

# Distribution of Dissolved Pesticides and Other Water Quality Constituents in Small Streams, and their Relation to Land Use, in the Willamette River Basin, Oregon

U.S. Department of the Interior  
U.S. Geological Survey  
Water-Resources Investigations Report 97-4268



Prepared in cooperation with the  
Oregon Department of Environmental Quality and  
Oregon Association of Clean Water Agencies

**Cover photographs:**

**Upper left**—Filbert orchard near Mount Angel, Oregon, during spring, 1993.

**Upper right**—Irrigated cornfield near Albany, Oregon, during summer, 1994.

**Center left**—Road near Amity, Oregon, during spring 1996. The shoulder of the road has been treated with herbicide to prevent weed growth.

**Center right**—Little Pudding River near Brooks, Oregon, during spring, 1993.

**Lower left**—Fields of oats and wheat near Junction City, Oregon, during summer, 1994.

(Photographs by Dennis A. Wentz, U.S. Geological Survey.)

# Distribution of Dissolved Pesticides and Other Water Quality Constituents in Small Streams, and their Relation to Land Use, in the Willamette River Basin, Oregon, 1996

By CHAUNCEY W. ANDERSON, TAMARA M. WOOD, and  
JENNIFER L. MORACE

U.S. Department of the Interior  
U.S. Geological Survey  
Water-Resources Investigations Report 97-4268

Prepared in cooperation with the  
Oregon Department of Environmental Quality and  
Oregon Association of Clean Water Agencies



Portland, Oregon  
1997

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

Mark Schaefer, Acting Director

The use of firm, trade, and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

---

For additional information write to:

District Chief  
U.S. Geological Survey  
10615 SE Cherry Blossom Drive  
Portland, Oregon 97216  
E-mail: [info-or@usgs.gov](mailto:info-or@usgs.gov)

Copies of this report can be purchased from:

U.S. Geological Survey  
Information Services  
Box 25286  
Federal Center  
Denver, CO 80225

# CONTENTS

Abstract .....	1
Introduction .....	3
Study Background .....	3
Purpose and Scope.....	6
Methods.....	7
Streamflow .....	7
Sample Collection and Laboratory Analysis .....	7
Pesticides and Conventional Constituents .....	7
Immunoassay .....	12
Laboratory Analysis .....	12
Data Analysis.....	13
Quality Assurance .....	13
Statistical Methods .....	16
Site Selection .....	17
Crop Type and Pesticide Use Determination .....	17
Agricultural Fields .....	17
Pesticide Application Rates .....	18
Land Use .....	21
Site Selection .....	21
Agricultural Crop Surveys .....	22
Pesticide Applications .....	25
General water quality findings.....	30
Water Quality Criteria and Standards, and Toxicological Significance of Detected Pesticides .....	35
Pesticide Detections and Concentrations.....	30
Conventional Constituents .....	38
Pesticides .....	39
Relation of pesticide occurrence to land use.....	40
Pesticide Occurrence Relative to Urban and Agricultural Land Uses.....	44
Pesticide Occurrence Relative to Different Types of Agricultural Land Uses.....	46
Correlations with Estimated Application Rates .....	47
Other Correlations .....	51
Seasonal distribution of pesticides .....	55
Summary .....	58
References Cited .....	63
Appendixes 1. Quality Assurance Data and Figures.....	67
2.Toxicological Reference Data.....	73
3. Data Presentation .....	79

## COMPACT DISK (CD-ROM)

[CD-ROM is in pocket]

## FIGURES

Figure 1. Map Showing Willamette River Basin, Oregon.....	5
Figure 2. Graph showing comparison of immunoassay and gas chromatography/mass spectrometry (GC/MS) results for atrazine and metolachlor concentrations, Willamette Phase III, Oregon, 1996 .....	14
Figure 3. Map showing location of subbasins sampled in the Willamette River Basin, Oregon, during 1996.....	23
Figure 4. Diagram showing examples of agricultural study subbasins with diverse and nondiverse crop types, Willamette River Basin, Oregon, during 1996 .....	26
Figure 5. Graph showing relation between the percentage of the basin devoted to agricultural land use	

and the percentage of the basin planted in grass seed crops for 16 agricultural subbasins, Willamette Basin, Oregon, 1996.....	27
Figure 6. Graph showing concentrations of all compounds detected with 10% or greater frequency in the Willamette Valley during 1996 that had significant differences in concentration between urban and agricultural land uses .....	45
Figure 7. Graph showing concentrations of compounds detected with 10% or greater frequency at 16 agricultural sites in the Willamette Basin during 1996 that had significant differences in concentration between the northern and southern sites .....	46
Figure 8. Graph showing relation between the concentration of four pesticides and their estimated seasonal application to 16 agricultural subbasins in the Willamette River Basin during 1996.....	50
Figure 9. Graph showing comparison of atrazine concentrations with concentrations of metolachlor, bromacil, and pronamide in samples collected from 16 agricultural sites in the Willamette Basin during 1996 .....	53
Figure 10. Graph showing short-term temporal variability of atrazine and metolachlor concentration at Senecal Creek in October 1996 and Lake Creek in November 1996 .....	54
Figure 11. Graphs showing seasonal patterns of pesticide concentrations, unit discharge, and suspended sediment concentrations measured at 16 agricultural sites in the Willamette Valley during 1996 .....	56
Figure 12. Graphs showing concentrations of atrazine and metolachlor measured with enzyme immunoassays at 20 sites in the Willamette Basin in January 1997 .....	57

TABLES

Table 1. Selected reports from Phases I and II of the Willamette River Basin Water Quality Study, Oregon, and related reports from the U.S. Geological Survey, 1992–97 .....	4
table 2. Description of pesticides analyzed during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996.....	9
Table 3. Water quality analyses conducted by U.S. Geological Survey, Oregon Department of Environmental Quality, and Association of Clean Water Agency laboratories during Phase III of the Willamette River Basin Water Quality Study, 1996.....	11
table 4. Method used to estimate chemical applications—example using tall fescue in Marion, Yamhill, Washington and Polk Counties, Oregon, during 1996.....	19
Table 5. Method used to estimate mass of pesticide applications—example using applications of an herbicide (diuron) to different crop types in a hypothetical subbasin in the Willamette River Basin, Oregon, during 1996 .....	20
Table 6. Description and location of sampling sites for Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996.....	22
Table 7. Acreages of each crop or land use type in 16 agricultural subbasins, Willamette River Basin, Oregon, 1996 .....	24
Table 8. Estimated nominal rate of application of herbicides to crops in study subbasins during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996 .....	28
Table 9. Estimated nominal rate of application of insecticides to crops in study subbasins during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996.....	29
Table 10. Total mass of the 20 pesticides included in the study that were estimated to have the highest application quantities in the 16 agricultural study subbasins. Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996.....	30
Table 11. Summary statistics for pesticides detected during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996.....	31

Table 12. Comparison of concentrations of herbicides and insecticides from the Phase III study with concentrations from previous U.S. Geological Survey studies in the Willamette River Basin, Oregon.....	33
Table 13. Summary statistics of immunoassay analyses of atrazine and metolachlor concentrations in samples collected at Phase III sites in Willamette River Basin, Oregon, during 1996.....	36
Table 14. Exceedances of Oregon Department of Environmental Quality standards or criteria for streams sampled during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996.....	37
Table 15. Pesticide detections at each sampling site for Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996.....	42
Table 16. Summed ranks of detections in the upper quartile of pesticide concentrations, by sampling site, for Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996 43	
Table 17. Compounds whose detection or nondetection in Phase III of the Willamette River Basin Water Quality Study did not agree with estimated application in 1996.....	47
Table 18. Correlations of pesticide concentrations, loads, and estimated application rates with several independent variables at agricultural sites for Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996.....	49
Table 19. Correlation statistics for pesticide concentrations, unit discharge, and suspended sediment concentrations at agricultural sites, Willamette River Basin, Oregon, 1996 .....	52

### CONVERSION FACTORS

[SI = International System of units, a modernized metric system of measurement]

*Factors for converting SI metric units to inch/pound units*

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
<b>Length</b>		
micrometer (mm)	0.00003937	inch (in)
meter (m)	3.281	foot (ft)
kilometer (km)	0.621	mile (mi)
<b>Volume</b>		
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart
liter (L)	0.2642	gallon (gal)
<b>Mass</b>		
microgram (µg)	0.0000003527	ounce
milligram (mg)	0.00003527	ounce
gram (g)	0.03527	ounce
kilogram (kg)	2.205	pound (lb)
<b>Area</b>		
square kilometers (km <sup>2</sup> )	0.3861	square miles (mi <sup>2</sup> )
hectares (ha)	2.471	acres (ac)
square kilometers (km <sup>2</sup> )	247.105	acres (ac)
<b>Temperature</b>		
degrees Celsius (°C)	( <sup>1</sup> )	degrees Fahrenheit (°F)
<b>Concentration, in Water</b>		
nanograms per liter (ng/L)	1	parts per trillion (ppt)
micrograms per liter (µg/L)	1	parts per billion (ppb)
milligrams per liter (mg/L)	1	parts per million (ppm)

1. Temperature °F = 1.8 (Temperature °C) + 32

## SYMBOLS AND ABBREVIATIONS USED IN THIS REPORT

303(d)	Section 303(d) of the Clean Water Act
ACWA	Association of Clean Water Agencies
BOD <sub>5</sub>	5-day biochemical oxygen demand
CD-ROM	compact disk—read only memory
DO	dissolved oxygen
<i>E. coli</i>	<i>Escherichia coli</i> bacteria
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
GC/MS	gas chromatography/mass spectroscopy
GCC	1 liter amber glass bottle
GIS	Geographical Information System
HPLC	high pressure liquid chromatography
MDL	method detection limit
mi <sup>2</sup>	square miles
MRL	minimum reporting level
NAWQA	U.S. Geological Survey's National Water Quality Assessment Program
NH <sub>4</sub> <sup>+</sup> -N	ammonia nitrogen
NO <sub>2</sub> <sup>2-</sup> -N	nitrite nitrogen
NO <sub>3</sub> <sup>-</sup> -N	nitrate nitrogen
NWIS	National water information system
NWQL	U.S. Geological Survey's National Water Quality Laboratory
ODEQ	Oregon Department of Environmental Quality
ODL	U.S. Geological Survey's Oregon District Laboratory
ODOT	Oregon Department of Transportation
Phase I	Phase I of the Willamette River Basin Water Quality Study, 1991–1993
Phase II	Phase II of the Willamette River Basin Water Quality Study, 1993–1995
Phase III	Phase III of the Willamette River Basin Water Quality Study, 1995–1997
PO <sub>4</sub> <sup>3-</sup> -P	orthophosphate phosphorus
QC	quality control
QUAL2E-UNCAS	Enhanced Stream Water Quality Model with Uncertainty Capabilities
SMPTOX3	Simplified Method Program—Two Phase Toxics Model with Bed Interactions
STORET	U.S. Environmental Protection Agency's Storage and Retrieval System
TKN	total kjeldahl nitrogen
TP	total phosphorus (as phosphorus)
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UT	Unnamed Tributary
WRTASC	Willamette River Technical Advisory Steering Committee
<	Less than
>	Greater than
%	Percent

## ACKNOWLEDGMENTS

**Project development and financial support**—Members of the Willamette River Basin Technical Advisory Steering Committee; Oregon Association of Clean Water Agencies; Oregon Department of Environmental Quality

**Site Reconnaissance**—Eugene Foster (Oregon Department of Environmental Quality); Gayle Killam (Oregon Environmental Council); Joan Rothlein (Oregon Health Sciences University, Center for Research in Environmental and Occupational Toxicology); Stuart McKenzie and Kenneth Skach (U.S. Geological Survey).

**Data Collection**—Kurt Carpenter, Micelis Doyle, Howard Harrison, Nora Herrera, Mary Janet, Bruce Fisher, Matt Johnston, Antonius Laenen, Karl Lee, Kenneth Skach, John Risley, Dwight Tanner, and Mark Uhrich (U.S. Geological Survey); Brandon Reich (Oregon State University)

**Pesticide Use Estimation**<sup>1</sup>—Thomas Mayer (Asplundh Corp.); Neil Michael (Linn County Department of Transportation); Janet Fults (Oregon Department of Agriculture); David Hannaway, Jeffrey Jenkins, Russell Karow, Jan McNeilan, Daniel McGrath and Jeff Olsen (Oregon State University Extension Service); Jim Green (Oregon State University Department of Horticulture); Jay Pscheidt (Oregon State University Plant Disease Clinic); Bette Coste, Steve Hande, David Humphries, Dennis Joll, and Bill Manning (Oregon Department of Transportation); Chuck Gilbert (Portland and Western Railroad)

**Technical Review**—Eugene Foster (Oregon Department of Environmental Quality); David Buckwalter, Jeffrey Jenkins, and Jennifer Fields (Oregon State University); Members of the Willamette River Basin Technical Advisory Steering Committee; Bernadine Bonn and Frank Rinella (U.S. Geological Survey)

**Editing and Report Publication**—Thelma Parks, Donita Parker, and John Williams (U.S. Geological Survey)

---

1. The findings expressed in this report are those of the authors and U.S. Geological Survey and do not necessarily represent the views of individuals outside the U.S. Geological Survey who contributed to the development of pesticide use estimates.

# Distribution of Dissolved Pesticides and Other Water Quality Constituents in Small Streams, and their Relation to Land Use, in the Willamette River Basin, Oregon, 1996

By Chauncey W. Anderson, Tamara M. Wood, and Jennifer L. Morace

## ABSTRACT

Water quality samples were collected at sites in 16 randomly selected agricultural and 4 urban subbasins as part of Phase III of the Willamette River Basin Water Quality Study in Oregon during 1996. Ninety-five samples were collected and analyzed for suspended sediment, conventional constituents (temperature, dissolved oxygen, pH, specific conductance, nutrients, biochemical oxygen demand, and bacteria) and a suite of 86 dissolved pesticides. The data were collected to characterize the distribution of dissolved pesticide concentrations in small streams (drainage areas 2.6–13 square miles) throughout the basin, to document exceedances of water quality standards and guidelines, and to identify the relative importance of several upstream land use categories (urban, agricultural, percent agricultural land, percent of land in grass seed crops, crop diversity) and seasonality in affecting these distributions.

A total of 36 pesticides (29 herbicides and 7 insecticides) were detected basinwide. The five most frequently detected compounds were the herbicides atrazine (99% of samples), desethylatrazine (93%), simazine (85%), metolachlor (85%), and diuron (73%). Fifteen compounds were detected in 12–35% of samples, and 16 compounds were detected in 1–9% of samples.

Water quality standards or criteria were exceeded more frequently for conventional constituents than for pesticides. State of Oregon water quality standards were exceeded at

all but one site for the indicator bacteria *E. coli*, 3 sites for nitrate, 10 sites for water temperature, 4 sites for dissolved oxygen, and 1 site for pH. Pesticide concentrations, which were usually less than 1 part per billion, exceeded State of Oregon or U.S. Environmental Protection Agency aquatic life toxicity criteria only for chlorpyrifos, in three samples from one site; such criteria have been established for only two other detected pesticides. However, a large number of unusually high concentrations (1–90 parts per billion) were detected, indicating that pesticides in the runoff sampled in these small streams were more highly concentrated than in the larger streams sampled in previous studies. These pulses could have had short term toxicological implications for the affected streams; however, additional toxicological assessment of the detected pesticides was limited because of a lack of available information on the response of aquatic life to the observed pesticide concentrations.

Six pesticides, including atrazine, diuron, and metolachlor, had significantly higher ( $p < 0.08$  for metolachlor,  $p < 0.05$  for the other five) median concentrations at agricultural sites than at urban sites. Five other compounds—carbaryl, diazinon, dichlobenil, prometon, and tebuthiuron—had significantly higher ( $p < 0.05$ ) concentrations at the urban sites than at the agricultural sites. Atrazine, metolachlor, and diuron also had significantly higher median concentrations at south-

ern agricultural sites (dominated by grass seed crops) than northern agricultural sites. Other compounds that had higher median concentrations in the south included 2,4-D and metribuzin, which are both used on grass seed crops, and triclopyr, bromacil, and pronamide.

A cluster analysis of the data grouped sites according to their pesticide detections in a manner that was almost identical to a grouping made solely on the basis of their upstream land use patterns (urban, agricultural, crop diversity, percentage of basin in agricultural production). In this way inferences about pesticide associations with different land uses could be drawn, illustrating the strength of these broad land use categories in determining the types of pesticides that can be expected to occur. Among the associations observed were pesticides that occurred at a group of agricultural sites, but which have primarily noncropland uses such as vegetation control along rights-of-way. Also, the amount of forested land in a basin was negatively associated with pesticide occurrence, suggesting that riparian growth or runoff from forested lands helped reduce pesticide concentrations.

Estimates of pesticide application also were made for the 16 agricultural study basins. Concentrations of pesticides in streams were significantly (albeit weakly) correlated ( $p < 0.05$ ) with estimated use for only a few compounds that are applied to a wide variety of crop types. Because of the large acreages involved, several compounds that are applied to grass seed were better correlated with the fraction of upstream land use in agricultural production or in grass seed crops than with their respective estimated applications. Application estimates for some compounds, including atrazine and metolachlor, were probably low because of uses that are not indicated in current literature.

Significant correlations were also found among certain individual compound concentrations, and between these and concentrations of suspended sediment. Included in both groups were atrazine and metolachlor, suggesting that environmental factors that mobilize atrazine and metolachlor can mobilize other compounds, and that hydrologic conditions are as important as the specific amount and timing of application in determining the transport of many compounds to the streams. The suspended sediment concentration was not, however, significantly correlated with discharge, and concentrations of only one pesticide were correlated with discharge. Even though correlations between discharge and pesticide concentration were poor, the similar seasonal pattern in both variables is evidence that transport to the streams is related to discharge and consequently to the amount of runoff.

Median concentrations of atrazine, metolachlor, diuron, metribuzin, pronamide, and suspended sediment were significantly higher in the late fall than in the summer. Additionally, winter "baseline" sampling for both atrazine and metolachlor confirmed that median concentrations as high as those in the fall or spring were maintained well past any periods of initial flushing, suggesting that a steady supply of atrazine and metolachlor is retained in soils in the study basins.

Two intensive immunoassay studies illustrated variations in pesticide concentration over storm hydrographs. During a large storm with localized flooding, atrazine concentration increased on the rising limb of the hydrograph, started to decrease just prior to peak stage (indicating dilution), and continued to decrease as the water level decreased. Metolachlor concentrations decreased throughout the storm by a factor of two from their concentrations prior to the storm.

The future prospects for successfully correlating the stream loads of certain pesticides with estimates of application rates may be good if current and locally specific rates of application to various crop types can be obtained. Alternatively, atrazine concentration appears to be at least a rough indicator for conditions that move several other compounds, and it was shown that it can be measured relatively cheaply and with good accuracy and precision, with enzyme immunoassays. However, the prevalence of atrazine in stream water throughout the basin precludes its use for prediction of occurrence or concentrations of specific compounds in the absence of other information.

## INTRODUCTION

A series of recent reports produced under the auspices of the Willamette River Basin Water Quality Study, a three phase, multidimensional study, has highlighted a variety of water quality issues in the Willamette River Basin (table 1). The study, which was administered by the Oregon Department of Environmental Quality (ODEQ) through the Willamette River Technical Advisory Steering Committee (WRTASC), focused on many issues during its first two phases, including assessments of habitat, biological communities, point- and nonpoint-source pollution, and modeling of flow and water quality. Overall findings through Phase II were summarized by Tetra Tech, Inc. (1995d) and Leland and others (1997). Additional data and findings in the basin for ground water, nutrients, trace elements and organochlorine compounds in bed sediments and aquatic biota, and nonpoint runoff of pesticides, have been reported by the U.S. Geological Survey's National Water Quality Assessment (NAWQA) program.

