year study period. For example, spring runoff concentrations of nutrients and pesticides typical of conditions immediately following application of fertilizers and pesticides during March and April are not represented in this northern-southern basin comparison.

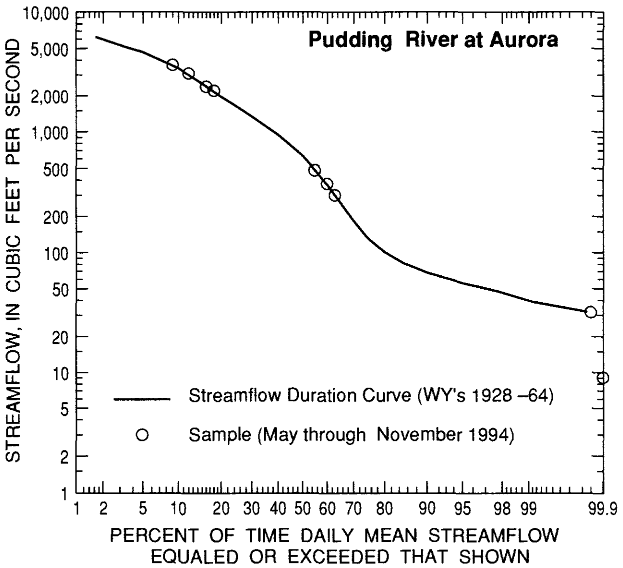

**Figure 23.** Instantaneous streamflow at time of sample collection at Pudding River at Aurora, May through November 1994, compared to the percentage of time that streamflow amount was equaled or exceeded at that site, water years 1928–64.

All samples collected in the northern Willamette Basin had detections for TN, $NO_3$-N, TP, and SRP, whereas not all samples collected in the southern Willamette Basin had nutrient detections (87–100 percent; fig. 24A). Maximum concentra-

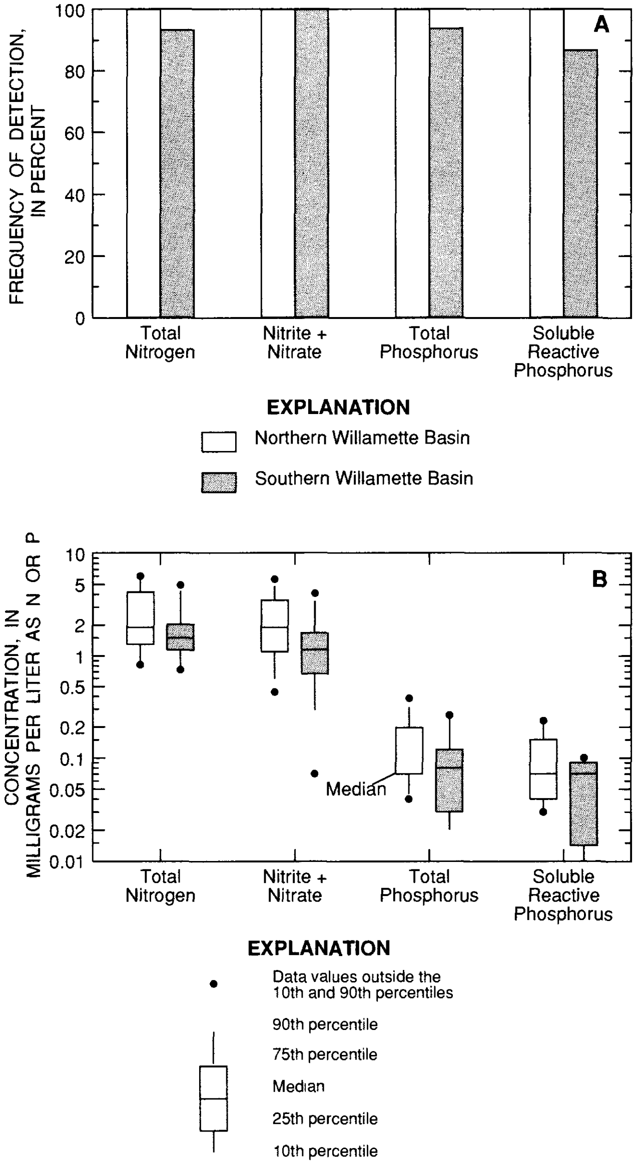

**Figure 24.** (A) Frequencies of detection and (B) statistical distribution of detected concentrations of total nitrogen, nitrite plus nitrate, total phosphorus, and soluble reactive phosphorus for sites sampled in the northern and southern Willamette Basin, May through November 1994.