Among the issues that have received attention is the nonpoint-source runoff of synthetic organic compounds to rivers and streams, and the role of land use in contributing to this runoff. The presence of these compounds in Willamette River Basin streams has raised concern because:

- Concentrations exceeding aquatic toxicity criteria have been reported (Anderson and others, 1996) at a variety of site types throughout the basin,
- Water from the Willamette River may be increasingly used to meet regional drinking water needs in the future (Water Providers of the Portland Metropolitan Area, 1996),
- Skeletal deformities and external lesions of unknown origin or cause have been reported in resident fish (Markle, 1995), and
- The Willamette River is considered a source of many contaminants to the lower Columbia River (Fuhrer and others, 1996).

This report, from Phase III of the Willamette River Basin Water Quality Study, describes the results of a study to relate pesticide concentrations in small streams to land use and to estimates of pesticide applications in the Willamette River Basin.

## Study Background

The Willamette River Basin (fig. 1) is renowned for containing a highly productive agricultural valley. Economically important crops include, among others, grass seed, wheat and other grains, hops, row crops, berries, fruits, nuts, and nursery plants. The basin is also home to a large percentage of Oregon's population and includes the cities of Portland, Eugene, and Salem, the State's three largest population centers. With increasing growth pressures, much of the basin's agricultural lands are being converted to urban and suburban land uses. Previous reports have described the climate, hydrogeology, and surface hydrology of the basin (Hines and others, 1976; McFarland, 1983; Gonthier, 1985; Bonn and others, 1995).

Previous reports on water quality in streams in the Willamette River Basin have listed detections of a variety of pesticides; although most concentrations have been considered low, they have sometimes been higher than U.S. Environmental

**Table 1.** Selected reports from Phases I and II of the Willamette River Basin Water Quality Study, Oregon, and related reports from the U.S. Geological Survey, 1992–97 [WRTASC, Willamette River Technical Advisory Steering Committee; USGS, U.S. Geological Survey; NAWQA, USGS National Assessment of Water Quality Program; OSU, Oregon State University]

<b>Study Focus</b>			
<b>Topic</b>	<b>Area in Willamette River Basin</b>	<b>Reference</b>	<b>Sponsoring organization</b>
<b>Physical and ecological Investigations</b>			
Physical habitat	Main stem	Tetra Tech, Inc., 1995a	WRTASC
Stream velocity and dye tracer study	Main stem and tributaries	Lee, 1995	WRTASC, USGS
Aquatic communities and biological indices	Main stem	Tetra Tech, Inc., 1995b	WRTASC
Bacteria	Main stem	Tetra Tech, Inc., 1993a	WRTASC
Periphyton algal dynamics	Main stem	Gregory, 1993	WRTASC, OSU
Interactions of periphyton algae, nutrients, and water quality	Main stem, McKenzie River, Coast Fork Willamette	Pogue and Anderson, 1995	WRTASC, USGS
Sediment oxygen demand	Lower main stem	Caldwell and Doyle, 1995	WRTASC, USGS
<b>Point and nonpoint source pollution</b>			
Point source discharges	Main stem and tributaries	Tetra Tech, Inc., 1992	WRTASC
Toxic contaminants	Main stem	Tetra Tech, Inc., 1993b	WRTASC
Nonpoint-source runoff of sediments and nutrients	Main stem and tributaries	Tetra Tech, Inc. and E&S Environmental Chemistry, 1993a	WRTASC
Nutrients (analysis of historical data)	Main stem and tributaries	Bonn and others, 1995	USGS (NAWQA)
Data report for nonpoint toxics studies from Phases I and II	Main stem and tributaries	Harrison and others, 1995	WRTASC, USGS
Interpretation of data from Phases I and II on nonpoint source runoff of toxic constituents in relation to land uses	Main stem and tributaries	Anderson and others, 1996	WRTASC, USGS
Nonpoint-source runoff of toxic constituents in relation to land uses	Fixed stations on main stem and tributaries	Rinella and Janet, in press	USGS (NAWQA)
Trace elements and organochlorine compounds in bed sediment and aquatic biota	Main stem and tributaries	Wentz and others, in press	USGS (NAWQA)
<b>Ground water</b>			
Ground water quality	Basinwide	Hinkle, 1997	USGS (NAWQA)
<b>Modelling</b>			
Toxic contaminants from point sources using SMPTOX3 (steady state)	Main stem	Tetra Tech, Inc., 1993c	WRTASC
Nonpoint-source runoff of sediments and nutrients in relation to land use (steady state)	Tributary Ranking	Tetra Tech, Inc. and E&S Environmental Chemistry, 1993b	WRTASC
Nonpoint-source runoff of sediments and nutrients in relation to land use (nonsteady state)	Pudding River Basin	Tetra Tech, Inc., and E&S Environmental Chemistry, 1995	WRTASC
Flow in relation to precipitation, and basis for water quality modelling (nonsteady state)	Main stem and tributaries	Laenen and Risley, 1997	WRTASC, USGS
Nutrients, algae, dissolved oxygen, pH using QUAL2E-UNCAS (steady state)	Main stem	Tetra Tech, Inc., 1995c	WRTASC

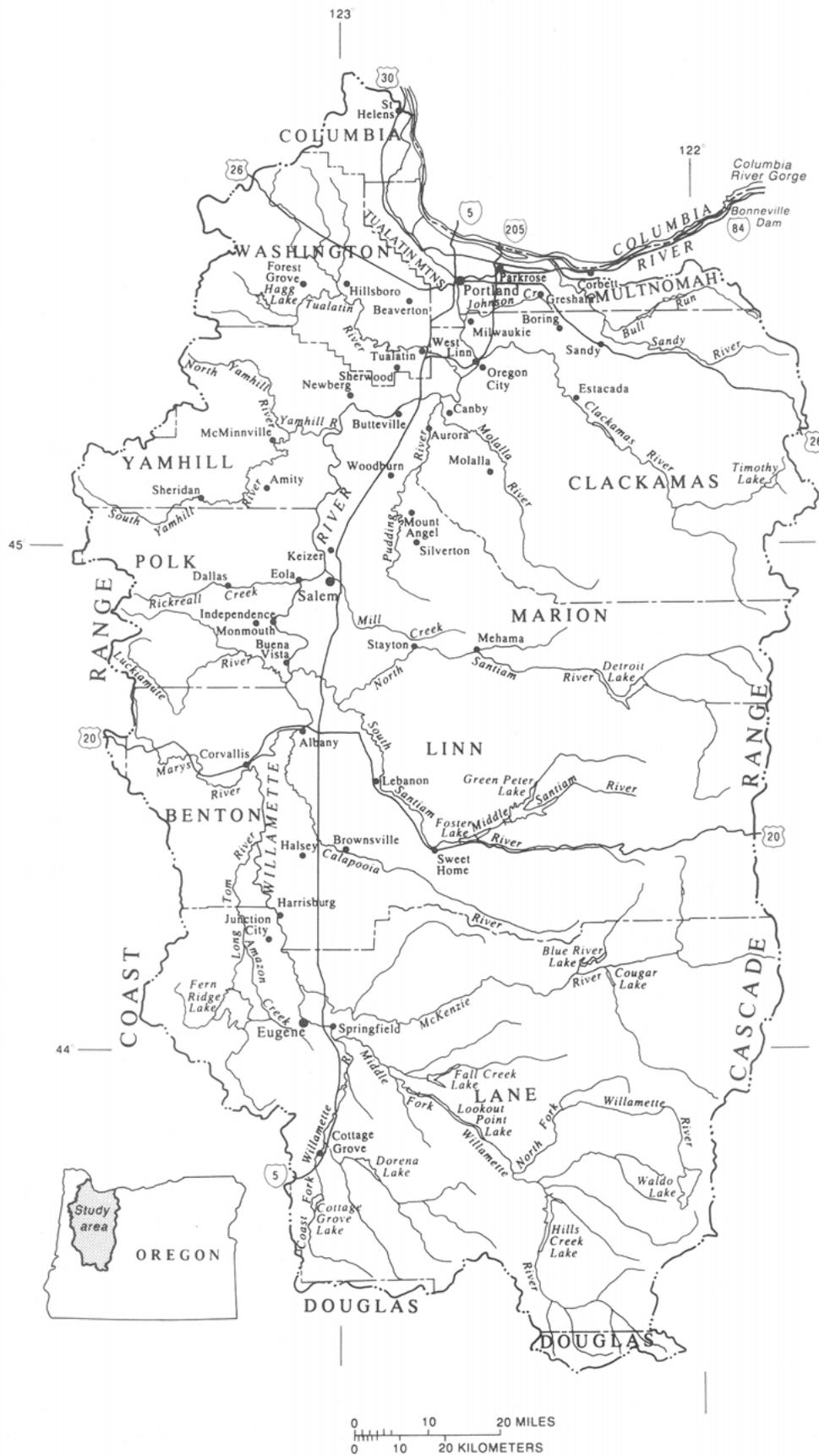


Figure 1. Willamette River Basin, Oregon.

Protection Agency aquatic life toxicity criteria (Anderson and others, 1996; Rinella and Janet, in press). The highest concentrations, and the transport of the greatest amounts of these compounds, have typically been found during periods of high rainfall runoff, particularly in the spring and fall. There have, however, been some high concentrations noted during summer low flow periods. Some compounds have been detected in more than 50% (percent) of the samples taken, at sites representing runoff from diverse upstream land uses. For instance, during Phases I and II of the Willamette River Basin Water Quality Study, Anderson and others (1996) found the herbicides atrazine, simazine, metolachlor, and diuron in 90, 82, 81, and 54% of samples, respectively, collected between 1992 and 1994; distributions were indistinguishable among urban, agricultural, and mixed land uses. Other compounds detected in that study showed distinct signatures of urban or agricultural use: diazinon, prometon, and tebuthiuron were found more frequently and at generally higher concentrations at urban sites than at agricultural sites, whereas carbofuran, ethoprop, fonofos, napropamide, and terbacil were associated primarily with agricultural land uses. A breakdown of agricultural sampling sites by geographic location indicated that a greater number of unique pesticides were detected in the northern than in the southern part of the basin. This finding has been attributed to the higher diversity of crops grown in the northern part of the basin, where row crops, berries, orchards, nurseries, and vineyards are common, than in the southern areas, where grass seed and other seed crops predominate (Anderson and others, 1996).

The Phase III study of pesticide occurrence in small streams was an outgrowth of needs identified from the results of the Phase I and II studies of toxic constituents. The Phase I study of trace elements and organic compounds was a reconnaissance-level investigation of many different compound types in a variety of media (unfiltered and filtered water, suspended and streambed sediments), and was intended to determine the need for additional, more detailed investigations into toxic constituent occurrence in the basin. The Phase II study provided additional spatial coverage for trace elements and for pesticides in filtered water, in stream sizes

ranging from small creeks to large rivers. Although the Phase I and II studies provided an indication of concentrations of pesticides, and those found with the highest frequency in the Willamette River Basin, it remained unclear to what extent the results held true for the streams in agricultural and urban areas throughout the basin.

Results from Phases I and II suggested that a wider variety of compounds at higher concentrations were found in the smaller streams in the basin, particularly those that had relatively intensive (that is, a high percentage of) agricultural or urban upstream land uses. However, correlations between pesticide detections and gross estimates of pesticide applications in the basin as a whole were poor. One reason for the poor correlation with pesticide use was that there was insufficient resolution in the available land use data to estimate pesticide applications upstream of individual sampling sites, and the estimates of the total amounts applied in the basin were not current. In addition, it was unknown whether the most affected sites from Phases I and II were representative of streams with similar land uses or if they were unique because of site specific considerations such as soils, slopes, or contributions from individual practices upstream. Finally, additional data were needed by ODEQ concerning other water quality constituents that were under increased scrutiny as part of the State's requirements under section 303(d) of the Clean Water Act (Oregon Department of Environmental Quality, 1996). These constituents—nutrients, bacteria, five day biochemical oxygen demand (BOD<sub>5</sub>), stream temperature, dissolved oxygen (DO), and pH—are hereafter referred to as “conventional constituents.”

On the basis of these data requirements, and with the guidance and cooperation of the WRTASC, the USGS undertook a study of water quality in small agricultural and urban streams in the Willamette River Basin.

## **Purpose and Scope**

The primary purposes of this report are to (1) describe the distribution of dissolved pesticide concentrations in selected small streams throughout the basin, (2) document exceedances of water

quality guidelines for the targeted pesticides, and (3) identify the relative importance of broad measures of land use and seasonality in determining those concentrations. Secondary objectives are to (4) describe relations, where they exist, between selected pesticide applications and stream concentrations or loads and, (5) for those relations identified, to further describe their dependence on seasonality and on selected site and compound characteristics. A final objective is to further characterize water quality at the chosen sampling sites with respect to conventional constituents.

The sampling sites were on 16 small, randomly selected agricultural streams and on 4 urban streams. The constituents investigated were suspended sediment, conventional constituents, and a suite of 86 pesticides in filtered water that included 18 of the 25 most heavily used organic pesticides in the basin (on the basis of previous use estimates). Small streams were chosen in order to assess whether these were the locations of the higher concentrations of pesticides, and because it was anticipated that these subbasins would have more well defined upstream land uses with which to make comparisons. In this report, the term "pesticide" is used to refer in a general sense to any synthetic organic compound used as an herbicide, insecticide, or fungicide, or to a combination of such compounds, and also at times includes some of their degradation products.

Water quality data collected for this study are provided on a CD-ROM accompanying this report, with a description of those data given both on the CD-ROM and in appendix 3. Included on the CD-ROM are data for several miscellaneous samples that were collected during the course of the study but that were excluded from the final dataset used for data analysis in this report because they were not collected according to the sampling design.

## **METHODS**

### **Streamflow**

Discharge was measured according to standard USGS guidelines as described by Rantz

and others (1982). No sites were gaged. Discharge was measured twice during each of spring and fall and once during summer, when a complete set of samples were collected for analytical chemistry. However, many sites were visited at other times for a rapid collection of samples for immunoassay analysis of triazine (primarily atrazine) or chloroacetamide (primarily metolachlor) herbicides. In order to estimate the relative stage of streams when time constraints prohibited a full discharge measurement, reference points were established at each site from which to consistently measure either the depth of the water or the distance to the water surface. These reference point depths were noted at the time of each discharge measurement and also at any time that immunoassay samples were taken.

### **Sample Collection and Laboratory Analysis**

Samples were collected at each site twice during spring and fall in order to assess stream responses to runoff, and once during summer to assess low-flow conditions. Basinwide samplings during spring and fall were timed to correspond to periods of rainfall runoff, with minimum intervals of approximately 1 week of dry weather required between samplings in each season, to allow pesticide applications to occur and stream discharges to return to steady flows. Rain storms during spring 1996 that produced runoff were well spaced, and samplings for successive storms were conducted in mid-April and mid-May. During fall, basinwide samplings were conducted in mid-October and in mid-November. Constituents collected during basinwide samplings in spring, summer, and fall included pesticides, conventional constituents, and suspended sediment; additional samplings were conducted at individual sites, and basinwide during the winter, using immunoassays as a screening tool to expand the number of samples for atrazine and metolachlor.

### **Pesticides and Conventional Constituents**

Water samples for pesticides and conventional constituents were collected as grab samples from midstream. Samples for suspended sediment were collected using the equal-width-increment method, a depth- and width-integrating technique described

by Edwards and Glysson (1988). Water temperature, DO, pH, and specific conductance were measured in place using Hydrolab™ multiparameter probes that were calibrated in the field according to the manufacturer's suggested methods. All samples were processed at the USGS Oregon District Laboratory prior to shipment to laboratories for analysis.

Grab samples were generally collected at the centroid of flow by wading. When safety considerations prevented wading, samples were collected using weighted bottle holders suspended from a bridge or culvert above the stream. Sampling personnel wore plastic gloves to minimize contamination. At each site, pesticide samples were collected into cleaned and baked (350 degrees Celsius, 12 hours) amber glass (GCC) bottles, nutrients and BOD<sub>5</sub> were collected in polypropylene bottles, and bacteria samples were collected in autoclaved polycarbonate bottles. Additional samples for immunoassays were collected in GCC bottles as needed. GCC and bacteria bottles were not rinsed in the field, whereas bottles for nutrients and BOD<sub>5</sub> were rinsed three times with stream water prior to filling. All sample bottles except those for suspended sediment were stored on ice until they were returned to the Oregon District Laboratory for processing, usually a period of 1 to 6 hours.

At the Oregon District Laboratory, pesticide samples were immediately filtered into clean GCC bottles through 0.7 μm (micrometer) pore-size baked glass-fiber filters and subsequently chilled. Small aliquots of the filtrate were subsampled for analysis of herbicides using immunoassay methods. The remaining filtrate was extracted onto a solid-phase sorbent material (Sandstrom, 1989), which was then shipped within 4 days of collection to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado, for elution and subsequent analysis. Pesticide analysis was performed using gas chromatography/mass spectroscopy (GC/MS—USGS schedule 2010) or high-pressure liquid chromatography (HPLC—USGS schedule 2051). Procedures for filtration, solid-phase extraction, elution, and analysis of pesticides by GC/MS have been detailed by Zaugg and others (1995),

and similar procedures describing sample preparation and analysis by HPLC are described by Werner and others (1996). The suite of 86 pesticides analyzed by the two methods is listed in table 2, and other constituents and their methods are listed in table 3. Units of concentration used in this report are in terms of micrograms per liter (μg/L, equivalent to parts per billion, or ppb) for pesticides, and milligrams per liter (mg/L, equivalent to parts per million, or ppm) for nutrients, BOD<sub>5</sub>, and suspended sediment.

The lower limits of the NWQL's analytical capabilities are generally reported by one of two methods. The minimum reporting level (MRL) is the lowest measured concentration of a constituent that may be reliably reported using a given analytical method (Timme, 1994). For methods such as nutrient analyses (table 3) that use MRLs, concentrations less than the MRL are censored, and the data are reported as being less than the value of the MRL. The method detection limit (MDL) is a statistically derived minimum concentration that can be identified, measured, and reported with a 99% confidence as being greater than zero (Sandstrom, 1989). That is, there is no more than a 1% chance that a concentration greater than the MDL was reported for a sample that actually did not contain the analyte (false positive). Concentrations may be reported that are less than the MDL, but the chance of a false positive detection is greater than 1%. In contrast, the actual concentration in a sample reported as a nondetection has up to a 50% chance of being equal to or greater than the MDL (false negative). Concentrations for compounds listed in table 2 are reported using MDLs.

Pesticide analysis of several stream samples were qualified by NWQL analysts as particularly difficult due to interferences from nontarget compounds, sometimes at relatively high concentrations. As a special analysis, extracts from three of these "dirty" samples were re-analyzed by custom, high-resolution electron-capture negative-ion mass spectrometry in order to investigate the causes of the interferences. Identification of additional compounds observed in these samples

**Table 2.** Description of pesticides analyzed during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996

[Italics indicate trade names. Only principal trade names are listed here; however, many additional trade names or formulations with other compounds exist for some pesticides. The compounds chlorothalonil and esfenvalerate had poor analytical performance and were dropped from subsequent consideration in this report. STORET codes are accounting codes specific for each parameter as listed in the U.S. Environmental Protection Agency's Storage and Retrieval system database. GC/MS, gas chromatography/mass spectroscopy; HPLC, high pressure liquid chromatography; MDL, method detection limit; µg/L, micrograms per liter, or parts per billion; —, not applicable; (E), concentrations are estimates; H, Herbicide, I, Insecticide; F, Fungicide; M, metabolite]

GC/MS (USGS Schedule 2010)				HPLC (USGS Schedule 2051)			
Compound	STORET code	MDL (µg/L)	Use	Compound	STORET code	MDL (µg/L)	Use
<b>Chloroacetamide compounds</b>				<b>Benoic acid compounds</b>			
Acetochlor	49260	0.002	H	Dicamba ( <i>Banvel</i> )	38442	0.035	H
Alachlor ( <i>Lasso</i> )	46342	.002	H	<b>Benzonitrile compounds</b>			
Metolachlor ( <i>Dual, Pennant</i> )	39415	.002	H	Bromoxynil ( <i>Buctril</i> )	49311	.035	H
Napropamide ( <i>Devrinol</i> )	82684	.003	H	Dichlobenil ( <i>Casoron</i> )	49303	(E).02	H
Pronamide ( <i>Kerb</i> )	82676	.003	H	<b>Carbamate compounds</b>			
Propachlor ( <i>Ramrod</i> )	04024	.007	H	Aldicarb ( <i>Temik</i> )	49312	.016	I
Propanil ( <i>Stampede, Prostar</i> )	82679	.004	H	Aldicarb Sulfone	49313	.016	M <sup>a</sup>
<b>Carbamate compounds</b>				Aldicarb Sulfoxide	49314	.021	M <sup>a</sup>
Carbaryl ( <i>Sevin</i> )	82680	(E).003	I	Carbaryl ( <i>Sevin</i> )	49310	.008	I
Carbofuran ( <i>Furadan</i> )	82674	(E).003	I	Carbofuran ( <i>Furadan</i> )	49309	.028	I
<b>Thiocarbamate compounds</b>				3-hydroxy-carbofuran	49308	.014	M <sup>b</sup>
Butylate ( <i>Sutan +</i> )	04028	.002	H	Methiocarb ( <i>Grandslam</i> )	38501	.026	I
EPTC ( <i>Eptam, Eradicane</i> )	82668	.002	H	Methomyl ( <i>Lannate</i> )	49296	.017	I
Molinate ( <i>Ordram</i> )	82671	.004	H	Oxamyl ( <i>Vydate</i> )	38866	.018	I
Pebulate ( <i>Tillam</i> )	82669	.004	H	Propham ( <i>Tuberite</i> )	49236	.035	H
Thiobencarb ( <i>Bolero</i> )	82681	.002	H	Propoxur ( <i>Baygon</i> )	38538	.035	I
Triallate ( <i>Far-go</i> )	82678	.001	H	<b>Chlorophenoxy acid compounds</b>			
<b>Dinitroaniline compounds</b>				Bentazon ( <i>Basagran</i> )	38711	.014	H
Benfluralin ( <i>Balan, Bonalan</i> )	82673	.002	H	2,4-D	39732	.035	H
Ethalfuralin ( <i>Sonolan, Curbit</i> )	82663	.004	H	2,4-DB ( <i>Butyrac</i> )	38746	.035	H
Pendimethalin ( <i>Prowl</i> )	82683	.004	H	Dacthal, mono-acid- ( <i>Dacthal</i> )	49304	.017	H, M <sup>c</sup>
Trifluralin ( <i>Treflan</i> )	82661	.002	H	Dichlorprop (2,4-DP)	49302	.032	H
<b>Miscellaneous compounds</b>				MCPA	38482	.05	H
2,6-Diethylaniline	82660	.003	M <sup>d</sup>	MCPB ( <i>Thistol</i> )	38487	.035	H
Propargite ( <i>Omite</i> )	82685	.013	I	Silvex (2,4,5-TP)	39762	.021	H
<b>Organochlorine compounds</b>				2,4,5-T	39742	.035	H
DCPA ( <i>Dacthal</i> )	82682	.002	H	<b>Dinitroaniline compounds</b>			
Dieldrin	39381	.001	I	Oryzalin ( <i>Surflan</i> )	49292	.019	H
p,p'-DDE	34653	.006	M <sup>e</sup>	<b>Dinitrophenol compounds</b>			
alpha-HCH	34253	.002	I	Dinoseb ( <i>DNBP</i> )	49301	.035	H,I
Lindane ( <i>gamma-HCH</i> )	39341	.004	I	2,6-Dinitro-o-cresol ( <i>DNOC</i> )	49299	(E).035	H,I

**Table 2.** Description of pesticides analyzed during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996—Continued

[Italics indicate trade names. Only principal trade names are listed here; however, many additional trade names or formulations with other compounds exist for some pesticides. The compounds chlorothalonil and esfenvalerate had poor analytical performance and were dropped from subsequent consideration in this report. STORET codes are accounting codes specific for each parameter as listed in the U.S. Environmental Protection Agency's Storage and Retrieval system database. GC/MS, gas chromatography/mass spectroscopy; HPLC, high pressure liquid chromatography; MDL, method detection limit; µg/L, micrograms per liter, or parts per billion; —, not applicable; (E), concentrations are estimates; H, Herbicide, I, Insecticide; F, Fungicide; M, metabolite]

GC/MS (USGS Schedule 2010)				HPLC (USGS Schedule 2051)			
Compound	STORET code	MDL (µg/L)	Use	Compound	STORET code	MDL (µg/L)	Use
<b>Organophosphorus compounds</b>				<b>Diphenyl ether compounds</b>			
Chlorpyrifos ( <i>Dursban, Lorsban</i> )	38933	.004	I	Acifluorfen ( <i>Bazer, Tackle</i> )	49315	.008	H
Diazinon	39572	.002	I	<b>Miscellaneous</b>			
Disulfoton ( <i>Di-syston</i> )	82677	.017	I	1-Naphthol	49295	(E) .007	M <sup>f</sup>
Ethoprop ( <i>Mocap</i> )	82672	.003	I	<b>Phenoxy acid compounds</b>			
Fonofos ( <i>Dyfonate</i> )	04095	.003	I	Chloramben ( <i>Amiben</i> )	49307	.011	H
Malathion ( <i>Cythion</i> )	39532	.005	I	<b>Phenyl urea compounds</b>			
Azinphos-Methyl ( <i>Guthion</i> )	82686	(E) .001	I	Diuron ( <i>Karmex</i> )	49300	.02	H
Methyl Parathion ( <i>Penncap-M</i> )	82667	.006	I	Fenuron ( <i>Dybar</i> )	49297	.013	H
Parathion	39542	.004	I	Fluometuron ( <i>Cotoran</i> )	38811	.035	H
Phorate ( <i>Thimet</i> )	82664	.002	I	Linuron ( <i>Lorox, Linex</i> )	38478	.018	H
Terbufos ( <i>Counter</i> )	82675	.013	I	Neburon ( <i>Neburyl</i> )	49294	.015	H
<b>Permethrin compounds</b>				<b>Phthalimide compounds</b>			
cis-Permethrin	82687	.005	I	Chlorothalonil ( <i>Bravo</i> )	49306	(E) .035	F
<b>Phenyl Urea compounds</b>				<b>Pyrethroid compounds</b>			
Linuron ( <i>Lorox, Linex</i> )	82666	.002	H	Esfenvalerate ( <i>Asana</i> )	49298	(E) .019	I
Tebuthiuron ( <i>Spike</i> )	82670	.01	H	<b>Pyridazinone compounds</b>			
<b>Triazine compounds</b>				Norflurazon ( <i>Evitol</i> )	49293	.024	H
Atrazine ( <i>AAtrex</i> )	39632	.001	H	<b>Pyridine compounds</b>			
Cyanazine ( <i>Bladex</i> )	04041	.004	H	Clopyralid ( <i>Reclaim, Stinger</i> )	49305	.05	H
Desethylatrazine	04040	(E) .002	M <sup>g</sup>	Picloram ( <i>Tordon</i> )	49291	.05	H
Metribuzin ( <i>Lexone, Sencor</i> )	82630	.004	H	<b>Pyridyloxyacetic acid compounds</b>			
Prometon ( <i>Pramitol</i> )	04037	.018	H	Triclopyr ( <i>Garlon, Crossbow</i> )	49235	.05	H
Simazine ( <i>Princep</i> )	04035	.005	H	<b>Uracil compounds</b>			
<b>Uracil compounds</b>				Bromacil ( <i>Bromax</i> )	04029	.035	H
Terbacil ( <i>Sinbar</i> )	82665	(E) .007	H				

<sup>a</sup> Parent compound is aldicarb.

<sup>b</sup> Parent compound is carbofuran.

<sup>c</sup> Parent compound is dacthal.

<sup>d</sup> Parent compound is alachlor.

<sup>e</sup> Parent compound is DDT.

<sup>f</sup> Parent compound is carbaryl.

<sup>g</sup> Parent compound is atrazine.

**Table 3.** Water quality analyses conducted by U.S. Geological Survey, Oregon Department of Environmental Quality, and Association of Clean Water Agency laboratories during Phase III of the Willamette River Basin Water Quality Study, 1996 [See table 2 for method detection limits for pesticide analyses. NWQL, U.S. Geological Survey National Water Quality Laboratory in Arvada, Colorado; ODEQ, Oregon Department of Environmental Quality Laboratory in Portland, Oregon; ACWA, Association of Clean Water Agency laboratories in Portland, Tualatin, and Eugene, Oregon; APHA, American Public Health Association; USEPA, U.S. Environmental Protection Agency; WA; USGS Sediment Laboratory, Vancouver, Washington; SPE, solid-phase extraction, GC/MS, gas chromatography/mass spectroscopy; HPLC, high-performance liquid chromatography; MDL, method detection limit; MRL, minimum reporting level; mg/L, milligrams per liter, or parts per million; MF, membrane filtration; —, not applicable]

Constituent	MDL/ MRL (mg/L)	Laboratory	Laboratory Schedule or Method Number	Reference
<b>Constituents analyzed at the NWQL only</b>				
Pesticides in filtered water analyzed by SPE and GC/MS	Various	NWQL	Schedule 2010	Zaugg and others, 1995
Pesticides in filtered water analyzed by SPE and HPLC	Various	NWQL	Schedule 2051	Werner and others, 1996
<b>Constituents analyzed at both NWQL and ODEQ/ACWA laboratories</b>				
Phosphorus in unfiltered, digested water (total phosphorus, or TP, as P)	0.01	NWQL	I-4607-90	Fishman (1993)
	.01	ODEQ/ACWA	424F	APHA (1995)
Nitrate plus nitrite nitrogen in filtered water (NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-2</sup> , as N)	.05	NWQL	I-2543-85	Fishman and Friedman (1989)
	.02	ODEQ/ACWA	353.2	USEPA (1983)
<b>Constituents analyzed at ODEQ/ACWA laboratories only</b>				
Phosphorus in filtered water (PO <sub>4</sub> <sup>3-</sup> , as P)	.005	ODEQ/ACWA	365.2	USEPA (1983)
Organic plus ammonia nitrogen in unfiltered, digested water (TKN, as N)	.2	ODEQ/ACWA	351.2	USEPA (1983)
Nitrite nitrogen in filtered water (NO <sub>2</sub> <sup>2-</sup> , as N)	.02	ODEQ/ACWA	353.2	USEPA (1983)
Ammonium nitrogen in filtered water (NH <sub>4</sub> <sup>+</sup> , as N)	.02	ODEQ/ACWA	350.1	USEPA (1983)
5-day Biochemical Oxygen Demand (BOD <sub>5</sub> )	.1	ODEQ/ACWA	507	APHA (1995)
<i>Escherichia coli</i> ( <i>E. coli</i> ) (mTEC agar, MF)	—	ODEQ/ACWA	9213 D	APHA (1995)
Fecal coliform (FC agar, MF)	—	ODEQ/ACWA	9222 D	APHA (1995)

(using a GC/MS spectral library) was provided where possible, and inferences about their sources were made with the assistance of NWQL analysts. Results of these special analyses are used in this report to aid in the understanding of pesticides in runoff and their sources.

Subsamples for filtered-water nutrient analysis were passed through 0.45µm cellulose-nitrate filters using “clean” techniques modified from Horowitz and others (1994). Nutrient, BOD<sub>5</sub>, and bacteria samples were chilled unpreserved until they could be delivered to a laboratory for

analysis. Suspended sediment concentrations and the percentage of sediment finer than sand (less than 62 µm sieve diameter) were determined gravimetrically at the USGS sediment laboratory in Vancouver, Washington, as outlined by Guy (1969).

Analytical results from pesticide analyses were stored in the USGS National Water Information System (NWIS). Data in NWIS are periodically transferred to the U.S. Environmental Protection Agency’s Storage and Retrieval System (STORET). Pesticide data in this report

were retrieved from NWIS and were current as of May 1997. Owing to periodic updates to NWIS from the NWQL, data in NWIS are subject to change in the future.

Nutrient analyses included total phosphorus (TP), orthophosphate (termed soluble reactive phosphorus, or SRP, in this report); total ammonia plus organic nitrogen (total Kjeldahl nitrogen), nitrite plus nitrate nitrogen (nitrate), nitrite nitrogen, and ammonium nitrogen ( $\text{NH}_4^+\text{-N}$ ). Bacterial analyses included *Escherichia coli* (*E. coli*) and fecal coliform bacteria. *E. coli* are used as the indicator bacteria by the State of Oregon, whereas fecal coliform bacteria, which include *E. coli* among others, were the indicator bacteria prior to 1996 (Oregon Administrative Rules, Chapter 340, Division 41, 1996). To the extent possible, nutrient, BOD<sub>5</sub>, and bacteria samples were analyzed at laboratories operated by ODEQ and the Oregon Association of Clean Water Agencies (ACWA); however, some nutrient samples from early spring or late fall 1996, for TP and nitrate only, were submitted to the NWQL (table 3).

There are differences in methods used for nutrient analyses between the NWQL and the ODEQ or ACWA laboratories. For samples submitted to the NWQL, dissolved constituents such as  $\text{NH}_4^+\text{-N}$  were analyzed from water that was filtered shortly after collection and stored chilled and unpreserved. In contrast, in the USEPA method used by ODEQ and ACWA for dissolved nutrients (except SRP) samples are acidified upon collection and filtered just prior to analysis. SRP is the only analyte in that method that is filtered immediately after collection. This method difference is expected to affect primarily the dissolved  $\text{NH}_4^+\text{-N}$  concentrations, as hydrolysis of certain adsorbed or organically bound compounds containing  $\text{NH}_4^+\text{-N}$  may occur in the acidified, unfiltered sample; evidence of this phenomenon was observed previously in studies involving nutrient concentrations in the upper Willamette River (Pogue and Anderson, 1995; Tetra Tech, Inc., 1995b). However, the resulting concentration differences are likely to be small compared with concentrations observed in this study, so such potential differences are not considered in this report.

## Immunoassay

Water samples were also collected for the measurement of atrazine and metolachlor concentrations by enzyme-linked immunoabsorbent assays. This method, often referred to as “immunoassay,” uses antibodies selective for the compound being analyzed for, making it possible to isolate the target compound and determine the concentrations at low levels (less than 1 part per billion). Immunoassay samples were collected for two purposes: (1) to assess the agreement between the immunoassay and GC/MS methods and (2) to provide better resolution of temporal variability, especially during storms and midwinter “baseline” conditions. The advantages of the immunoassay method over the more comprehensive GC/MS analysis include the lower cost and the timeliness of the data. However, the immunoassay method is less compound specific than GC/MS.

## Laboratory Analysis

Immunoassays for atrazine and metolachlor were chosen for this study because these compounds were expected to be commonly detected on the basis of previous studies (Anderson and others, 1996) and because reliable test kits were available for them. Immunoassay kits were used according to the manufacturer’s specifications (Ohmicron Environmental Diagnostics, Inc., written commun., March 1996). Analyses were performed in triplicate with the RPA-I RaPID Photometric Analyzer™ (Ohmicron Environmental Diagnostics, Inc., 1992).

Because the tests’ antibody binding sites are also available to compounds with structures similar to the target compound, immunoassays have an inherent amount of cross-reactivity. The atrazine immunoassay responds primarily to atrazine, but may also be affected by other triazine analogues and their degradation by-products (propazine, prometryn, prometon, ametryn, terbutylazine, simazine, desethylatrazine, terbutryn, cyanazine, desisopropylatrazine, and 6-hydroxyatrazine (Hottenstein and others, 1996). Similarly, the metolachlor immunoassay may also respond to other chloroacetanilide analogues (acetochlor, metalaxyl, butachlor, propachlor, and alachlor)

(Lawruck and others, 1993). These cross-reactivities are expected to have a larger effect at lower concentrations, when there are fewer binding sites occupied by the target compound and therefore more sites left open for structurally related compounds to react (E. Mike Thurman, U.S. Geological Survey, oral commun., April 1997). For this study, however, cross-reactivities did not appear to be a large problem (see “Data Analysis” section), and concentrations were not corrected for the cross-reactivities.

#### Data Analysis

MDLs for the immunoassay samples were established with a procedure similar to that used by the NWQL for the GC/MS analyses (Zaugg and others, 1995). The resulting MDLs used to censor the data set were 0.028 µg/L for atrazine and 0.06 µg/L for metolachlor. Analytical error for both atrazine and metolachlor was greater at lower concentrations. Coefficients of variation (cv's) for atrazine were approximately 16% and 8% for concentrations below and above 0.5 µg/L, respectively, and cv's for metolachlor were approximately 20% and 7% below and above 2 µg/L, respectively. Spike recoveries for both immunoassay methods were lower and more variable for spike concentrations of 0.1 and 0.5 µg/L, respectively. Matrix effects of the sample water appeared to contribute to the lower recoveries at the lower concentrations.

**Comparison of immunoassay and GC/MS results**—Immunoassay analyses were not intended to replace the more comprehensive GC/MS analyses of organic compounds but rather were used in this study as a screening tool for a selected group of target compounds. Immunoassays are, however, advantageous because they are less expensive (about one-tenth to one-fifth of the GC/MS cost) and have a quick turnaround time. The disadvantages of the immunoassays are the cross-reactivities that may decrease their specificity and the limited number of compounds that can be analyzed at once (the GC/MS schedule analyzed by the NWQL provides analyses of over 40 compounds for each sample).