tions for all four nutrient species were slightly larger in the northern Willamette Basin (fig. 24B), with the largest concentrations for TP (0.38 mg/L) and SRP (0.23 mg/L) ranking in the upper 90th percentile of all sample detections in the Willamette Basin. However, there was sufficient overlap of the nutrient distributions overall to suggest little difference between nutrient concentrations observed in the northern and southern parts of the Willamette Basin during the sampling period.

A total of 34 pesticides was detected in the 6 agricultural subbasins: 32 were detected in the northern Willamette Basin, and 18 were detected in the southern Willamette Basin (fig. 25). Two of the pesticides detected in the southern basin—bromacil (1 detection, 0.20 µg/L) and oxamyl (1 detection, 0.07 µg/L)—were not found in the northern basin. Twenty-four of the 34 pesticides were more frequently detected in the northern Willamette Basin, 7 pesticides (diuron, terbacil, pronamide, metribuzin, trichlopyr, bromacil, and oxamyl) were more frequently detected in the southern basin, and three pesticides (atrazine, 2,4-D, and dinoseb) were detected equally in both parts of the basin.

Detections of atrazine, simazine, desethylatrazine, and metolachlor ranged from 80 to 100 percent of the northern and southern Willamette Basin samples, and detections for diuron and terbacil ranged from 50 to 75 percent of the samples (fig. 25). Pesticides detected only in the northern Willamette Basin included napropamide, diazinon, DCPA, trifluralin, carbofuran, *p,p'*-DDE, ethoprop, dieldrin, lindane, tebuthiuron, propachlor, bentazon, oryzalin, dichlobenil, pebulate, and pendimethalin. Similar frequencies of detection were noted previously by Anderson and others (1996) for spring and fall samples collected in the northern and southern agricultural areas of the Willamette Basin during calendar year 1994. Differences between the northern and southern basin in the number of pesticides detected and pesticide concentrations may result from differences in agricultural practices between the northern part of the

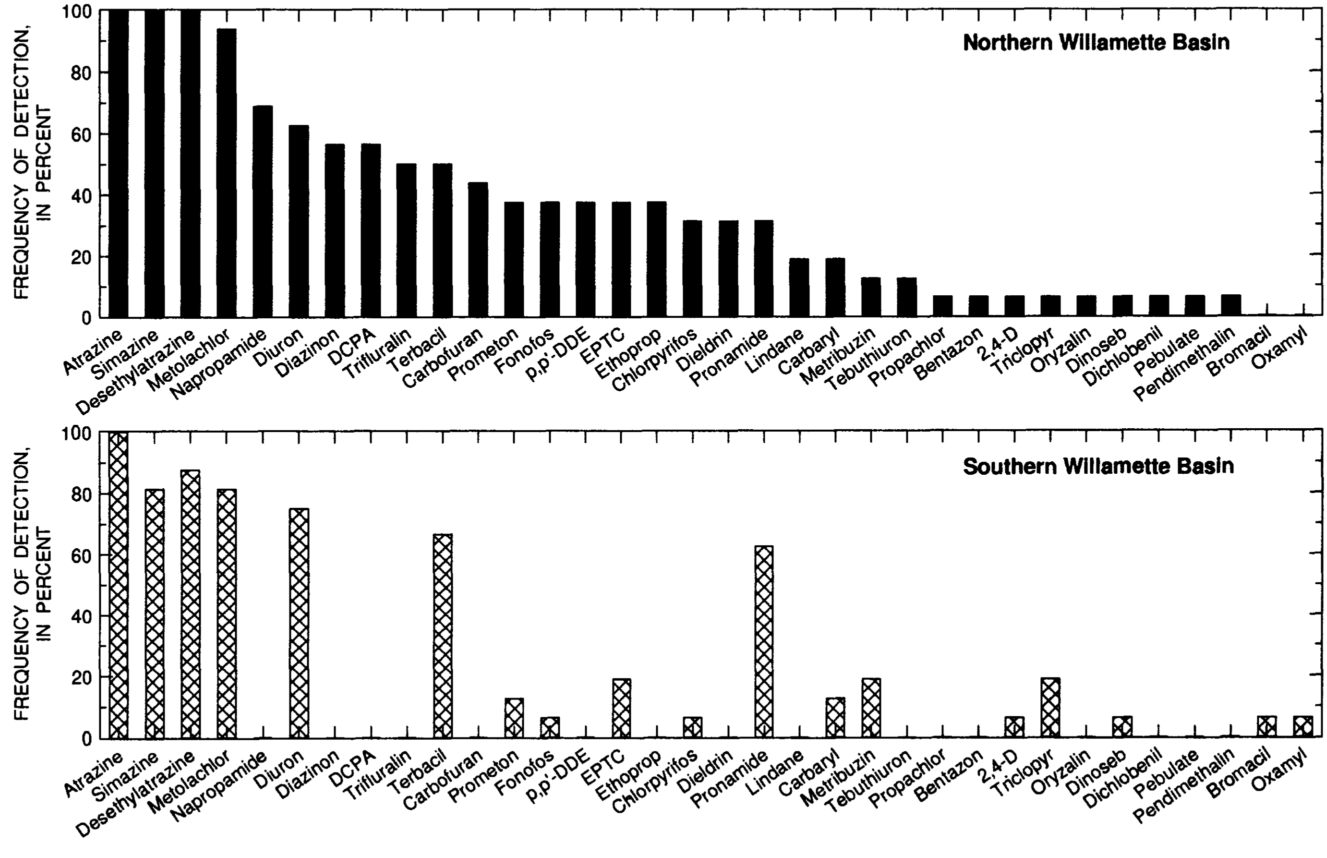

**Figure 25.** Frequencies of detection of pesticides and degradation products in the northern and southern Willamette Basin, May through November 1994.

basin, where more row crop fields, orchards, vineyards, and nurseries are located, and the southern parts of the basin, where more grains, hays and silages, and grass and legume seeds are produced.

Maximum pesticide concentrations for 21 of the pesticides were greatest in the northern agricultural river subbasins, 12 pesticides had their greatest concentrations in the southern agricultural river subbasins, and 1 pesticide was detected at the same concentration in both areas (fig. 26). Maximum concentrations for metolachlor (3.3 µg/L), *p,p'*-DDE (0.004 µg/L), dieldrin (0.021 µg/L), dichlobenil (0.42 µg/L), and pebulate (0.007 µg/L) in the northern agricultural river subbasins, and terbacil (0.11 µg/L), pronamide (0.065 µg/L), carbaryl (2.0 µg/L), trichlopyr (0.72 µg/L), bromacil (0.20 µg/L), and oxamyl (0.07 µg/L) in the southern agricultural river subbasins ranked as the largest recorded values for all detections in the Willamette Basin.