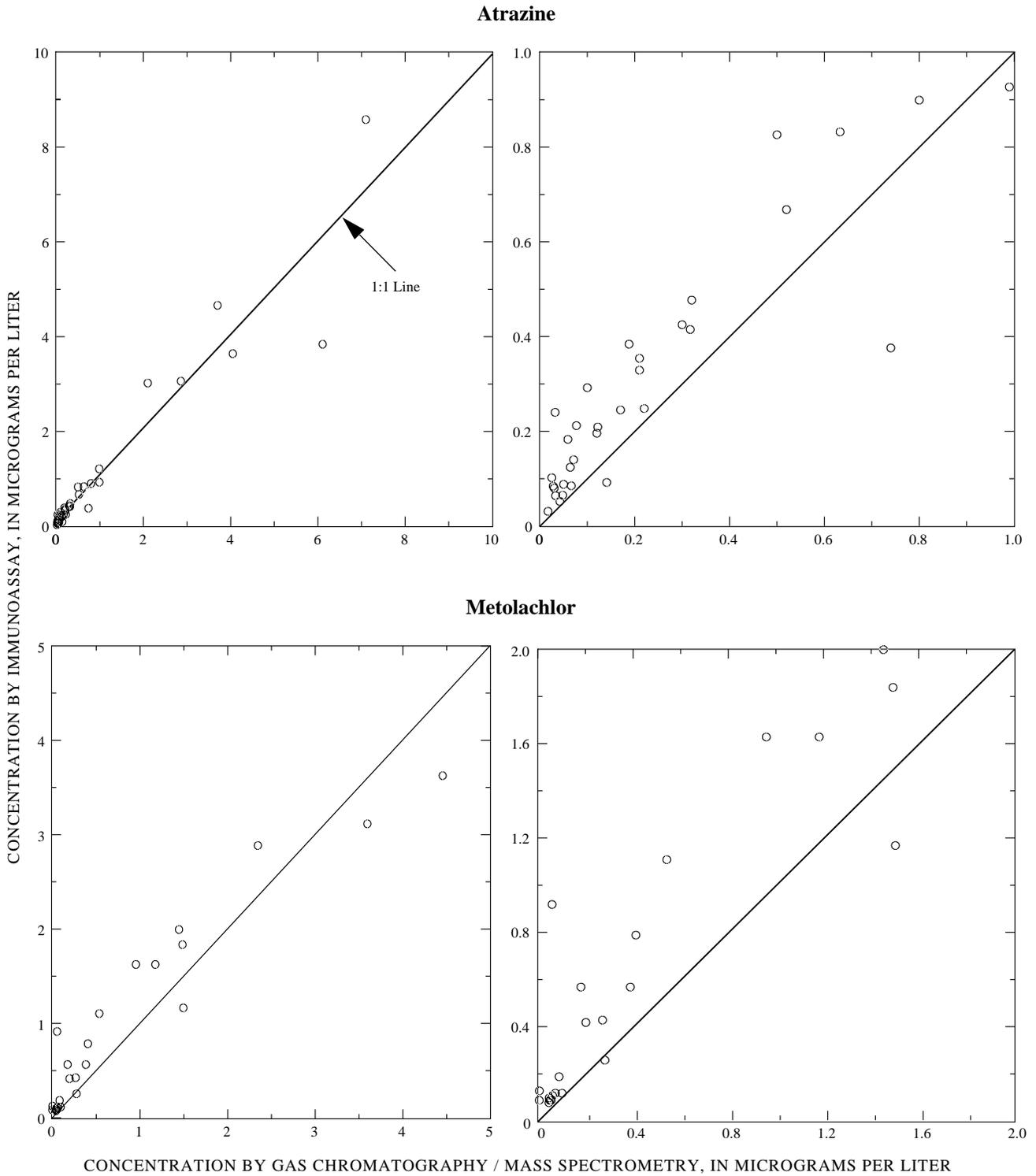
Forty-five atrazine samples and 40 metolachlor samples were analyzed by both immunoassay and GC/MS (fig. 2). The immunoassay

values were consistently slightly higher than the GC/MS values, most likely due to the cross-reactivities of the immunoassays. Overall, the immunoassay data correlated well with the GC/MS values ( $r^2 > 0.90$ ,  $p < 0.001$ ). These correlations were similar to the findings of other studies comparing immunoassay and GC/MS data (Thurman and others, 1990; Gruessner and others, 1995; Lydy and others, 1996).

#### Quality Assurance

In order to estimate variability in sampling and laboratory techniques, quality control (QC) samples were submitted to the NWQL for pesticides, and to the ODEQ and ACWA laboratories for the conventional constituents. Most QC samples were used to evaluate the potential for problems from the combination of field and laboratory procedures. QC samples for both pesticides and conventional constituents included (1) field and equipment blanks to test for contamination, (2) replicate native-water grab samples to test for precision, (3) depth and width integrated samples collected as replicates to compare with grab samples, and (4) distinct compounds, representing relevant pesticide families (surrogates), added in known amounts to each pesticide sample to monitor the analytical method's ability to quantify those sample types. Additional QC samples for pesticides included (5) native-water samples spiked with pesticide mixtures to test for accuracy, done at a range of concentrations (low, medium, and high), and (6) replicate spike samples to test for accuracy and precision. Water for blank samples was carefully selected to be free of the constituents of concern: organic-free water was used for pesticide, immunoassay, and BOD<sub>5</sub> samples; inorganic-free water was used for nutrient samples; a peptone buffer solution was used for fecal coliform bacteria, and a sterile saline solution was used for *E. coli* bacteria blanks. QC data for this study are presented in Appendix 1 and summarized below.

**Field Blanks**—Contamination of samples is not considered a problem for the current study. No pesticides were detected in any of the three blank samples submitted, which is consistent with blank results, collected from 1992 to 1996, for pesticide methods in the USGS Oregon District that were the



**Figure 2.** Comparison of immunoassay and gas chromatography/mass spectrometry (GC/MS) results for atrazine and metolachlor concentrations, Willamette Phase III, Oregon, 1996.

same as those used in this study (Anderson and others, 1996; Rinella and Janet, in press). Immunoassay analysis of two field blanks also had no detections for either atrazine or metolachlor. In two blank samples for conventional constituents, submitted to ACWA and ODEQ laboratories, there were low-level detections of  $\text{NO}_3^-$ -N and  $\text{PO}_4^{3-}$ -P (0.011 and 0.005 milligrams per liter, respectively). However, these concentrations were substantially lower than typical nutrient concentrations detected during this study and did not indicate an important problem. Two blank samples for bacteria had no *E. coli* colonies; one of two fecal coliform samples had only one colony, indicating that contamination of bacterial samples also was not a problem.

**Replicate Samples**—Replicate native-water analytical results indicated generally good agreement for most compound concentrations, with a range of 10-20% except at concentrations close to the MDLs; exceptions were for simazine, desethylatrazine, 2,4-D, and triclopyr at one sampling each. However, in eight cases compounds were detected in a sample but not its replicate. As a result of verification requests to the NWQL, six of the nondetections were revised to indicate detections at concentrations similar to those in the original samples. Original data in these cases thus represented false negatives. One exception was for 2,4-D, in a sample in which chemical interferences prevented the compound from being positively identified even when results from the other replicates for that sample indicated that 2,4-D was present. Although there appears to have been a slightly higher incidence of false negatives in the HPLC method than in the GC/MS method, the overall extent of this problem in the complete data set is unknown but is expected to be small.

Analytical differences between depth- and width-integrated samples and grab samples were minor for the dissolved compounds examined in this study. The comparison of the two sampling methods assessed the variability over the stream cross section, which could be large if pesticide concentrations were locally influenced by stream mixing. Differences between these samples were attributed to chemical interferences or analytical error and did not appear to be related to the

sampling method (table 1-1 in Appendix 1). On the basis of these results, the depth- and width-integrated samples are treated here as replicate samples.

**Field Matrix Spikes**—Spike recoveries were used qualitatively to identify compounds for which reported concentrations may substantially underestimate or overestimate actual concentrations and to assess the repeatability of the laboratory analyses. Ten native water samples were spiked with mixtures of pesticides at moderate, known concentrations (Appendix 1-1). Overall, recoveries for compounds analyzed by GC/MS were more consistent and closer to 100% than those analyzed by HPLC. Two compounds detected in stream samples, carbaryl and carbofuran, had median spike recoveries that were higher than the range generally considered acceptable (60-140% recovery), whereas six detected compounds (desethylatrazine, bentazon, dicamba dichlobenil, diuron, and MCPA) had median recoveries of less than 60%. Several other compounds, which were estimated as having been applied in the basin but were never detected, had median recoveries of less than 50%. These included chlorothalonil, chlopyralid, esfenvalerate, and oxamyl. The first three of these have had consistently poor performance and were therefore not considered further for this report. The median recovery for azinphos-methyl, for which an application rate was estimated but which was not detected, was higher than 140%.

**Surrogates**—Surrogate compounds are not expected to be found in stream water; however, they represent different families of pesticides that may be found there. Because of chemical similarities, surrogates are expected to behave similarly to the other compounds in their respective families, and they are thus used to monitor the method's performance for the those families of compounds. Surrogate recoveries for the GC/MS method were consistently in the range of 90-120%. The highest recoveries for each surrogate were recorded for the same sample (West Fork Palmer Creek on April 19, 1996), indicating that the sample may have been poorly spiked with the surrogate solution. No temporal trends were noted over the course of the study. Overall, surrogate recoveries for pesticide analysis by GC/MS

indicate that the process was acceptably precise and accurate for the pesticide families represented. Recoveries for the surrogate representing samples analyzed by HPLC were less precise; however, they have historically been poor, and the compound's utility as a surrogate has previously been questioned (Werner and others, 1996). Surrogate recoveries for analysis by GC/MS are summarized in Appendix 1-2.

**Custom Analysis**—Custom GC/MS analysis by the NWQL of several samples that had laboratory interferences, as previously described, provided insights into the ability to accurately quantify concentrations of some compounds when they are abnormally high. In particular, several nontarget compounds in the samples, when identified after a search of a database of GC/MS spectral responses, appeared to be degradation products of the herbicide diuron; these compounds were evidently formed in the analytical process itself, as the samples were injected into the mass spectrometer (Mark Sandstrom, USGS, written commun., 1997). In one case the concentrations of these compounds were high enough to saturate the electronics of the mass spectrometer, and probably represented a significant fraction of the original mass of diuron in the sample. Therefore diuron in that sample, originally quantified at 29  $\mu\text{g/L}$ , was in fact potentially much higher; it thus appears that other reported diuron concentrations in the range of several micrograms per liter or higher are likely to represent underestimated concentrations as well.

## Statistical Methods

Nonparametric statistical techniques were used to analyze the data in this report; these techniques are often more appropriate than parametric techniques for environmental data, which may not be normally distributed. For example, the central tendency and spread of the data are described by the median and the interquartile range, respectively. A Spearman's  $\rho$  (rho) statistic is used to measure the correlation between two data sets; this statistic is a measure of the degree to which larger and smaller values of one variable tend to be paired with larger and

smaller values of another (Helsel and Hirsch, 1992). Pairwise testing for the difference in medians was done using a Wilcoxon test statistic (Helsel and Hirsch, 1992), and testing for a seasonal difference in medians was done using a 2-way ANOVA test on the rank-transformed data (Helsel and Hirsch, 1992).

MDLs were carefully accounted for during rank transformations, hypothesis testing, and the calculation of percentile statistics. For those calculations that involved ranking the data, the following rules were applied: (1) Censored data at the standard MDL (table 2) were assigned one tied rank. (2) Detected or censored values below the standard MDL were assigned the same rank as values censored at the standard MDL. (3) Detected values at the standard MDL were assigned the next higher rank.

An additional consideration was introduced because analytical data were occasionally censored at an MDL different from the standard MDL for a given compound (table 2). For calculations that involved ranking data with multiple MDLs, the following rules were applied beyond those already stated: (4) A censored value above the standard MDL was assigned the same rank as censored values at the standard MDL *if* there were few or no detected values between the standard MDL and the higher MDL. In the former case, the detected values between the two MDLs were also assigned the same rank. (5) In a very few cases, a censored value was dropped before ranking the data. Those values were censored at a concentration much higher than the standard MDL for that compound, and could not be properly ranked with detected values. A total of five such values were dropped (for ranking purposes only), affecting four compounds. As an example of how these rules were applied, the following dataset consisting of 18 data values—0.012, 0.018,  $6 \times <0.02$ , 0.02, 0.022, 0.024,  $<0.025$ , 0.025, 0.03, 0.035, 0.05, 0.08, 0.1—has the following ranks— $12 \times 6.5$ , 13, 14, 15, 16, 17, 18.

Multiple MDLs were accounted for in pairwise testing by using a data set that was transformed to allow the use of survival testing techniques to calculate the Wilcoxon test statistic (She, 1997).

Percentile statistics for compounds with data censored at high, nonstandard MDLs within the range covered by the uncensored data were computed using a statistical procedure that fits a probability distribution to the data set using both the detections and the nondetections (Helsel and Cohn, 1988).

For one analysis, loads were calculated from the discharge and concentration data. In the rank transformation, loads calculated from censored concentration values were treated as a load value censored at a new MDL equal to the discharge times the concentration MDL. Loads were calculated only for the most frequently detected compounds (detection frequency > 70%), because only in those cases could the resulting load values be meaningfully ranked with respect to the rest of the load distribution using the same rules that applied to the ranking of the concentration data.

### **Site Selection**

The study design called for sample collection from 16 randomly selected subbasins that each had predominantly agricultural land uses upstream of the sampling site, and 4 subbasins having predominantly urban land use. In order to minimize inputs of water from undefined or highly varied sources, small drainage basins ranging from approximately 3 to 15 mi<sup>2</sup> (square miles) were selected.

Initial identification of potential sampling sites was made from a geographic information system (GIS) coverage of streams in the Willamette River Basin (U.S. Geological Survey, 1990). USGS topographic maps (1:24,000 scale) were used in conjunction with the GIS to identify potential sampling sites on streams at points where the drainage area was between 5 and 15 mi<sup>2</sup>. The initial identification of subbasins that had primarily agricultural land yielded a pool of 110 potential sites, from which the agricultural sites were chosen at random. Several of the sites that were originally selected were disqualified after an initial reconnaissance visit, and replacement sites were identified. Reasons for disqualifying sites included poor or unsafe

access, a judgement that the stream was likely to be intermittent (dry during summer), an upstream reservoir that might significantly modify the stream's hydrologic response, or an estimated land use distribution that did not meet the criteria set for the study. The land-use criteria for agricultural subbasins, which were established in consultation with representatives of the WRTASC, stipulated that the basin's land use would be at least 50% intensive agriculture (not including fallow land or pasture), and not more than 30% residential use.

The four urban sites were selected from a set of urban subbasins drawn on topographic maps, and the final choice was based primarily on the desire to sample urban drainages that had not been extensively sampled previously, the desire to sample sites in urban areas in the northern, central, and southern Willamette Basin, and the suitability of a site for sampling. Land use information for the urban sites was derived from the GIS, with coverages for urban lands most recently updated on the basis of the 1990 census (Hitt, 1994). Due to rapid growth in many of western Oregon's cities during the 1990's, data for urban land use taken from the GIS is expected to somewhat underestimate the proportion of urban lands and overestimate the proportion of agricultural or forested lands in the Phase III urban subbasins. However, these data were considered adequate for the purposes of this report.

### **Crop Type and Pesticide Use Determination**

#### **Agricultural Fields**

Crop surveys were conducted by observation from roads in the selected drainage basins and, when feasible, by talking with local land owners. The surveys were conducted over a 3-week period beginning June 24, 1996, and ending July 15, 1996. The southernmost basins were, in general, surveyed first in order to conduct field observations before harvest. USGS 7.5 minute topographic maps were used as base maps for the crop survey. Field boundaries were drawn onto the maps by using topographical and geographical landmarks as references and also by using commercially available aerial photographs. The photographs were

taken during flights made in 1994; nonetheless, most field boundaries were unchanged.

The field boundaries were later digitized, and the identified crops were placed into a GIS coverage. In all, more than 40 crop types were identified, as well as other land uses, including forested, urban or rural residential, and riparian zones. When riparian areas were heavily forested they were classified as forested. Fields that could not be seen from the roads were assigned the crop type “unknown.” Of the total 68,164 agricultural acres surveyed, 643 acres were identified as unknown. The largest percentage of land identified as unknown in any single basin was 4.5%.

### **Pesticide Application Rates**

The initial estimates of the pesticide application rates were based primarily on estimates for the Willamette Basin for previous years published by Oregon State University (Rinehold and Witt, 1989; Rinehold and Jenkins, 1993a; 1993b; 1994; 1996; 1997). The application rates in these publications were supplemented with rates from publications devoted to pesticide use on crops in the Pacific Northwest, but not specific to the Willamette Valley or Oregon (Fisher and others, 1996; Pscheidt, 1996; William and others, 1996). Information about specific formulations was obtained from the Herbicide Handbook (Ahrens, 1994) and from Page and Thomson (1997).

Whenever possible, the initial estimates of pesticide application rates were reviewed by experts, such as agricultural extension agents, who have first-hand knowledge of practices not accurately reflected in the published literature; such practices might be particular to a specific crop, pest, geographic area, or time of year. In this way, the published estimates were modified to more accurately reflect the current practices of growers in the Willamette Valley. The timing of stream samplings was divided into periods that corresponded with the intervals between application and periods of rainfall runoff; these intervals were designated “early spring” (mid-February to April 19), “spring” (April 20 to May

14), “summer” (May 15 to July 25), “fall” (July 26 to mid October), and “winter” (mid-October to mid-February). Whenever the published application rate was given as a range, the amount of pesticide applied to the study basins was calculated as a range as well. For most analyses, however, the final estimate for each pesticide was the average of the minimum and maximum values of the given range. Compounds that are not included in the list of target pesticides were not included in the use estimates.

Not all land planted with a given crop is treated identically because of such complications as variable pest problems and grower preferences. Therefore, the published application estimates were used to determine the percentage of land area planted in each crop type receiving treatment with each pesticide. Those percentages (not the acreages themselves) were multiplied by the specific acreages determined from the crop surveys of Phase III study basins, and by the application rate (in pounds of active ingredient per acre [lb. a.i./ac]) to obtain a *nominal* application rate for each pesticide.

Table 4 shows an example of the method used to estimate nominal application rates for one crop type, tall fescue grass seed in the northern Willamette Basin counties of Marion, Yamhill, Washington, and Polk. In this case, geographic-area-specific data indicated that application rates and timing of application for some pesticides differed between northern and southern counties. For example, 2,4-D, a broadleaf weed control agent that is typically applied in spring, can damage nursery plants, which are commonly grown in northern counties. Therefore MCPA, an alternative to 2,4-D that is not as damaging to nursery plants, is applied in the spring in the basin’s northern counties.

The total mass of a particular pesticide applied to each agricultural subbasin was calculated as the sum of the mass applied to each crop type in the basin. As an example, table 5 includes each crop type in a hypothetical subbasin to which diuron was estimated to have been applied and the percentage of the acres planted in that crop type receiving the indicated rate of treatment. In order to calculate the total amount of diuron applied to a

**Table 4.** Method used to estimate chemical applications—example using tall fescue in Marion, Yamhill, Washington and Polk Counties, Oregon, during 1996

[The October application of metribuzin or diuron is indicative of a situation where multiple compounds may be used for control of a particular pest. Both metribuzin and diuron would be included in the final use estimate. Pesticide application information for Time of application, Formulated rate of application and Percentage of crop area treated are from Rinehold and Jenkins (1993a; 1993b; 1994; 1996; and 1997). lb ai/ac, pounds of active ingredient per acre; pt, pint; gal, gallon; fl. oz, fluid ounce. The formulated rate of application is the amount of the product mixture applied to an acre of land. The rate of application of active ingredient (E) is determined, after unit conversion, as the product of the Concentration of active ingredient (C) and the Formulated rate of application (D), or  $E=C \times D$ . The Nominal rate of application (G) is determined as the product of the Rate of application (E) and the Percentage of crop area treated (F), or  $G=E \times F$ ]

A	B	C	D	E	F	G
Pesticide active ingredient (trade name)	Time of application	Concentration of active ingredient in formulation	Formulated rate of application	Rate of application of active ingredient (lb ai/ac)	Percentage of crop area treated	Nominal rate of application (lb ai/ac)
Dicamba (Banvel)	Spring	4 lb/gal	4 fl. oz/ac	0.13	60	0.08
MCPA	Spring	4 lb/gal	1 pt/ac	.5	60	.3
Diuron (Karmex 80W)	Early fall	80% by weight	3.0 lb/ac	2.4	23	.55
Metribuzin (Lexone, Sencor DF)	October	75% by weight	0.25–0.5 lb/ac	0.19–0.38	19	0.04–0.07
— or —		— or —	— or —	— or —	— or —	— or —
Diuron 4L		4 lb/gal	2.0–3.0 pt/ac	1.0–1.5	53	0.53–0.8
Diuron 4L	December	4 lb/gal	1.5–3.0 pt/ac	0.75–1.5	72	0.54–1.08
Dicamba (Banvel)	January	4 lb/gal	0.5–1.0 lb/ac	0.25–0.5	13	0.03–0.07
Chlorothalonil (Bravo 720)	Summer	6 lb/gal	1.3–3 pt/ac	1.1–2.3	2	0.02–0.05

given subbasin, the *nominal* rate of application was determined for each crop type and multiplied by the acreage of that crop planted in the subbasin. The mass of active ingredient applied (in this case diuron) was then summed over each crop type. Compounds used on row crops are often applied to only the rows or the areas between the rows (“banded” spray); nominal application rates for these situations were adjusted to account for the decreased land area treated. Likewise, pest problems that are treated with spot spraying result in decreases in the area treated, and nominal application rates were reduced in these cases as well.