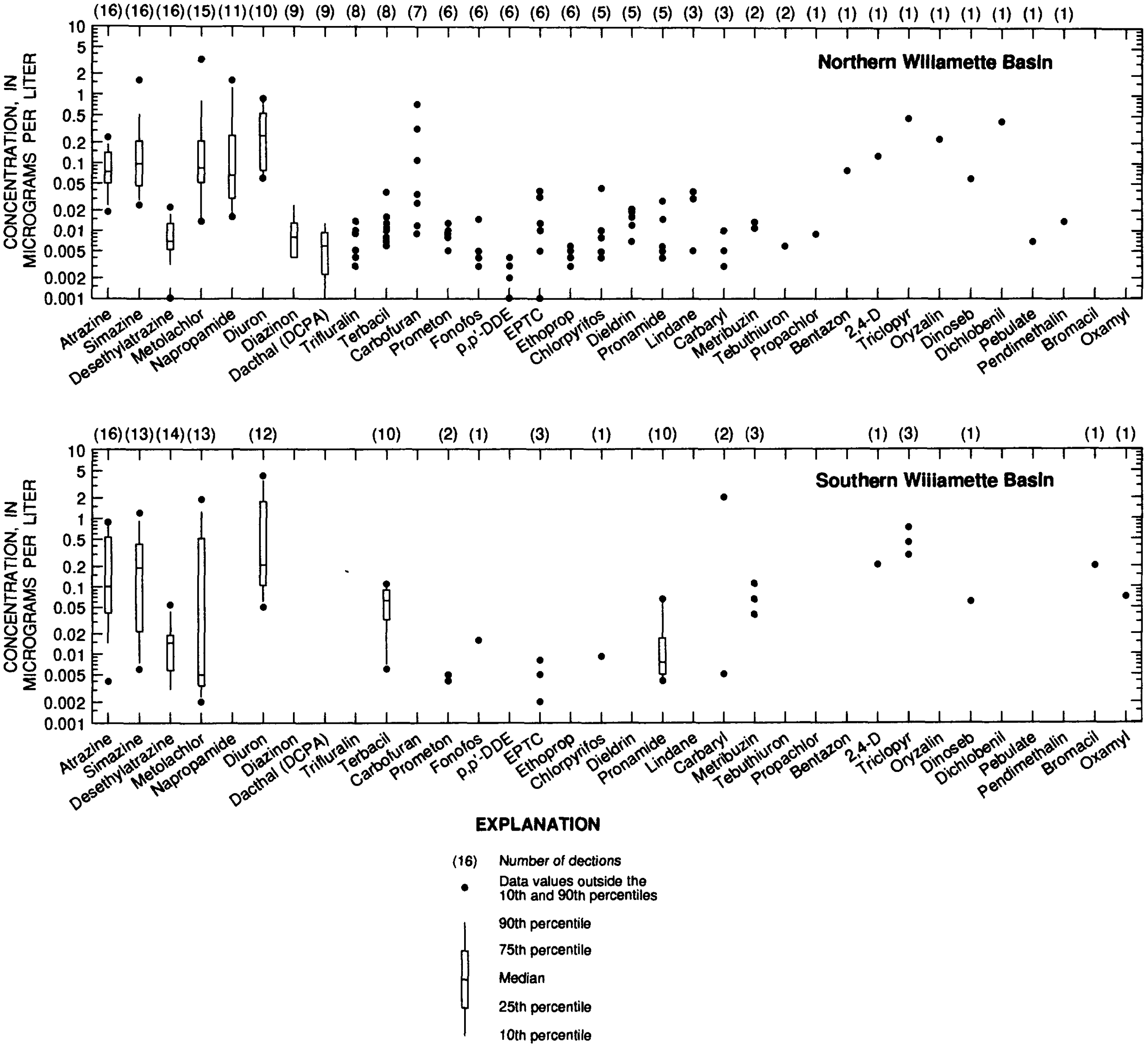

**Figure 26.** Statistical distributions of concentrations of pesticides and degradation products in the northern and southern Willamette Basin, May through November 1994. (Boxplots were constructed if nine or more data points were available, otherwise individual data points were plotted.)

# SUMMARY

The Willamette Basin, Oregon, was selected for study in 1991 as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. The goals of the NAWQA program are to (1) describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers, (2) describe how water quality is changing over time, and (3) improve our understanding of the primary natural and human factors that affect water-quality conditions.

The objective of the Willamette Basin study was to increase the understanding of the distribution and amounts of nutrients and pesticides in runoff, primarily from agricultural areas within the basin. To accomplish this objective, data from fixed-station and synoptic-station networks were collected and analyzed. Sampling at the seven fixed-station sites during the 2-1/2 years of study was designed to record seasonal water-quality variations resulting from agricultural, urban, and forested land used, and mixtures of these. Sampling at the fixed-station sites was done monthly and during periods when extremes in water quality were expected (spring runoff following application of pesticides and fertilizers, and fall/winter runoff following the heaviest seasonal rains). Shorter duration, synoptic sampling was done at an additional 44 sites within the Willamette Basin, primarily to evaluate spatial water-quality variations in agricultural areas during high- and low-flow hydrologic conditions. Water-quality samples collected at a total of 51 stream sampling sites during April 1993through September 1995 were analyzed primarily for 4 nutrient species and 86 pesticides.

## Nutrients

More than 260 nutrient samples were collected; about 70 percent of these was collected as part of the fixed-station network sampling. Calculated total nitrogen (TN) concentrations and detected nitrite plus nitrate ($NO_3$-N) concentrations in filtered water ranged from 0.25 to 24 mg/L and from 0.054 to 22 mg/L, respectively, with most $NO_3$-N concentrations in the upper 10th percentile (greater than 5.9 mg/L) occurring at sites receiving predominantly agricultural runoff. About 3-1/2 percent of the $NO_3$-N concentrations exceeded the 10 mg/L maximum contaminant level (MCL) established by the U.S. Environmental Protection Agency for drinking water. Total phosphorus (TP) and soluble reactive phosphorus (SRP) detections ranged in concentration from 0.01 to 7.0 mg/L and from 0.01 to 5.8 mg/L, respectively, with most SRP concentrations in the upper 10th percentile (greater than 0.22 mg/L) occurring at sites receiving predominantly agricultural runoff. About 47 percent of the TP concentrations equaled or exceeded the 0.10 mg/L desired limit suggested by Mackenthun (1973) for the prevention of nuisance plant growth in flowing streams.

### Seasonal Variability

The seasonal variability of nutrient concentrations at the fixed-station sites generally was related to surface- and subsurface-water runoff following winter and spring rains. Early November through December storms generally produced the largest surface-water TN and $NO_3$-N concentrations; storms that followed also produced elevated nitrogen concentrations that tended to be smaller in concentration than those measured during the first storm. Seasonal variability of TN mirrored that of $NO_3$-N because $NO_3$-N accounted for a most of the TN concentration. TN and $NO_3$-N concentrations rose 25 to 50 percent at the Pudding River at Aurora site during the summer of each year, possibly because of discharge of nutrients from an upstream sewage treatment plant and the decrease in streamflow. The largest TP concentrations also occurred during the winter high-flow period; however, the largest SRP concentrations did not necessarily occur at the same time as for TP because SRP represented a variable portion of the TP concentration over time. The largest SRP concentrations occurred at two of the agricultural sites (Pudding River at Aurora and Zollner Creek near Mount Angel) during summer low flow, probably as a result of ground-water contributions and, in the case of one site, from the discharge of nutrients from an upstream sewage treatment plant.

### Spatial Variability

Water samples were collected near the outflows of six large, predominantly agricultural

river subbasins in the Willamette Basin during May through November 1994. Three of the subbasins were located in the northern Willamette Basin, and three were located in the southern Willamette Basin. Although maximum concentrations of TN, $NO_3$-N, TP, and SRP were slightly larger at sites in the northern Willamette Basin, sufficient overlap existed in the two concentration distributions to suggest that nutrient concentrations in the northern and southern Willamette Basin were similar.

### Relations to Land Use

Nutrient concentrations appeared to relate to land use, including the percentage of drainage area in forest and in agriculture, and point-source discharge. During the fixed-station sampling, sites on Little Abiqua Creek and Gales Creek, with 96 and 100 percent of their areas in forest, respectively, had among the smallest nutrient concentrations of all fixed-station sites sampled, whereas the fixed-station site on Zollner Creek, with 99 percent of its area in agriculture, had the largest nutrient concentrations of all fixed-station sites sampled. During the synoptic sampling, forested sites at Molalla River at Wilhoit, North Fork Silver Creek at Van Handle Road, and Ferguson Creek at Ferguson Road (all 100 percent forested) had among the smallest nutrient concentrations of all synoptic sites sampled. The two agricultural Zollner Creek sites, at Boehmer Road and near Mount Angel (100 and 99 percent of their drainage areas in agriculture, respectively), Flat Creek at Noraton Road site (87 percent agricultural), and Muddy Creek near Peoria (71 percent agricultural) had among the largest nutrient concentrations of all sites sampled. Further evidence of the relation between the percentage of drainage area in agriculture and magnitude of the nutrient concentrations also was observed in a nutrient sampling of 20 sites in the Pudding River and Molalla River Subbasins during high flow. Affects of a point-source discharge were seen at the Pudding River at Aurora site, where nutrient concentrations (such as, TN and $NO_3$-N) were observed to rise in excess of 25 to 50 percent in July through early September of each year during summer low flow, when dilution was minimal.