Rights-of-way in the agricultural basins, which include county and state roads, railroads, and power transmission lines, were treated more qualitatively than agricultural fields because previously published estimates of application rates and compounds (Reinhold and Witt, 1989) for rights-of-way did not appear to agree with current practices. Conversations with district spray managers for the Oregon Department of Transportation (ODOT) indicated that ODOT has been reducing roadside pesticide applications in recent

years, and the primary chemical applied during 1996 for weed control along Federal and State highways was glyphosate, a nontarget compound. Chemicals that were used along rights-of-way in 1987 that are no longer in use include atrazine, dicamba, diazinon, picloram, prometon, pronamide, and simazine. Although late summer and fall spot spraying with triclopyr (Garlon) occurred along roadways in most districts in the Willamette River Basin, the amounts applied in the study subbasins could not be estimated on the basis of available information. Krovar (a formulation of diuron and bromacil) was applied in 1996 in one ODOT district in the southern Willamette Basin, but apparently not in other districts. Oryzalin, dichlobenil, and triclopyr were used on a case by case basis in 1996 for ornamental landscaping by ODOT, but no quantitative application rates could be determined for the individual subbasins.

Recent estimates of applications along railroads were also changed from previously published

**Table 5.** Method used to estimate mass of pesticide applications—example using applications of an herbicide (diuron) to different crop types in a hypothetical subbasin in the Willamette River Basin, Oregon, during 1996  
[Pesticide application information from Rinehold and Jenkins (1993a; 1993b; 1994; 1996; and 1997); lb ai/ac, pounds of active ingredient per acre; qt, quart; pt, pint; gal, gallon. Total mass applied is the product of the Nominal rate of application and the total area in crop type, which for this table is hypothetical. See table 4 for explanation of method to calculate Nominal rate of application. Tall fescue, orchard grass, and ryegrass have different fall application rates for crops in different stages of growth; however, winter applications to these crops are similar for both new and established stages]

<b>Crop Type</b>	<b>Time of application</b>	<b>Nominal rate of application (lb ai/ac)</b>	<b>Hypothetical total area in crop type (acres)</b>	<b>Total mass of diuron applied (lb ai)</b>
Alfalfa hay	Spring	0.03–.05	125	5
Barley	Winter	.03	0	0
Beans	None	0	250	0
Caneberries	Fall (banded)	0.27–0.54	150	61
Clover	Fall	0.58–0.73	100	66
Corn	None	0	425	0
Tall fescue (new)	Fall	.55	300	166
Tall fescue (established)	Fall	0.53–0.8	150	100
Tall fescue	Winter	0.54–1.08	450	365
Hazelnuts	Spring	0.53–1.06	150	120
Orchard grass (new)	Fall	.55	25	14
Orchard grass (established)	Fall	0.48–0.72	0	0
Orchard grass	Winter	0.54–1.08	25	20
Oats	Spring	0.19–0.29	150	36
Raspberries	Early spring (banded)	0.18–0.36	75	20
Perennial ryegrass (new)	Fall	.7	1,000	700
Perennial ryegrass (established)	Fall	0.55–0.66	1,500	908
Ryegrass	Winter	0.40–0.79	2,500	1,485
Wheat	Winter	0.26	600	156
<b>TOTAL</b>			<b>5,000</b>	<b>4,222</b>

literature. The 1989 estimates by Reinhold and Witt indicated that 2,4-D, atrazine, dicamba, diuron, picloram, and triclopyr were used for control of weeds along railroads; however, in 1996 the compounds used that were analyzed in this study were diuron, bromacil, triclopyr, and tebuthiuron (T. Mayer, Asplundh Corp., written commun., 1996).

Because of the problems in quantitatively estimating chemical use along rights-of-way, these uses are not accounted for in the basin-by-basin estimates. However, the appearance of compounds used along rights-of-way, and in other such noncropland uses, is considered together with comparisons of pesticide occurrence with estimated uses.

Three pesticides included in the study, 2,4-D, DCPA, and dicamba, are applied in different forms depending on the crop, pest, or formulation in which they are used. To varying degrees they may be applied as either acids, esters, or amines, although the amines (and to a lesser extent the esters) tend to hydrolyze rapidly in soils into the acid forms (Ahrens, 1994). Only the acid forms of these compounds were analyzed by the methods used in this study. Thus, it is possible that some form of these compounds may have been present in a given water sample but that they were not fully quantified because they were present either as amines or esters. This was probably most important for 2,4-D because it is applied widely as the both an ester and an amine salt in the Willamette River Basin. When making pesticide use estimates, it was often unclear in what form 2,4-D would be applied, so no effort was made to account for these different forms. However, although pesticide use estimates for 2,4-D may be somewhat high compared with the actual use of the form analyzed, it is assumed that degradation and hydrolysis reactions would increase the amount of acid present, making any overestimates minor.

## LAND USE

### Site Selection

The sites chosen by the random selection process were distributed relatively evenly around the low elevations of the Willamette River Basin

(table 6, fig. 3). Drainage areas of the upstream subbasins ranged in size from 2.6 mi<sup>2</sup> to 13.0 mi<sup>2</sup>. The total land area incorporated by the subbasins is 141.4 mi<sup>2</sup> (90,468 acres), with about 75% of that area (106.5 mi<sup>2</sup>) in the 16 agricultural subbasins. Of the agricultural sites, 10 were located north of the city of Albany. No sites were located south of Eugene. Major tributary drainages represented by the sampling sites included the Pudding River, the Tualatin River, the Yamhill River, and the Long Tom River, which have all been classified as having severe nonpoint-source pollution problems on the basis of sediment and nutrient runoff (Tetra Tech, Inc., 1995d). The Calapooia River drains land having similar types of uses as the Long Tom River and has also been documented as having substantial pesticide loading and high nutrient concentrations (Anderson and others, 1996, Bonn and others, 1996, Rinella and Janet, in press). Several sites were on tributaries to smaller streams, such as Champoeg Creek or Mill Creek, or enter the main stem of the Willamette River directly. Several streams are unnamed; these streams are herein designated as "Unnamed Tributaries" (UT) to the indicated creeks or rivers. For convenience, the shortened names in table 6 are used throughout the text of this report.

On basis of the results of the crop use surveys conducted in July, 1996, several of the selected subbasins did not meet the initial criteria for potential sampling sites, indicating that the reconnaissance surveys conducted in spring 1996 did not always properly account for all land use in the subbasins. Baker, Chicken, UT Ash Swale, and SF (South Fork) Ash each had less than 50% of the upstream land in intensive agricultural use in 1996, with a minimum of 31% at UT Ash Swale. However, these same sites, together with Shafer and UT S (South) Yamhill, have relatively high proportions of forested (or riparian) areas and provide an opportunity to qualitatively evaluate the influence of forested areas in determining the distribution and concentrations of pesticides in nonpoint source runoff. Six sites had 80% or more of the upstream land in active agricultural production, including two sites in the northern part of the Willamette River Basin (W [West] Champoeg, WF [West Fork] Palmer) and four sites in the southern part (UT

**Table 6.** Description and location of sampling sites for Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996

[Agricultural sites are listed in order of increasing percentage of upstream agricultural land use. Source for urban land use data: Hitt, 1994. \*, "Residential" category used for all urban land in urban basins, including combined urban residential, commercial, industrial, and transportation areas. Map Index Numbers (refer to sites on figure 3. Nonintensive, relatively small percentage (less than 60 percent) of agricultural land use in subbasin; Intensive, relatively large (more than 60 percent) amount of agricultural land use in subbasin; Diverse, relatively large number of crop types grown in subbasin; Nondiverse, relatively small number of crop types grown in subbasin. Refer to table 7 for crop diversity information. "(direct)," streams enters Willamette River directly. mi<sup>2</sup>, square miles; Cr., Creek; nr, near; trib; tributary; N, North; R, River; Rd., Road]

Map index numbers	Site name	Short name	Tributary subbasin to Willamette River	Subbasin size (acres/ mi <sup>2</sup> )	Upstream land use (percent of subbasin area)			
					Agriculture	Forest	Residential*	Other
<b>URBAN SITES</b>								
U1	Dixon Cr. at 5th St. at Corvallis	Dixon	(direct)	3,041 / 4.8	18	20	62	0
U2	Beaverton Cr. at Wetlands Park nr Aloha	Beaverton	Tualatin River	8,326 / 13.0	5	2	93	0
U3	Pringle Cr. at Bush Park at Salem	Pringle	(direct)	5,484 / 8.6	20	0	80	0
U4	Claggett Cr. at N. River Rd. at Salem	Claggett	(direct)	5,451 / 8.5	0	0	100	0
<b>AGRICULTURAL SITES</b>								
<b>Nonintensive, diverse</b>								
43	Unnamed trib to Ash Swale at Old Bethel Rd nr Amity	UT Ash Swale	Yamhill River	2,903 / 4.5	31	51	6	11
9	Baker Cr. at Highway 210 nr Scholls	Baker	Tualatin River	6,173 / 9.7	40	49	7	4
10	Chicken Cr. at Edy Rd. nr Scholls	Chicken	Tualatin River	2,662 / 4.2	40	23	13	24
69	South Fork Ash Cr. at Monmouth Hwy nr Monmouth	SF Ash	(direct)	4,122 / 6.5	45	44	2	9
104	Shafer Cr. at Territorial Rd. nr Monroe	Shafer	Long Tom River	1,666 / 2.6	55	26	9	10
<b>Intensive, diverse</b>								
37	Senecal Cr. at Fellers Rd nr Donald	Senecal	Pudding River	5,558 / 8.7	60	5	21	15
48	Unnamed trib to S. Yamhill R. at Dejong Rd. nr Ballston	UT S Yamhill	Yamhill River	6,301 / 9.9	69	21	2	8
27	Deer Cr. at Fargo Rd nr Aurora	Deer	Pudding River	3,819 / 6.0	70	11	11	8
39	West Champoeg Cr. at Hwy 219 nr Woodburn.	W Champoeg	Champoeg Creek	3,699 / 5.8	80	8	7	5
40	West Fork Palmer Cr. at Webfoot Rd. nr Dayton	WF Palmer	Yamhill River	5,639 / 8.8	83	3	8	6
<b>Intensive, nondiverse</b>								
61	Simpson Cr. at Brownell Dr. nr Aumsville	Simpson	Mill Creek	1,856 / 2.9	72	6	8	14
86	Truax Cr. at Scravel Hill Rd nr Draperville	Truax	(direct)	4,292 / 6.7	77	4	16	4
94	Unnamed trib to Shedd Slough at Fayetteville nr Shedd	UT Shedd	Calapooia River	2,167 / 3.8	84	0	5	10
106	Unnamed trib to Flat Cr. at High Pass Rd. nr Junction City	UT Flat	(direct)	5,364 / 8.4	84	0	11	4
80	Unnamed trib to Oak Cr. at Looney Dr. nr Albany	UT Oak	Calapooia River	5,011 / 7.8	87	0	8	5
81	Lake Cr. nr Tangent	Lake	Calapooia River	6,934 / 10.9	95	0	2	3

Oak, Lake, UT Shedd, and UT Flat). Outside of the urban subbasins, the greatest amount of upstream residential land use was 21% at Senecal, which did meet the initial selection criteria of 30% (or less) residential land use in agricultural subbasins.

### Agricultural Crop Surveys

Results of the land use surveys and mapping of the agricultural subbasins (table 7) illustrate the wide variety of crop types found within the

Willamette River Basin. A total of 44 land use categories were identified, of which 5 (forests, industrial, other, urban residential, and rural residential) are not intensive agricultural activities, leaving 39 crop types in the study subbasins during 1996. By far the most abundant crop type was ryegrass seed, accounting for 30% of the land in the agricultural subbasins overall. The total grass seed area, including rye, orchard, tall fescue, and the unidentified grass seed, was 26,217 acres (39% of the agricultural land). Forested and rural

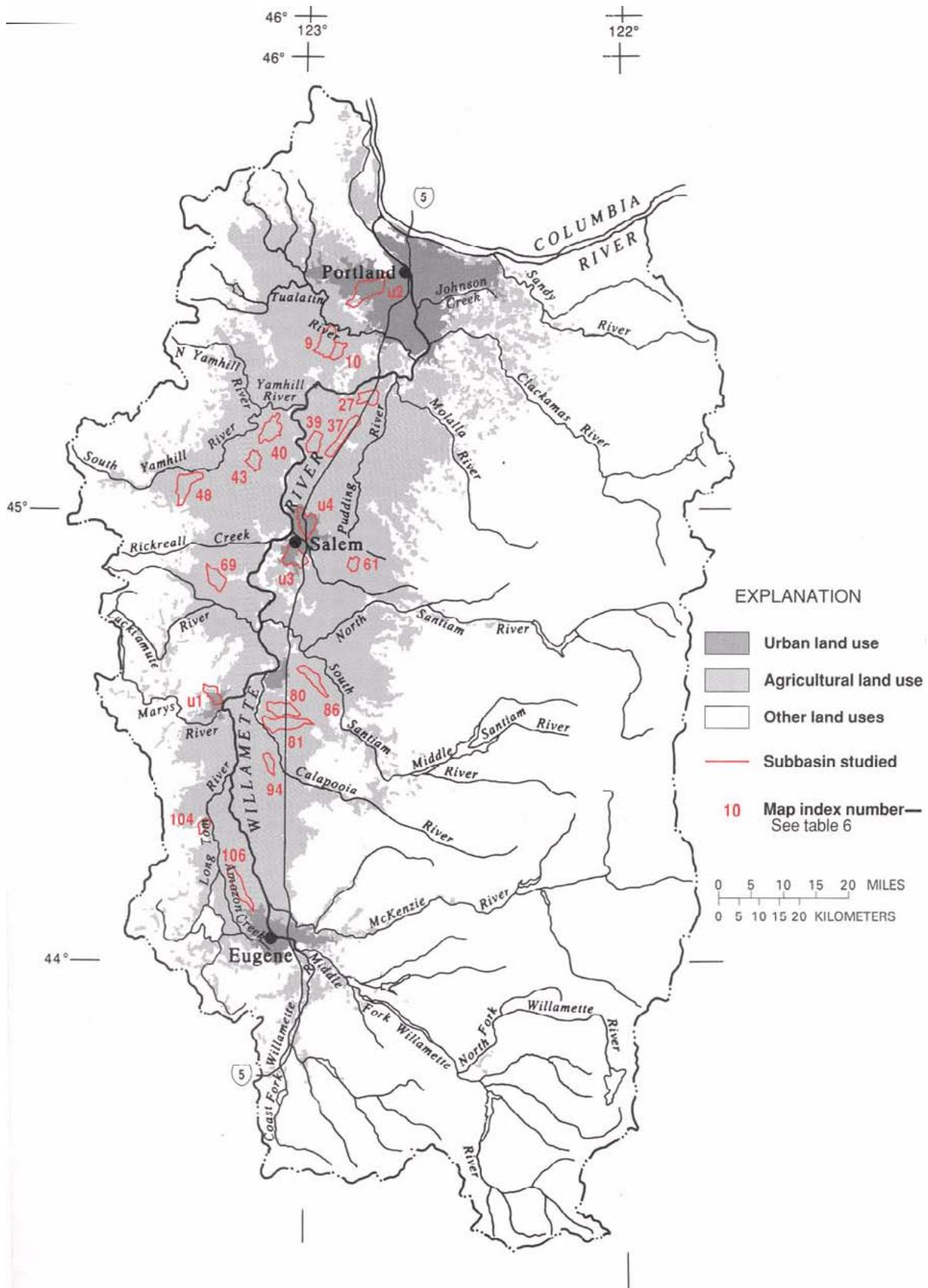


Figure 3. Location of subbasins sampled in the Willamette River Basin, Oregon, during 1996.

**Table 7.** Acreages of each crop or land use type in 16 agricultural subbasins, Willamette River Basin, Oregon, 1996

[Refer to table 3 for complete listing of site names and locations and table 6 for data on relative agricultural intensity. The “other” category includes fallow ground, riparian area, rights of way, and unknown land uses. “Grass seed” is a grass seed crop that could not be specifically identified as orchard grass seed, fescue seed, or ryegrass seed. “Organic” includes organic farms that do not use pesticides. “Not Yet Planted” is land that was in preparation for planting but for which a specific crop could not be identified. The total agricultural acres and total number of crop types do not include land uses listed as “forest,” “industrial,” “other,” “rural residential,” or “urban residential”]

Crop or land use type	Nonintensive, diverse					Intensive, diverse					Intensive nondiverse					Total (acres)	
	UT Ash Swale	Baker	Chicken	SF Ash	Shafer	Senecal	UT S Yamhill	Deer	W Champoeg	WF Palmer	Simpson	Truax	UT Sheild	UT Flat	UT Oak		Lake
Alfalfa	0	22	0	0	0	25	0	0	50	0	0	0	0	0	0	0	97
Barley	0	0	0	0	0	0	42	0	0	0	0	0	0	0	0	40	82
Snap Beans	0	0	0	0	0	131	5	44	251	109	0	0	0	0	0	0	540
Beet seed	0	0	0	0	0	0	15	0	0	119	0	0	0	0	0	0	134
Blueberries	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1
Broccoli	0	0	0	0	0	47	0	67	0	54	0	0	0	0	0	0	168
Caneberries	0	99	10	0	0	64	5	82	39	64	0	0	0	0	0	0	363
Cherries	106	301	29	24	0	0	0	0	0	33	0	0	0	0	0	0	493
Christmas trees	27	385	308	27	627	3	277	122	0	0	103	0	0	0	0	0	1,879
Clover	0	0	7	0	0	0	42	9	0	231	0	82	0	0	0	294	665
Corn	0	0	0	0	0	87	0	246	110	791	0	102	0	0	0	0	1,336
Fescue seed	56	24	50	126	224	166	293	52	171	0	595	462	271	606	226	1,512	4,834
Forest	1,494	3,050	620	1,823	428	277	1,339	425	313	176	108	164	0	0	0	27	10,244
Grapes	0	6	79	0	8	0	13	0	0	21	0	0	0	0	0	0	127
Grass seed	70	22	30	106	0	152	61	0	160	0	0	0	282	2	171	0	1,094
Hay	258	499	106	737	8	202	1,059	107	0	640	0	97	41	612	54	5	4,425
Hazelnuts	73	448	156	131	0	147	0	76	122	193	4	0	0	25	0	0	1,375
Hops	0	0	0	0	0	228	0	0	960	0	0	0	0	0	0	0	1,188
Industrial	0	0	0	0	0	0	0	83	0	10	0	0	0	105	0	0	198
Meadowfoam	0	0	24	0	0	14	0	22	0	0	0	0	0	0	0	0	60
Mint	0	0	0	0	0	0	0	0	0	7	41	0	0	0	0	71	119
Mustard seed	0	0	0	0	0	11	0	33	0	0	0	0	0	0	0	0	44
Not yet planted	117	5	0	27	17	13	40	71	3	188	75	23	55	35	0	46	715
Nursery (container)	0	0	0	0	0	0	0	0	0	515	0	0	0	0	0	0	515
Nursery (in-ground)	0	62	57	0	0	217	0	303	44	31	0	0	0	0	0	0	714
Orchard grass	0	0	0	36	0	0	64	0	0	0	0	2	0	165	0	0	267
Oats	11	443	8	0	0	34	521	0	0	0	16	0	0	0	0	159	1,192
Organic	0	0	0	0	0	0	0	19	0	0	0	0	0	0	0	0	19
Other	330	219	628	359	173	814	517	298	174	344	257	167	324	234	258	213	5,209
Pasture	31	94	165	23	27	48	355	361	57	154	35	20	21	273	15	26	1,705
Peaches	0	0	0	0	0	41	7	41	0	0	0	0	0	0	0	0	89
Prunes	5	0	0	0	0	0	10	0	0	25	0	0	0	0	0	0	40
Raspberries	0	0	0	0	0	0	0	3	43	0	0	0	0	0	0	0	46
Rural residential	170	420	352	87	132	1,143	116	341	268	454	150	668	118	512	395	50	5,376
Rye grain	0	17	0	0	0	0	45	0	0	0	0	0	0	0	0	0	62
Rye grass	23	0	0	614	0	1,091	538	977	915	611	456	2,390	1,436	2,731	3,893	4,347	20,022
Sod	0	0	0	0	0	236	0	0	0	0	0	0	0	0	0	0	236
Squash	0	0	0	0	0	70	0	0	0	21	0	0	0	0	0	0	91
Strawberries	0	0	11	0	0	46	0	4	13	0	0	0	0	0	0	0	74
Tomatoes	0	8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	8
Urban residential	0	0	0	0	21	0	12	0	0	0	0	0	0	0	0	67	100
Vegetables	0	0	0	0	0	0	45	0	0	0	0	0	0	0	0	0	45
Walnuts	14	12	20	0	0	0	0	0	0	0	0	0	0	0	0	0	46
Wheat	119	37	0	0	0	249	881	33	5	847	14	75	0	64	0	77	2,401
<b>Total agricultural acres</b>	<b>910</b>	<b>2,484</b>	<b>1,061</b>	<b>1,851</b>	<b>911</b>	<b>3,322</b>	<b>4,318</b>	<b>2,672</b>	<b>2,943</b>	<b>4,654</b>	<b>1,339</b>	<b>3,291</b>	<b>1,824</b>	<b>4,513</b>	<b>4,359</b>	<b>6,577</b>	<b>47,029</b>
<b>Total number of active crop types</b>	<b>12</b>	<b>17</b>	<b>17</b>	<b>9</b>	<b>6</b>	<b>23</b>	<b>20</b>	<b>20</b>	<b>15</b>	<b>18</b>	<b>8</b>	<b>9</b>	<b>5</b>	<b>8</b>	<b>5</b>	<b>9</b>	<b>39</b>

residential areas, the next largest combined land uses, comprised 15% and 8% of the agricultural subbasins, respectively.