## Pesticides

About 195 samples were collected for filtered-water pesticide analysis during this study; about 60 percent of the samples was collected at four sites in the fixed-station network. Of the 86 pesticides analyzed, 50 pesticides were detected. Forty-three of the 50 pesticides were detected at 1 predominantly agricultural fixed-station site, Zollner Creek near Mount Angel. From 72 to 94 percent of the samples had detections of atrazine, simazine, metolachlor and desethylatrazine; from 54 to 59 percent of the samples had detections of diuron and diazinon; and from 34 to 37 percent of the samples had detections of napropamide, EPTC, DCPA, and chlorpyrifos. Some concentrations of atrazine, azinphos-methyl, carbaryl, carbofuran, chlorpyrifos, *p,p'*-DDE, diazinon, dieldrin, diuron, lindane, and malathion exceeded concentrations established for the protection of freshwater aquatic life from chronic toxicity. Exceedances occurred at stream sites receiving agricultural and urban runoff; however, the largest concentrations occurred predominantly at the agricultural sites.

### Seasonal Variability

Concentrations for six of the most frequently detected pesticides—atrazine, simazine, metolachlor, diuron, desethylatrazine, and diazinon—at the four fixed-station sites showed variability related to seasonal streamflows, and possibly also related to the effects of differing land use; however, not all variations in pesticide concentrations could be explained by streamflow and land-use variations. Winter, spring, and summer storms generally produced increases in surface-water pesticide concentrations, with some noted exceptions. Peak pesticide concentrations at the predominantly agricultural site—Zollner Creek near Mount Angel—generally occurred during the spring storms following application of pesticides and fertilizers; some pesticide increases also were observed at the predominantly urban fixed-station site (Fanno Creek at Durham) during the same time, but generally at considerably lower concentrations.

### Spatial Variability

Thirty-four pesticides were detected in samples collected at six of the larger predominantly agricultural river subbasins in the northern and southern Willamette Basin from May through November 1994. Thirty-two pesticides were detected in the northern Willamette Basin, whereas 18 pesticides were detected in the southern Willamette Basin. More pesticides were detected in the northern Willamette Basin and at larger concentrations; however, some pesticide were detected in the southern Willamette Basin at larger concentrations. Differences in the number of pesticides detected and pesticide concentrations between the northern and southern Willamette Basin may result from differences in agricultural practices, where more row crop fields, orchards, vineyards, and nurseries are located in the north, and where more grains, hays and silages, and grass and legume seeds are produced in the south.

### Relations to Land Use

Frequencies of pesticide detections and pesticide concentrations appeared to be related to percentage of drainage area in forest, urban, or agriculture land use. In 11 samples collected at 6 predominantly forested sites, only 2 detections of atrazine and 1 detection of its degradation product, desethylatrazine, were observed at very low concentrations. In contrast, at a predominantly agricultural site Zollner Creek near Mount Angel, 43 pesticides were detected, and many of these were detected at concentrations larger than at any other sites sampled in the Willamette Basin. A relation between the percentage of drainage area in agriculture and magnitude of pesticide concentrations also was observed for atrazine and simazine concentrations in samples collected at 20 sites in the Pudding River and Molalla River Subbasins during a high-flow sampling in April 1993. An urban fixed-station site, Fanno Creek at Durham (92 percent of the drainage area urbanized), had 23 different pesticides detections, three of which—prometon, tebuthiuron, and dichlobenil—were more frequently detected there than at the Zollner Creek near Mount Angel, an agricultural site.