The agricultural subbasins studied can be loosely grouped according to the land use information shown in tables 6 and 7. One group of subbasins, referred to in the tables as “nonintensive, diverse,” has a high proportion of nonagricultural land (including 20 to 50% forested land), moderately diverse cropping patterns (12 to 17 different active crop types), and little dominance by any one crop type. A second group, referred to as “intensive, diverse,” is characterized by relatively little nonagricultural land, a high diversity of crop types (more than 17), and little dominance by any one crop type (fig. 4a). A third grouping, referred to as “intensive, nondiverse,” includes subbasins with little nonagricultural land, relatively few crop types (9 or fewer), and a predominance of one crop type (more than 50% of the land), usually grass seed crops (fig. 4b). Two sites, SF Ash and Shafer, do not fit completely into any one of these groups because they have much less than 50% of the upstream land in grass seed, and the amounts of nonagricultural lands in the two basins are close to 50%; however, they also have low crop diversity (6 to 8 crop types). They are included in the “nonintensive, diverse” group in tables 6 and 7 on the basis of their relatively high proportions of forested land upstream.

In general, the agricultural subbasins with the highest crop diversity were those located in the northern part of the Willamette River Basin (that is, north of Albany). In contrast, the “intensive, nondiverse” agricultural subbasins were mostly located south of Albany and were those in which grass seed crops dominated (fig. 5). This geographical distinction, which was used to partly explain differences in pesticide occurrences by Anderson and others (1996), is primarily a result of differences in soil types throughout the basin. In particular, the poorly drained Dayton soils of the southern Willamette River Basin are not suitable for the cultivation of row crops, whereas grass seed and grain crops can be grown in them (Herbert Huddleston, Oregon State University, oral commun., 1997). The relative amount of grass seed grown in the

study basins is a potentially important component driving the distribution of certain pesticides found in the streams because the acreages can be so large. These site groupings are discussed in greater detail in the section “Relation of Pesticide Occurrence with Land Use.”

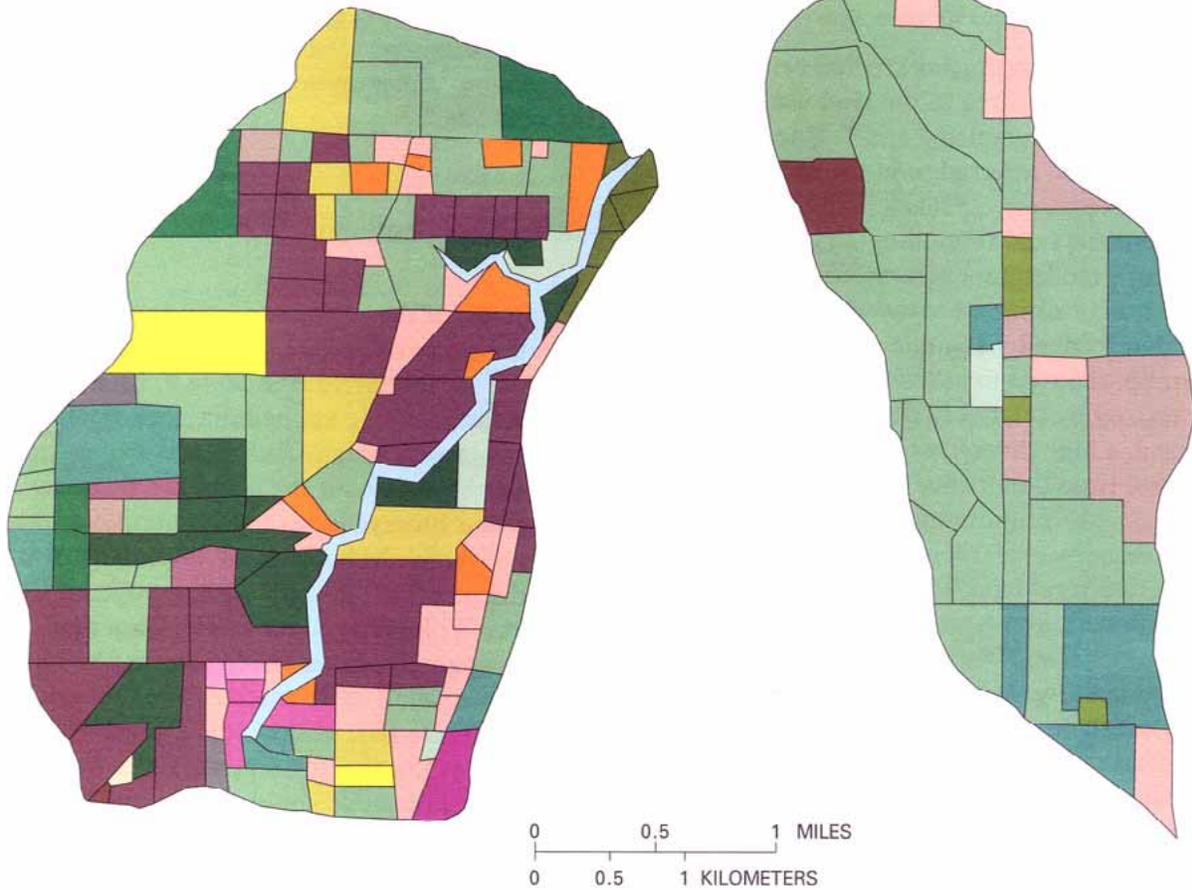
## **Pesticide Applications**

Estimates of the nominal pesticide application rates in the study basins are given for herbicides in table 8 and for insecticides in table 9. Literature estimates for pesticide application rates to crops were based largely on answers to surveys, so the results may be skewed if the subgroup that chose to answer the surveys is not representative of the group as a whole. Probably more important, however, is the fact that the data were aggregated from all over the Willamette River Basin. Data that have been aggregated basinwide may not be representative on a small scale (such as the subbasins sampled in Phase III), where local right-of-way applications or the specific practices of a few growers for a few fields could disproportionately influence water quality. Literature estimates of pesticide usage can also become outdated as customs or regulations change in response to emerging pests and as new pesticides not yet accounted for in the literature are developed. These influences, along with undocumented noncropland applications—such as rights-of-way, road construction, residential and commercial landscaping, and homeowner use—may contribute to underestimates of pesticide use for some compounds analyzed in this study. The influences of those activities to the occurrence of selected pesticides are evaluated qualitatively in a later section.

Estimates for several compounds reflect use on many different crop types. The herbicides 2,4-D, diuron, and napropamide were estimated to have been used on 16, 15, and 13 different crop types, respectively. Of the insecticides, 4 (carbaryl, chlorpyrifos, diazinon, and malathion) were estimated to have been used on more than 10 crop types each. Likewise, several crop types receive applications of a variety of different pesticides. For

**DIVERSE CROP TYPES**  
(West Champoeg Creek near Woodburn)

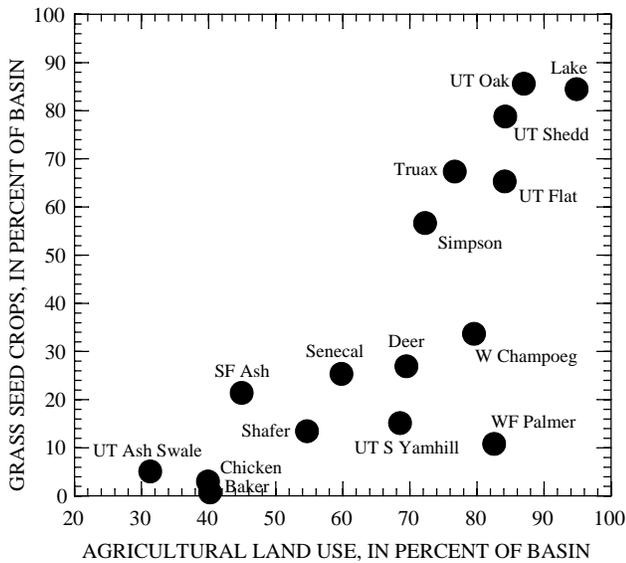
**NONDIVERSE CROP TYPES**  
(Unnamed tributary to Shedd Slough)



**EXPLANATION**

BERRIES	GRASS SEED CROPS	OTHER CROPS	OTHER USES
Caneberries	Unidentified grass seed	Hazelnuts	Not yet planted
Raspberries	Fescue seed	Hops	Fallow
Strawberries	Ryegrass seed	Nursery	Forest
		Snap beans	Pasture
FORAGE CROPS	GRAIN CROPS		Rural residential
Hay	Sweet corn		Riparian
Alfalfa	Wheat		Unknown

**Figure 4.** Examples of agricultural study subbasins with diverse and nondiverse crop types, Willamette River Basin, Oregon, during 1996.



**Figure 5.** Relation between the percentage of the basin devoted to agricultural land use and the percentage of the basin planted in grass seed crops for 16 agricultural subbasins, Willamette Basin, Oregon, 1996.

instance, the use of up to nine herbicides and nine insecticides was estimated for various berry crops. The fact that most compounds are applied to a variety of crops, and that most crops receive applications of a variety of pesticides, means that the occurrence of a compound in streams cannot, in general, be linked to one specific crop when many crops are grown in a given drainage basin.

The estimated load of the targeted pesticides applied to each study subbasin (table 10) was calculated (as shown for the examples in tables 4 and 5) as the product of the area of each crop type (table 7) and the estimated nominal application rates (tables 8 and 9), summed over each sampling season. The compound estimated to be applied in the far greatest amount in the entire study area was diuron, which was applied almost four times as much as the compound with the next highest use, 2,4,-D. These two herbicides, along with MCPA, are commonly used on many crops, including grass seed crops; their high rankings were partly a reflection of the relatively large amount of grass seed production in the study area as a whole. Similarly, chlorpyrifos, dicamba, and atrazine, though estimated to be applied in much lesser amounts, ranked fifth, sixth, and eighth in total application, respectively, largely because of their use on grass seed.

Atrazine, diuron, and 2,4-D were also among the four most heavily used compounds in pesticide use estimates for the Willamette River Basin from 1987, whereas MCPA ranked 11th overall according to the 1987 estimates (Reinhold and Witt, 1989; Anderson and others, 1996). Diuron, bromacil, and triclopyr are sometimes used along roadside rights-of-way, and estimates of their applications in this study are assumed to be low because these uses were not accounted for.

Of interest for their relative lack of estimated application were compounds frequently observed in past studies, notably atrazine and metolachlor. Although estimated atrazine usage ranked eighth on the list of compounds examined in this study, it ranked second in total applications in the Willamette River Basin in 1987 (Anderson and others, 1996). The sale of most formulations of atrazine has been restricted since 1993 (Meister, 1995), and the literature used for this study (Reinhold and Jenkins, 1993a, 1993b, 1994, 1996, 1997; Fisher and others, 1996; Pscheidt, 1996) reflects these restrictions. Nonetheless, atrazine remains available for purchase by individuals with pesticide application licenses, a group that includes commercial applicators and many growers. The sale and use of atrazine therefore may have remained prevalent in the Willamette River Basin in 1996 despite the increased regulatory restrictions. Similarly, although its sale is not restricted, the use of metolachlor may be much more widespread than is indicated by literature derived application rates.

An important source of potential discrepancies for the estimated application rates compared to actual use are special registrations for specific compounds. Under emergency conditions, these registrations allow the use of certain compounds on crops or for pests for which they may not have been previously registered, and for which no accounting may have been made in the available literature. For instance, metolachlor and pronamide have been approved for special registration under section 18 of the Federal Insecticide, Fungicide, and Rodenticide Act, or FIFRA (U.S. Environmental Protection Agency, 1972) for use on grass seed in 1996 and for several years prior. Many of these uses do not appear in published pesticide application estimates, despite the fact that the estimates are based on user

**Table 8.** Estimated nominal rate of application of herbicides to crops in study subbasins during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996

[Units are in pounds of active ingredient per acre. Compounds analyzed (table 3) that had no estimated application to crops in the basin are not included. Rates are adjusted for percent of acreage applied to. See table 4 for method to determine nominal rate of application. “—”, not applied. Rates for 2,4-D and MCPA are for reference purposes only; either 2,4-D or MCPA would be used on grass seed crops, but not both. Sources: Rinehold and Witt, 1989; Rinehold and Jenkins, 1993a, 1993b, 1994, 1996, 1997]

Crop type	2,4-D	2,4-DB	Alachlor	Atrazine	Bentazon	Bromoxynil	Butylate	Chloramben	Clopyralid	Dicamba	Dichlobenil	Diuron	EPTC	Ethalfuralin	MCPA	Metolachlor	Metribuzin	Napropamide	Norflurazon	Oryzalin	Pendimethalin	Pronamide	Simazine	Terbacil	Triallate	Triclopyr	Trifluralin
Alfalfa	—	0.05	—	—	—	0.01	—	—	—	—	—	0.55	0.35	—	—	—	0.15	—	—	—	—	0.07	—	—	—	—	—
Barley	—	—	—	—	—	.09	—	—	—	0.06	—	.71	—	—	0.49	—	.11	—	—	—	—	—	—	—	0.40	—	—
Snap beans	—	—	—	—	0.14	—	—	0.13	—	—	—	—	3.30	—	—	1.62	—	—	—	—	—	—	—	—	—	—	0.55
Beet seed	—	—	—	—	—	—	—	—	0.01	—	—	—	—	—	—	—	—	—	—	—	—	.75	—	—	—	—	—
Blueberries	0.02	—	—	—	—	—	—	—	—	—	0.20	.18	—	—	—	—	—	0.92	0.23	0.72	—	.03	0.12	0.04	—	—	—
Broccoli	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.20	—	—	—	—	—	—	—	.65	
Caneberries	—	—	—	—	—	—	—	—	—	—	.04	.41	—	—	—	—	—	.32	.15	.03	—	.07	.59	.04	—	—	—
Cherries	.19	—	—	—	—	—	—	—	—	—	.02	—	—	—	—	—	—	—	.12	.66	.01	—	.56	—	—	—	—
Christmas trees	.02	—	—	0.29	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.08	—
Clover	—	—	—	—	—	—	—	—	—	—	—	.66	.59	—	.09	—	—	—	—	—	—	.79	—	—	—	—	—
Corn	—	—	0.15	1.48	.20	—	0.08	—	—	—	—	—	—	1.11	—	.54	—	—	—	—	—	—	—	—	—	—	—
Fescue seed	.34	—	—	—	—	—	—	—	—	.13	—	2.02	—	—	.30	—	.05	—	—	—	—	—	—	—	—	—	—
Grapes	.01	.02	—	—	—	—	—	—	—	—	.05	.05	—	—	—	—	—	.01	—	.12	—	—	.31	—	—	—	—
Grass seed	.46	—	—	—	—	.01	—	—	.02	.13	—	1.43	—	—	.42	—	.03	—	—	—	—	—	—	—	—	—	—
Hay	—	.05	—	—	—	.01	—	—	—	—	—	.55	.35	—	—	—	.15	—	—	—	—	.07	—	—	—	—	—
Hazelnuts	.46	—	—	—	—	—	—	—	—	—	.08	.79	—	—	—	—	—	.04	.10	—	—	—	1.20	—	—	—	—
Hops	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.15	—	—	—	—	—	—	—	—
Meadowfoam	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mint	—	—	—	—	.75	.16	—	—	.10	—	—	—	—	—	—	—	—	.12	—	—	—	—	—	1.96	—	—	—
Mustard Seed	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Nursery	—	—	—	—	—	—	—	—	.01	—	.20	—	—	—	—	.02	—	.65	—	1.03	.05	—	.38	—	—	—	—
Nursery, container	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.25	—	.60	—	1.65	1.04	—	.12	—	—	—	—
Oats	—	—	—	—	—	.09	—	—	—	.07	—	.75	—	—	.66	—	—	—	—	—	—	—	—	—	—	—	—
Orchard grass seed	.36	—	—	—	—	—	—	—	—	.14	—	1.95	—	—	.33	—	.06	—	—	—	—	—	—	—	—	—	—
Pasture	.07	—	—	—	—	—	—	—	.01	.01	—	—	—	—	.03	—	—	—	—	—	—	—	—	—	—	—	—
Peaches	.03	—	—	—	—	—	—	—	—	—	.02	—	—	—	—	—	—	.04	—	.07	—	—	.12	—	—	—	—
Prunes	.07	—	—	—	—	—	—	—	—	—	.06	—	—	—	—	—	—	.03	—	.04	—	—	.14	—	—	—	—
Raspberries	—	—	—	—	—	—	—	—	—	—	.20	.35	—	—	—	—	—	.28	.12	.12	—	.11	.56	.17	—	—	—
Rye grain	.21	—	—	—	—	—	—	—	—	—	—	—	—	—	.01	—	—	—	—	—	—	—	—	—	—	—	—
Rears seed	.52	—	—	.02	—	.01	—	—	.04	.12	—	.99	—	—	.47	—	.02	—	—	—	—	—	—	—	—	—	—
Sod	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Squash	.07	—	—	—	—	—	—	.77	—	—	—	—	—	0.91	—	—	—	—	—	—	—	—	—	—	—	—	—
Strawberries	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.80	—	—	—	—	.92	—	—	—	—
Tomatoes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.24	—	—	—	—	—	—	—	—	—
Vegetables	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Walnuts	.04	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Wheat	.03	—	—	—	—	.14	—	—	—	.06	—	.71	—	—	.53	—	.11	—	—	—	—	—	—	—	.43	—	.05

**Table 9.** Estimated nominal rate of application of insecticides to crops in study subbasins during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996

[Values are in pounds of active ingredient per acre. Compounds analyzed (table 3) that had no estimated application to crops in the basin are not included. Rates are adjusted for percent of acreage applied to. See table 4 for method to determine nominal rate of application. —, not applied. Sources: Rinehold and Witt, 1989; Rinehold and Jenkins, 1993a, 1993b, 1994, 1996, 1997]

Crop type	Carbaryl	Carbofuran	Chlorpyrifos	Diazinon	Disulfoton	Ethoprop	Fonofos	Malathion	Methomyl	Methyl Azinphos	Methyl Parathion	Oxamyl	Parathion	cis-Permethrin	Phorate	Propargite	Terbufos
Alfalfa	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Barley	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Snap beans	1.05	—	0.05	0.38	—	0.33	0.17	0.04	—	—	—	—	—	—	—	—	—
Beet seed	.05	—	.50	.10	—	—	.10	—	—	—	—	—	—	—	—	0.07	—
Blueberries	.29	—	—	.48	—	—	—	.44	0.05	0.04	—	—	0.02	—	—	—	—
Broccoli	.15	—	1.60	.13	0.20	—	.62	—	.04	—	—	—	—	0.01	—	—	—
Caneberries	.82	—	—	.95	—	—	—	.53	—	.10	—	—	—	—	—	—	—
Cherries	—	—	.13	.65	—	—	—	3.62	—	.01	0.12	—	.86	—	—	—	—
Christmas trees	—	—	.06	.01	—	—	—	.01	—	—	—	—	—	—	—	—	—
Clover	—	—	.30	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Corn	—	—	.45	—	—	.50	.42	—	—	—	—	—	—	.03	—	—	0.01
Fescue seed	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Grapes	.06	0.01	—	—	—	—	—	.02	—	—	—	—	.04	—	—	—	—
Grass seed	—	—	.04	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hay	.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hazelnuts	.04	—	1.06	.07	—	—	—	—	—	.19	—	—	—	—	—	—	—
Hops	—	—	1.00	1.50	—	—	—	—	—	—	—	—	—	—	—	1.73	—
Meadowfoam	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mint	—	—	.78	—	—	—	1.42	.01	—	—	—	0.68	—	—	—	.57	—
Mustard seed	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Nursery	—	—	.25	.11	—	—	.10	—	—	—	—	—	—	—	—	.05	—
Nursery, container	—	—	.40	.04	—	—	—	—	—	.03	—	—	—	—	—	—	—
Oats	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Orchard grass seed	—	—	.88	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pasture	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Peaches	—	—	—	.38	—	—	—	—	—	—	—	—	—	—	—	—	—
Prunes	.46	—	.30	.75	—	—	—	—	—	—	—	—	.25	—	—	—	—
Raspberries	.14	—	—	.77	—	—	—	.92	—	.02	—	—	.01	—	—	—	—
Rye grain	—	—	—	—	—	—	—	—	—	—	—	—	.05	—	—	—	—
Ryegrass seed	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sod	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Squash	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Strawberries	.18	.30	.72	.04	—	—	.02	.03	—	.22	—	—	—	—	—	.22	—
Tomatoes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Vegetables	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Walnuts	—	—	—	.26	—	—	—	2.70	—	—	—	—	—	—	—	—	—
Wheat	—	—	—	—	.01	—	—	—	—	—	—	—	—	—	0.02	—	—

**Table 10.** Total mass of the 20 pesticides included in the study that were estimated to have the highest application quantities in the 16 agricultural study subbasins. Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996  
 [Values are in pounds of active ingredient]

Compound	Nonintensive, diverse subbasins					Intensive, diverse subbasins					Intensive, nondiverse subbasins					All Basins	
	UT Ash Swale	Baker	Chicken	SF Ash	Shafer	Senecal	UT S Yamhill	Deer	W Champoeg	WF Palmer	Simpson	Truax	UT Shedd	UT Flat	UT Oak		Lake
Diuron	528	1,120	345	1,593	458	2,103	2,994	1,256	1,610	1,891	1,679	3,518	1,992	4,654	4,585	7,757	38,083
2,4-D	61	283	97	67	91	85	70	66	4	137	7	1,422	841	1,720	2,181	2,779	9,912
MCPA	128	331	38	383	1	782	1,232	503	553	761	412	48	1	41	0	192	5,405
EPTC	90	182	41	258	3	610	413	462	1,012	1,600	0	196	14	214	19	175	5,289
Chlorpyrifos	97	554	214	180	38	600	99	390	1,049	1,012	43	74	0	172	7	143	4,671
Dicamba	27	38	12	109	29	190	216	130	153	129	134	357	208	437	518	736	3,427
Diazinon	81	333	53	25	4	511	21	161	1,611	199	1	0	0	2	0	0	3,004
Atrazine	8	112	89	20	182	151	91	417	180	1,183	39	197	27	52	74	83	2,904
Simazine	148	790	266	171	3	344	9	266	76	372	5	0	0	30	0	0	2,480
Malathion	422	1,179	170	88	8	40	7	50	70	157	2	0	0	0	0	1	2,193
Propargite	0	4	6	0	1	416	1	16	1,666	14	24	0	0	0	0	40	2,189
Oryzalin	70	266	88	16	1	229	3	318	52	908	0	0	0	0	0	0	1,950
Metolachlor	0	1	1	0	0	264	9	210	467	733	0	55	0	0	0	0	1,740
Metribuzin	57	84	19	134	12	96	291	42	57	201	40	95	48	194	102	176	1,649
Napropamide	3	92	79	5	0	308	2	254	89	370	5	0	0	1	0	8	1,217
Carbaryl	10	110	24	20	1	216	37	131	307	215	0	2	1	13	1	0	1,088
Triallate	51	16	0	0	0	107	396	14	2	364	6	32	0	28	0	49	1,065
Fonofos	0	6	6	0	0	111	2	183	94	410	58	43	0	0	0	100	1,014
Pronamide	18	43	14	52	1	20	119	21	20	321	0	72	3	43	4	233	982
Ethoprop	0	0	0	0	0	87	2	137	138	432	0	51	0	0	0	0	847

surveys (Rinehold and Jenkins, 1993a, 1993b, 1994, 1996, 1997). Also, special registrations for other compounds may have been enacted since these estimates were published.

## GENERAL WATER QUALITY FINDINGS

Water quality results are given here as an overview of the study's findings taken as a whole. These include summaries of concentrations, a comparison with other studies, an evaluation of the conformance to water quality standards and criteria, and implications for toxicity in the study streams. Subsequent sections address specific findings regarding pesticide detections at certain sites, land use and seasonal components of the data, and the relation between estimated pesticide applications and occurrence in streams.

## Pesticide Detections and Concentrations

A total of 36 pesticides (29 herbicides and 7 insecticides) were detected during the Phase III study (table 11). There were slightly fewer than 100 samples (5 at each of the 20 sites) because 5 sites (UT Shedd, UT S Yamhill, Lake, UT Oak, and SF Ash) were dry or had no flowing water during the summer. As a result of analytical interferences, pesticide concentrations for some compounds were occasionally censored at MDLs that deviated from the standard MDLs listed in tables 2 and 10; for four of these compounds the highest reported MDL was within the range of detected concentrations that included the lowest percentile shown in table 11. In these four cases the percentile statistics were computed using a statistical procedure that fits a probability distribution to the data set using both the detections and the nondetections (Helsel and

**Table 11.** Summary statistics for pesticides detected during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996 [All samples are included in calculations. One microgram per liter ( $\mu\text{g/L}$ ) is equal to one part per billion; The method detection limit (MDL) is defined as the concentration at which there is a 99% chance that a detected compound is actually present, and a 50% chance that a nondetected compound is actually present; \*, Compound had nondetections censored at values interspersed within a range of detected concentrations above the lowest indicated percentile, so summary statistics were computed according to Helsel and Cohn (1988); <, not detected at the MDL]

Compound	MDL ( $\mu\text{g/L}$ )	Number of samples	Number of detections	Detection frequency (percent of samples)	Concentration at indicated percentile ( $\mu\text{g/L}$ )				Maximum ( $\mu\text{g/L}$ )
					25	50	75	90	
Atrazine	0.001	95	94	99	0.027	0.071	0.26	1.3	90
Desethylatrazine	.002	95	88	93	.006	.012	.033	.1	.24
Simazine	.005	95	81	85	.008	.022	.069	.41	1.0
Metolachlor	.002	95	81	85	.004	.017	.14	.96	4.5
Diuron	.020	94	69	73	<	.26	1.5	4.2	29
Tebuthiuron *	.010	95	35	37	<	<	.021	.078	.32
Pronamide	.003	95	34	36	<	<	.01	.084	.62
Prometon *	.018	95	33	35	<	<	.013	.019	.046
Metribuzin	.004	95	29	31	<	<	.029	.17	5.3
Diazinon	.002	95	25	26	<	<	.007	.031	.31
Triclopyr	.050	94	22	23	<	<	<	.55	6.0
EPTC	.002	95	21	22	<	<	<	.016	.89
Ethoprop	.003	95	21	22	<	<	<	.014	.44
2,4-D	.035	94	20	21	<	<	<	.22	10
Dichlobenil *	.020	93	20	21	<	<	<	.036	.23
Terbacil	.007	95	15	16	<	<	<	.019	.97
Bromacil	.035	94	14	15	<	<	<	.31	51
Chlorpyrifos	.004	95	13	14	<	<	<	.009	3.3
Triallate	.001	95	12	13	<	<	<	.008	.070
Carbaryl *	.003	95	12	13	<	<	<	.027	.11
MCPA	.050	94	9	10	<	<	<	<	.98
Trifluralin	.002	95	6	6	<	<	<	<	.023
Dicamba	.035	94	5	5	<	<	<	<	14
Oryzalin	.019	94	4	4	<	<	<	<	3.2
Carbofuran	.003	95	4	4	<	<	<	<	.084
DCPA	.002	95	4	4	<	<	<	<	.003
Napropamide	.003	95	4	4	<	<	<	<	.011
Fonofos	.003	95	3	3	<	<	<	<	.012
Propachlor	.007	95	3	3	<	<	<	<	.051
Bentazon	.014	94	3	3	<	<	<	<	.24
Malathion	.005	95	1	1	<	<	<	<	.030
Alachlor	.002	95	1	1	<	<	<	<	.005
Norflurazon	.024	94	1	1	<	<	<	<	.02
Dinoseb	.035	94	1	1	<	<	<	<	.19
Bromoxynil	.035	94	1	1	<	<	<	<	.22
Propanil	.004	95	1	1	<	<	<	<	.066

Cohn, 1988). For example, one sample for atrazine was reported as  $< 0.010 \mu\text{g/L}$  even though its standard MDL is  $0.001 \mu\text{g/L}$ . In this case, the one nonstandard MDL is less than the 25<sup>th</sup> percentile of the distribution and there is no effect on the percentiles shown in table 11. In contrast, although the standard MDL for tebuthiuron is  $0.010 \mu\text{g/L}$  (table 2), concentrations for 2 of the 60 nondetections were reported as  $<0.047$  and  $<0.055 \mu\text{g/L}$ . These censored values are higher than 50% of the distribution values (including both detections and non-detections); hence, the upper quartile of the distribution for tebuthiuron was fitted to a probability distribution as described by Helsel and Cohn (1988).

Five compounds were detected in about three-quarters or more of all samples—those “frequently detected” compounds were atrazine, desethylatrazine, simazine, metolachlor, and diuron. Desethylatrazine is a degradation product of atrazine; as such its occurrence in conjunction with atrazine is expected and does not indicate direct application of the compound. Desethylatrazine is left out of some of the interpretive discussions that follow for that reason. Of the five frequently detected compounds, all but diuron were detected at every site, regardless of upstream land use; indeed, there was only one sample in which atrazine was *not* detected. An intermediate group of “occasionally detected” compounds, detected in approximately 10-40% of the samples, included tebuthiuron, pronamide, prometon, metribuzin, diazinon, EPTC, triclopyr, ethoprop, 2,4-D, dichlobenil, terbacyl, bromacil, chlorpyrifos, triallate, carbaryl, and MCPA. Finally, the most “rarely detected” compounds (operationally defined as detected in less than 10% of samples) included trifluralin, fonofos, dicamba, napropamide, oryzalin, carbofuran, DCPA, propachlor, bentazon, malathion, alachlor, norflurazon, dinoseb, bromoxynil, and propanil.

The list of detected compounds is similar to an aggregate of results from Phases I and II of the Willamette River Basin Water Quality Study (Anderson and others, 1996) and the Willamette NAWQA study (Rinella and Janet, in press) (table 12). In those basinwide studies, sites were selected and sampled with different objectives

than in the Phase III study, resulting in a combined data set that has sampling sites draining a wide range of basin sizes and upstream land uses, and unequal numbers of samples among sites. Nonetheless, with a total number of pesticide samples from 1992-96 that ranges from approximately 165 to 235, this “previous” dataset represents the best available data for comparison with the Phase III study results. Pesticides detected in the previous studies that were not detected during Phase III were not included in table 12.

No compounds were detected in this study that have not been previously found in streams in the Willamette River Basin, although the detection frequencies and relative rank, for compounds other than the frequently detected compounds, vary among the datasets. For instance, the herbicide bromacil, which is used in noncropland areas and along rights-of-way, was detected in 15% of the samples in this study, whereas its detection rate was 2% in the aggregated data from the previous studies. Other herbicides detected more frequently in the Phase III study than in the previous studies included tebuthiuron, pronamide, metribuzin, triclopyr, 2,4-D, dichlobenil, triallate, and MCPA. Conversely, several compounds, notably EPTC, terbacyl, DCPA, trifluralin, napropamide, and all insecticides, were detected less frequently during Phase III than previously.

Seventy-fifth percentile concentrations for many pesticides detected in Phase III were slightly higher than for those detected previously, but generally remained within a factor of two of the previous values. The most distinct difference in pesticide concentrations between Phase III and previous studies is not the median or 75th percentile concentrations, but rather the large number of concentrations that are particularly high (more than  $1 \mu\text{g/L}$ , for instance). Maximum concentrations were higher than previously observed for 16 of the 36 detected pesticides, including 13 for which there were multiple detections at concentrations greater than the previous maximum. Maximum concentrations were one to two orders of magnitude higher than previously observed for atrazine, metribuzin, triclopyr, 2,4-D, bromacil, dicamba, oryzalin, and chlorpyrifos. Pesticides for which the 75th percentile and maximum

**Table 12.** Comparison of concentrations of herbicides and insecticides from the Phase III study with concentrations from previous U.S. Geological Survey studies in the Willamette River Basin, Oregon

[Pesticides are arranged in order of decreasing detections in Phase III. Total number of samples for previous studies varies by constituent but ranged from approximately 165 to approximately 235. Data source U.S. Geological Survey's Water Storage and Retrieval System (WATSTORE); µg/L, micrograms per liter; \*, maximum concentration is from Zollner Creek near Mount Angel; <, not detected at the method detection limit (MDL). Refer to table 2 for listing of MDLs]

Compound Name	Value from previous studies in Willamette River Basin			Value from Phase III Study			Number of Phase III data points exceeding previous maximum
	Detection frequency (percent of samples)	75th percentile (µg/L)	Maximum (µg/L)	Detection frequency (percent of samples)	75th percentile (µg/L)	Maximum (µg/L)	
<b>Herbicides</b>							
Atrazine	91	0.15	4.5 *	99	0.26	90	17
Desethylatrazine	54	.013	.27 *	93	.033	.24	0
Simazine	79	.12	5.8 *	85	.069	1.0	0
Metolachlor	76	.049	3.3	85	.14	4.5	2
Diuron	53	.53	14 *	73	1.5	29	4
Tebuthiuron	21	<	.14	37	.021	.32	4
Pronamide	15	<	.098	36	.01	.62	8
Prometon	27	.006	.076	35	.013	.046	0
Metribuzin	18	<	.41	31	.029	5.3	5
Triclopyr	8	<	.72	23	<	6.0	8
EPTC	33	.005	1.0 *	22	<	.89	0
2,4-D	11	<	.79 *	21	<	10	5
Dichlobenil	4	<	.42	21	<	.23	0
Terbacil	28	.010	1.0	16	<	.98	0
Bromacil	2	<	.20	15	<	51	12
Triallate	3	<	.011	13	<	.070	5
MCPA	2	<	.63	10	<	.98	3
Trifluralin	15	<	.036	6	<	.023	0
Dicamba	2	<	.29	5	<	14	3
Oryzalin	1	<	.23	4	<	3.2	1
DCPA	31	.002	.061	4	<	.003	0
Napropamide	31	.012	1.7 *	4	<	.011	0
Propachlor	4	<	.024	3	<	.051	0
Bentazon	4	<	1.2	3	<	.24	0
Alachlor	6	<	.36 *	1	<	.005	0
Norflurazon	1	<	.45 *	1	<	.020	0
Dinoseb	5	<	1.0 *	1	<	.19	0
Bromoxynil	2	<	.11 *	1	<	.22	1
Propanil	1	<	.004	1	<	.066	1
<b>Insecticides</b>							
Diazinon	51	.017	1.2 *	26	.007	.31	0
Ethoprop	25	.003	3.1	22	<	.44	0
Chlorpyrifos	30	.006	.40 *	14	<	3.3	2
Carbaryl	22	<	2.0	13	<	.11	0
Carbofuran	25	.012	9.0 *	3	<	.084	0
Fonofos	22	<	.10 *	3	<	.012	0
Malathion	8	<	.24 *	1	<	.030	0

concentrations decreased in the Phase III study compared to the previous studies include primarily simazine, EPTC, DCPA, napropamide, bentazon, dinoseb, and all of the insecticides except chlorpyrifos.

Differences in detection frequency and maximum concentrations of the various pesticides are expected between studies in the basin because of differing study objectives, site types, and time periods encompassed. However, many of the differences between the Phase III and previous study results are obscured by data from one site: Zollner Creek near Mount Angel, a small subbasin (15 mi<sup>2</sup>) with intensive agriculture and diverse crop types (46% row crops, less than 50% grass and wheat, 4% forested [Tetra Tech, Inc. and E&S Environmental Chemistry, 1995]), which was sampled in both the Willamette NAWQA and the Phase I and II studies. For example, insecticides have been detected at unusually high frequencies at Zollner Creek—carbofuran, diazinon, fonofos, ethoprop, and chlorpyrifos were each detected in at least 66% of samples from Zollner Creek from 1993-95. In fact, many of the highest pesticide concentrations in the combined Phase I and II and NAWQA dataset were from the Zollner Creek site, and it was sampled many times (about 30) for long-term trend analysis and intensive surveys in the Pudding River Basin (Rinella and Janet, in press). To investigate that site's effect on the previous dataset, the summary statistics in table 12 were recomputed with Zollner Creek data excluded. This resulted in (1) lowering maximum concentrations for 16 of the pesticides, which increased the importance of the respective Phase III maximums for 6 pesticides (desethylatrazine, EPTC, norflurazon, dinoseb, bromoxynil, and diazinon), (2) lowering the detection frequency for 26 pesticides in the previous studies, including all insecticides, and (3) increasing the detection frequency for 3 herbicides (tebuthiuron, prometon, and triallate) in the previous studies that were rarely detected at Zollner Creek.