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# APPENDIXES

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# APPENDIX 1. METHOD DETECTION LIMITS FOR FILTERED PESTICIDES AND DEGRADATION PRODUCTS ANALYZED IN SURFACE-WATER SAMPLES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SCHEDULE 2010

[USEPA STORET number, U.S. Environmental Protection Agency's Storage and Retrieval System number; MDL, method detection limit; µg/L, micrograms per liter; P, degradation product; H, herbicide; I, Insecticide; DCPA, dimethyltetrachloroterephthalate; DDE, dichlorodiphenyldichloroethylene; EPTC, S-ethyl dipropylthiocarbamate; HCH, hexachlorocyclohexane; "filtered water" is an operational definition referring to the chemical analysis of that portion of a water-suspended sediment sample that passes through a nominal 0.7 micrometer filter (Fuhrer and others, 1995)]

| Pesticide or degradation product | Type | USEPA STORET number | MDL (µg/L) |
|---|---|---|---|
| Acetochlor | H | 49260 | 0.002 |
| Alachlor | H | 46342 | .002 |
| Atrazine | H | 39632 | .001 |
| Azinphos-methyl | I | 82686 | .001 |
| Benfluralin | H | 82673 | .002 |
| Butylate | H | 04028 | .002 |
| Carbaryl | I | 82680 | .003 |
| Carbofuran | I | 82674 | .003 |
| Chlorpyrifos | I | 38933 | .004 |
| Cyanazine | H | 04041 | .004 |
| DCPA | H | 82682 | .002 |
| *p,p'*-DDE | P | 34653 | .006 |
| Desethylatrazine | P | 04040 | .002 |
| Diazinon | I | 39572 | .002 |
| Dieldrin | I | 39381 | .001 |
| 2,6-Diethylaniline | P | 82660 | .003 |
| Dimethoate | I | 82662 | .004 |
| Disulfoton | I | 82677 | .017 |
| EPTC | H | 82668 | .002 |
| Ethalfluralin | H | 82663 | .004 |
| Ethoprop | I | 82672 | .003 |
| Fonofos | I | 04095 | .003 |
| *alpha*-HCH | I | 34253 | .002 |
| *gamma*-HCH (Lindane) | I | 39341 | .004 |
| Linuron | H | 82666 | .002 |
| Malathion | I | 39532 | .005 |
| Methyl Parathion | I | 82667 | .006 |
| Metolachlor | H | 39415 | .002 |
| Metribuzin | H | 82630 | .004 |
| Molinate | H | 82671 | .004 |
| Napropamide | H | 82684 | .003 |
| Parathion | I | 39542 | .004 |
| Pebulate | H | 82669 | .004 |
| Pendimethalin | H | 82683 | .004 |
| *cis*-Permethrin | I | 82687 | .005 |
| Phorate | I | 82664 | .002 |
| Prometon | H | 04037 | .018 |
| Pronamide | H | 82676 | .003 |
| Propachlor | H | 04024 | .007 |
| Propanil | H | 82679 | .004 |
| Propargite | I | 82685 | .013 |
| Simazine | H | 04035 | .005 |
| Tebuthiuron | H | 82670 | .010 |
| Terbacil | H | 82665 | .007 |
| Terbufos | I | 82675 | .013 |
| Thiobencarb | H | 82681 | .002 |
| Triallate | H | 82678 | .001 |
| Trifluralin | H | 82661 | .002 |
| Surrogate recoveries | | | Percent |
| Diazinon-$d_{10}$ | | 91063 | .100 |
| Terbuthylazine | | 91064 | .100 |
| *alpha*-HCH-$d_6$ | | 91065 | .100 |

## APPENDIX 2. METHOD DETECTION LIMITS FOR FILTERED PESTICIDES AND DEGRADATION PRODUCTS ANALYZED IN SURFACE-WATER SAMPLES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY/PHOTODIODE-ARRAY DETECTION FOR SCHEDULE 2051

[USEPA STORET number, U.S. Environmental Protection Agency's Storage and Retrieval System number; MDL, method detection limit; µg/L, micrograms per liter; P, degradation product; H, herbicide; I, Insecticide; 2,4-D, (2,4-dichlorophenoxy)acetic acid; 2,4-DB, 4-(2,4-dichlorophenoxy)butyric acid; DNOC, 4,6-Dinitro-o-cresol; MCPA, (4-chloro-2-methylphenoxy) acetic acid; MCPB, 4-(4-chloro-o-tolyloxy)butyric acid; DCPA, dimethyltetrachloroterephthalate; 2,4,5-T, (2,4,5-trichlorophenoxy)acetic acid; "filtered water" is an operational definition referring to the chemical analysis of that portion of a water-suspended sediment sample that passes through a nominal 0.7 micrometer filter (Fuhrer and others, 1995)]

| Pesticide or degradation product | Type | USEPA STORET number | MDL (µg/L) |
|---|---|---|---|
| Acifluorfen | H | 49315 | 0.035 |
| Aldicarb | I | 49312 | .016 |
| Aldicarb sulfone | P | 49313 | .016 |
| Aldicarb sulfoxide | P | 49314 | .021 |
| Bentazon | H | 38711 | .014 |
| Bromacil | H | 04029 | .035 |
| Bromoxynil | H | 49311 | .035 |
| Carbaryl | I | 49310 | .008 |
| Carbofuran | I | 49309 | .028 |
| 3-Hydroxy-carbofuran | P | 49308 | .014 |
| Chloramben | H | 49307 | .011 |
| Chlorothalonil | I | 49306 | .035 |
| Clopyralid | H | 49305 | .050 |
| 2,4-D | H | 39732 | .035 |
| 2,4-DB | H | 38746 | .035 |
| Dicamba | H | 38442 | .035 |
| Dichlobenil | H | 49303 | .020 |
| Dichlorprop | H | 49302 | .032 |
| Dinoseb | H | 49301 | .35 |
| Diuron | H | 49300 | .020 |
| DNOC | H | 49299 | .035 |
| Esfenvalerate | I | 49298 | .019 |
| Fenuron | H | 49297 | .013 |
| Fluometuron | H | 38811 | .035 |
| Linuron | H | 38478 | .018 |
| MCPA | H | 38482 | .050 |
| MCPB | H | 38487 | .035 |
| Methiocarb | I | 38501 | .026 |
| Methomyl | I | 49296 | .017 |
| Monoacid-DCPA | P | 49304 | .017 |
| 1-Naphthol | P | 49295 | .007 |
| Neburon | H | 49294 | .015 |
| Norflurazon | H | 49293 | .024 |
| Oryzalin | H | 49292 | .019 |
| Oxamyl | I | 38866 | .018 |
| Picloram | H | 49291 | .050 |
| Propham | H | 49236 | .035 |
| Propoxur | I | 38538 | .035 |
| Silvex | H | 39762 | .021 |
| 2,4,5-T | H | 39742 | .035 |
| Triclopyr | H | 49235 | .050 |

## APPENDIX 3. MINIMUM REPORTING LEVELS FOR NUTRIENTS ANALYZED IN SURFACE-WATER SAMPLES FOR SCHEDULE 2702

[USEPA STORET number, U.S. Environmental Protection Agency's Storage and Retrieval System number; mg/L, milligrams per liter; MRL, minimum reporting level; Kjeldahl nitrogen as N, sum of ammonia plus organic nitrogen; N, nitrogen; P, phosphorus; "filtered water" is an operational definition referring to the chemical analysis of that portion of a water-suspended sediment sample that passes through a nominal 0.45 micrometer filter (Fuhrer and others, 1995)]

| Compound | USEPA STORET number | MRL (mg/L) |
|---|---|---|
| Nitrogen, ammonia, filtered as N | 00608 | 0.01 |
| Nitrogen, nitrite, filtered as N | 00613 | .01 |
| Kjeldahl nitrogen, filtered as N | 00623 | .20 |
| Kjeldahl nitrogen, total as N | 00625 | .20 |
| Nitrite plus nitrate, filtered as N | 00631 | .05 |
| Phosphorus, total as P | 00665 | .01 |
| Phosphorus, filtered as P | 00666 | .01 |
| Soluble reactive phosphorus as P | 00671 | .01 |

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