The Zollner Creek subbasin is similar to the "intensive, diverse" Phase III subbasins (table 6) on the basis of upstream land uses and the relative lack of forested area. Although Zollner Creek

was not the only such subbasin represented in the combined dataset from the previous studies (see Anderson and others, 1996, or Rinella and Janet, in press for others), it was the smallest and was sampled much more often than most of the other sites in that dataset. Removing Zollner Creek from the previous dataset effectively makes table 12 a comparison of data from streams draining larger, more mixed-use subbasins (including a higher percentage of forested lands) and streams draining smaller subbasins with less forested lands and more intensive agricultural land uses. The large number of high concentrations in Phase III samples is not, therefore, an indication of declining water quality in the Willamette River Basin, but rather it indicates that the smaller streams sampled in Phase III were closer to the places of application of many of these pesticides than the larger or higher order streams generally sampled during Phases I and II or by NAWQA. Sampling during peak runoff conditions in the Phase III study apparently coincided with periods of high concentration pulses, whereas these pulses were probably somewhat attenuated by dilution or dispersion in the larger streams sampled previously.

It is noteworthy that no organochlorine insecticides such as *p,p'*-DDE (a metabolite of DDT), dieldrin, or lindane were detected during Phase III. These compounds have been previously observed in water, sediment, and tissues in Willamette River Basin streams ranging in size from small (Champoeg Creek, Johnson Creek) to large (Willamette River at Portland) (Rinella, 1993; Edwards, 1994; Oregon Department of Environmental Quality, 1994; Anderson and others, 1996; Oregon Department of Environmental Quality, 1996; Rinella and Janet, in press). For this reason the Willamette River Basin is commonly deemed an important potential source of such compounds to the lower Columbia River. The largest proportion of DDT (or its metabolites) is expected to be associated with suspended sediment, but *p,p'*-DDE often is detected in filtered water samples if total DDT and suspended sediment concentrations in the water column are high. DDT and its metabolites were the most commonly detected organic compounds in fish tissues from the Willamette Basin in studies conducted by ODEQ (1994) and by Wentz and others (in press). Therefore, although there could be

small concentrations of organochlorines that are preferentially located in stream sediments or the tissues of aquatic biota, the lack of detections in the water (despite sometimes high suspended sediment concentrations) implies that the Phase III study basins are not large sources for these compounds. This finding reinforces the conclusion from Anderson and others (1996) that the occurrence of DDT and other organochlorines in small streams in the Willamette River Basin is a site-specific phenomenon, dependent on local land and pesticide use history, rather than a basin-wide water quality problem. Larger streams in the basin, that are more subject to sediment deposition and that have had a wide variety of upstream land uses including historical use of organochlorines, may continue to store compounds such as DDT which can be transported during high flows.

**Immunoassay Analyses**—Results of immunoassay analysis are summarized in table 13. The conclusions obtained from the immunoassay data collected during Phase III are broadly similar to the conclusions based on the GC/MS data, although more processes (hydrologic response and winter baseline concentrations) were examined than would have been feasible with the more expensive GC/MS methods. Differing numbers of samples for immunoassays were collected from each site, making statistical comparisons difficult across sites. For this reason, the quantiles indicated in table 13 are based on the number of samples from each site. Samples from UT Oak, UT Shedd Slough, and Lake had the highest concentrations of both atrazine and metolachlor of the 16 agricultural sites sampled in this study, as measured by immunoassay. Samples from each of these three sites exceeded the MCL of 3 µg/L for atrazine at least once. Concentrations at UT Oak Creek exceeded the MCL in more than one-half of the immunoassay samples collected at this site and also had the maximum atrazine concentration measured by immunoassay in the basin (more than 100 µg/L, confirmed by the GC/MS as 90 µg/L). Samples from Shafer Creek had a maximum atrazine concentration of 2 µg/L (table 13). Christmas tree plantations make up 38 percent of the Shafer Creek drainage area, and weed control on Christmas tree plantations is one of the few unrestricted uses remaining for atrazine (William,

1996; American Crop Protection Association, 1996). Of the four urban sites, Beaverton Creek had the largest atrazine concentration (0.24 µg/L) measured by immunoassay. This is most likely not due to a large atrazine concentration (GC/MS value of 0.032 µg/L) but rather to the effect on the immunoassay of a large simazine concentration (GC/MS value of 1.0 µg/L). Simazine is a structurally related triazine compound used for nonselective weed control in industrial areas, fairways, and lawns (Meister, 1995), and Beaverton Creek had the largest simazine concentration measured in this study.

### **Water Quality Criteria and Standards, and Toxicological Significance of Detected Pesticides**

Constituents analyzed in this study for which water quality standards or criteria have been established by the State of Oregon or the U.S. Environmental Protection Agency, including conventional constituents, are shown in table 14. Exceedances of stream temperature and DO standards were determined after consultations with fisheries biologists from the Oregon Department of Fish and Wildlife to evaluate the fish species present in the study streams. The fish species are used by ODEQ to determine the applicable criteria for a particular stream segment (Oregon Administrative Rules, Chapter 340, Division 41, 1996). Only the pesticides that were detected in the study and for which there are established criteria are included in the table.

Maximum contaminant levels (MCLs, drinking water standards) are not shown in table 14 because the streams studied are not likely to be used for drinking water sources. However, there may be shallow wells used for drinking water in agricultural areas near the study streams, and stream concentrations may reflect short term water quality conditions in such wells. The MCL for atrazine, 3.0 µg/L, was exceeded in a total of 7 samples from UT Oak, Lake, and UT Shedd. Concentrations for no other pesticides exceeded their MCLs.

Water quality data collected for this study represent instantaneous concentrations, and streams

**Table 13.** Summary statistics of immunoassay analyses of atrazine and metolachlor concentrations in samples collected at Phase III sites in Willamette River Basin, Oregon, during 1996

[Statistics are based on all samples. Refer to table 6 for complete listing of site names; µg/L, micrograms per liter; —, too few samples taken for indicated statistic to apply]

Map Index number	Site name	Number of samples	Minimum (µg/L)	Concentration at indicated percentile (µg/L)			Maximum (µg/L)
				25	50	75	
<b>Atrazine immunoassays</b>							
U1	Dixon	4	<0.028	—	0.093	—	0.14
U2	Beaverton	3	.030	—	.16	—	.24
U3	Pringle	2	<.028	—	—	—	.028
U4	Claggett	11	<.028	<0.028	<.028	0.064	.094
43	UT Ash Swale	5	<.028	<.028	.065	.092	.096
09	Baker	5	<.028	<.028	.099	.18	.21
10	Chicken	4	<.028	—	<.028	—	.052
69	SF Ash	3	.080	—	.12	—	.12
104	Shafer	2	.67	—	—	—	2.0
37	Senecal	24	<.028	.030	.032	.098	.48
48	UT S. Yamhill	3	.34	—	.37	—	.42
27	Deer	6	.080	.12	.18	.29	.29
39	W Champoeg	8	.028	.069	.20	.37	.59
40	WF Palmer	8	.042	.11	.24	.26	.30
61	Simpson	3	.084	—	.085	—	.10
86	Truax	10	.11	.30	.36	.48	.90
94	UT Shedd	7	.43	.53	.90	8.6	62
106	UT Flat	3	.067	—	.085	—	.18
80	UT Oak	10	.83	2.0	4.1	17	>100 <sup>a</sup>
81	Lake	21	.13	.80	2.8	4.2	21
	<b>All sites</b>	142	<.028	.041	.18	.69	>100
<b>Metolachlor immunoassays</b>							
U1	Dixon	4	<.06	—	<.06	—	<.06
U2	Beaverton	3	<.06	—	.07	—	.13
U3	Pringle	2	<.06	—	—	—	.07
U4	Claggett	10	<.06	<.06	.10	.13	.64
43	UT Ash Swale	4	<.06	<.06	<.06	<.06	<.06
09	Baker	4	<.06	—	.08	—	.16
10	Chicken	4	<.06	—	<.06	—	<.06
69	SF Ash	3	<.06	—	.08	—	.12
104	Shafer	3	<.06	—	.07	—	.08
37	Senecal	23	<.06	<.06	<.06	.08	.26
48	UT S. Yamhill	3	<.06	—	<.06	—	.10
27	Deer	6	.07	.11	.13	.16	.19
39	W Champoeg	8	<.06	<.06	<.06	.09	.11
40	WF Palmer	7	.08	.24	.57	.92	1.0
61	Simpson	4	<.06	—	<.06	—	.08
86	Truax	10	.12	.24	.40	.80	1.6
94	UT Shedd	7	.26	.45	.98	2.0	3.6
106	UT Flat	3	.09	—	.10	—	.13
80	UT Oak	10	.41	.46	.95	1.7	3.1
81	Lake	20	.12	.49	1.7	2.0	2.9
	<b>All sites</b>	138	<.06	<.06	.11	.55	3.6

<sup>a</sup> Sample never diluted enough to determine final concentration.

**Table 14.** Exceedances of Oregon Department of Environmental Quality standards or criteria for streams sampled during Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996

[Pesticides that were not detected are not included; —, no exceedances noted; Standards and Criteria: water temperature standard, maximum temperature 20 degrees Celsius (68 degrees Fahrenheit); dissolved oxygen standard, absolute minimum (one time measurement) 4.0 milligrams per liter for streams supporting cool and warm water fish species; pH standard, maximum 8.5 pH units; nitrate-nitrogen standard, maximum 10.0 milligrams per liter; ammonia-nitrogen toxicity standard, based on revised tables of allowed ammonia concentration according to temperature and pH, for streams with salmonids absent; fecal coliform bacteria (standard prior to January 1996, 400 colonies/100 mL (milliliters); *E. coli* bacteria (standard after January 1996), maximum 406 colonies/100 mL; chlorpyrifos, aquatic life chronic toxicity criteria (CTC), 0.041 micrograms per liter (µg/L), aquatic life acute toxicity criteria (ATC), 0.083 µg/L; 2,4-D State of Oregon criteria for the protection of human health for ingestion of water and fish (HHP), 100 µg/L; malathion CTC, 0.1 µg/L. Sources: U.S. Environmental Protection Agency, written commun., revised tables for determining freshwater ammonia concentrations, 1992; Oregon Administrative Rules (OAR), Chapter 340, Division 41, 1996]

Site	Conventional constituents (number exceedances/number of samples)							Pesticides			
	Water temperature	Dissolved oxygen	pH	Nitrate-nitrogen	Ammonia-nitrogen	Fecal coliform bacteria	<i>E. coli</i> bacteria	Chlorpyrifos		2,4-D (HHP)	Malathion (CTC)
								(CTC)	(ATC)		
<b>Urban sites</b>											
Dixon	1/5	—	—	—	—	2/2	1/2	—	—	—	—
Beaverton	1/5	1/5	—	—	—	2/3	2/3	—	—	—	—
Pringle	1/5	—	—	—	—	2/2	2/2	—	—	—	—
Claggett	—	—	—	—	—	3/3	3/3	—	—	—	—
<b>Agricultural sites</b>											
UT Ash Swale	1/5	—	—	—	—	2/3	2/3	—	—	—	—
Baker	—	—	—	—	—	2/3	1/3	—	—	—	—
Chicken	—	—	—	—	—	1/2	—	—	—	—	—
SF Ash	—	—	—	—	—	2/4	2/4	—	—	—	—
Shafer	1/5	—	—	—	—	3/4	3/4	—	—	—	—
Senecal	—	3/6	—	—	—	2/4	2/4	—	—	—	—
UT S Yamhill	—	—	—	—	—	1/3	1/3	—	—	—	—
Deer	—	—	—	—	—	2/3	1/3	—	—	—	—
W Champoeg	1/5	2/5	—	2/5	1/4	3/3	4/4	—	—	—	—
WF Palmer	1/5	—	—	4/5	—	2/3	1/3	3/5	3/5	—	—
Simpson	1/5	—	—	—	—	1/4	2/4	—	—	—	—
Truax	1/5	1/4	—	1/5	—	3/4	3/4	—	—	—	—
UT Shedd	—	—	—	—	—	3/3	3/3	—	—	—	—
UT Flat	1/5	—	1/5	—	—	2/4	2/4	—	—	—	—
UT Oak	—	—	—	—	1/4	3/4	3/4	—	—	—	—
Lake	—	—	—	—	—	2/2	2/2	—	—	—	—

generally were sampled during transient conditions (stormflow), generally with a month or longer between samplings. Therefore, the standard for DO used in table 14 is based on an absolute minimum DO for surface water samples (4.0 mg/L for both “cool” and “warm” water streams) because the sampling strategy did not accommodate the time intervals required to evaluate the 7-day minimum mean concentration (5.0 mg/L for cool water streams) or the 30-day mean minimum concentration (6.5 mg/L for cool and 5.5 mg/L for warm water streams) specified in the regulations (Oregon Administrative Rules, Chapter 340, Division 41). For bacteria, the State standards (which are for water contact) are based on either a 30-day log-mean count of colonies with a minimum of five samples, or on an absolute maximum count. For table 14 only the maximum count was considered. Acute toxicity criteria for pesticides are based on either instantaneous concentrations or 1-hour-average concentrations that must not be exceeded more than once every 3 years, depending on the constituent. Likewise, chronic toxicity criteria are not to be exceeded for more than 24 hours or 4 days once every 3 years depending on the constituent. Consequently the results in table 14, although indicative of conditions at the time of sampling, technically represent only “potential” exceedances of the criteria, particularly the chronic toxicity criteria.

### Conventional Constituents

By far the most frequently exceeded standard was that for *E. coli* bacteria, which was exceeded at least once at each site except Chicken Creek. The former fecal coliform standard was also exceeded at all sites; however, it is no longer used by the State for regulatory purposes in fresh waters (Oregon Administrative Rules, Chapter 340, Division 41, 1996). Samples from several sites (W Champoeg, Lake, UT Shedd, Claggett, and Pringle) exceeded the *E. coli* standard in each sample. Most sites had individual samples with *E. coli* counts that were well over 1,000 colonies per 100 mL (milliliters); exceptions were Chicken, Simpson, and SF Ash. The highest *E. coli* counts, in excess of 10,000 colonies per 100 mL, were observed at W Champoeg and UT Oak. Most of the bacterial counts exceeding standards occurred in samples collected during high flow

(spring or fall) rather than low flow (summer); however, counts from samples at 9 of the 15 sites that had flowing water during the summer sampling also exceeded the standard.

Sources of the high bacterial counts are uncertain. Fecal coliform and *E. coli* bacteria are indicators of fecal contamination in water. These bacteria are found in the gut of warm blooded animals but fecal coliform bacteria may also be associated with soils. Therefore, the occurrence of fecal bacteria does not conclusively indicate the presence of fecal material. However, *E. coli* would not be from non-fecal sources, thus the presence of this indicator bacterium indicates a potential health hazard. Although livestock, waterfowl, and dairies could be sources of *E. coli*, and these sources were observed in many of the study basins, with animals sometimes within the riparian areas or streams themselves, no specific accounting was made of these animals. Also urban streams (presumably without livestock upstream) had bacterial counts that exceeded standards at similar frequencies to agricultural sites. Pringle Creek, for example, was previously known to frequently exceed bacterial standards (Keith Chapman, City of Salem, oral commun., 1996).

All of the temperatures that exceeded 20 degrees Celsius were measured during the summer low flow sampling. Of the 15 streams with flow during summer, 10 exceeded the temperature standard, including 3 of the 4 urban sites and 7 of 11 agricultural sites. Riparian conditions are important in maintaining cool water during the summer—each of the 4 agricultural streams that did not exceed the temperature standard has a relatively dense riparian canopy that shades much of the stream’s length, particularly near the sampling sites.

In contrast to temperature, summertime DO was below the State standard of 4.0 mg/L only at one site (Truax). Several other sites (Senecal, W Champoeg, UT Flat, Claggett) also had relatively low DO concentrations (between 4 and 6 mg/L) during the summer, indicating that they might have violated the standard on other days during the summer or early in the mornings. DO was below the State standard at both W Champoeg and Senecal in the spring and fall, suggesting that the water at

those sites was composed largely of anoxic ground water except during winter. This hypothesis was supported for Senecal by one suspended sediment sample from the fall in which a red flocculent material, presumably composed of iron minerals, precipitated after sampling and prior to analysis. This type of reaction occurs when iron-rich ground water that has little DO is exposed to atmospheric oxygen. DO in that sample was 0.8 mg/L. No ground water samples were taken, however, so the question of ground water contribution of low dissolved oxygen, nutrients, or pesticides to these streams cannot be answered with the current data.

Only one site had a pH value higher than the State standard (8.6 at UT Flat during spring). High pH values can exacerbate the toxicity of many constituents, particularly metals, to aquatic biota.

Nutrient concentrations were relatively high at several sites. Nitrate concentration exceeded 10 mg/L in four of the five samples at WF Palmer, and it was more than 9 mg/L in the other; two samples had nitrate concentrations higher than 20 mg/L. At W Champoeg, concentrations were as high as 18 mg/L. Likewise, ammonia concentrations in one sample each from W Champoeg and UT Oak were higher than the concentration determined by the USEPA to cause toxicity concerns (written commun.—revised tables for determining average freshwater ammonia concentrations, 1992). Additionally, ammonia concentrations were higher than 1 µg/L in six other samples (from Truax, UT Oak, Lake, WF Palmer, and W Champoeg), indicating the potential for ammonia toxicity at other times if temperature and pH were to be elevated. Although there are no Federal or State standards for phosphorus concentrations in water, the USEPA recommends that a desired goal for the prevention of excessive aquatic plant growth is 0.1 mg/L as P (U.S. Environmental Protection Agency, 1986). Total phosphorus concentrations were higher than 0.1 mg/L at least once at every site except Simpson and SF Ash, and were higher than 1.0 mg/L at W Champoeg, UT Oak, and UT Shedd. These concentrations are noteworthy because phosphorus is often considered the limiting nutrient in streams (Wetzel, 1983), and issues associated with nutrient

loading and eutrophication in the Willamette River Basin are a continuing concern (Tetra Tech, Inc., 1995d; Oregon Department of Environmental Quality, 1996).

### Pesticides

Toxicity criteria have been established by the U.S. Environmental Protection Agency (USEPA) for only 5 of the 86 pesticides analyzed in this study, and 2 of these were not detected in any samples (methoxychlor and parathion). Of the three remaining, there were exceedances only for chlorpyrifos at WF Palmer; chlorpyrifos was detected in each sample at that site, including the three highest concentrations (0.31, 0.87, and 3.3 µg/L, respectively) reported in the Willamette River Basin by the USGS (Anderson and others, 1996; Rinella and Janet, in press).

Other compounds were detected at concentrations that may be harmful to aquatic life, but for which the State of Oregon or the USEPA have not established aquatic toxicity criteria. For instance, the National Academy of Sciences and National Academy of Engineering (NAS/NAE) (1973) recommended instantaneous threshold values that are sometimes used as guidelines for aquatic toxicity for compounds for which more rigorous USEPA toxicity criteria have not been established. NAS/NAE values for carbaryl (0.02 µg/L) and diazinon (0.009 µg/L) were exceeded in 92 and 33 percent of the samples in which they were detected, respectively. Malathion was detected in only one sample; this concentration was 0.008 µg/L which is equal to the NAS/NAE guideline. The Canadian water quality guidelines, established by the Canadian Council of Resources and Environment Ministers (1996), or CCRM, are used for reference purposes in a manner similar to the NAS/NAE values. CCRM values for aquatic life criteria are established for 22 of the compounds studied in Phase III, but were exceeded for only 4. These exceedances were for atrazine (CCRM value 2 µg/L), 2,4-D (4 µg/L), dicamba (14 µg/L), and metribuzin (1 µg/L) in 9, 15, 20, and 7% of the samples in which they were detected, respectively.

Because there are few water quality criteria for the pesticides studied, it is difficult to assess the impact of observed concentrations on aquatic life.

In order to evaluate the toxicity of the waters sampled, a relatively consistent reference level was needed for comparison. Literature values for the concentration of a specific compound that is lethal to 50 percent of a population of aquatic animals ( $LC_{50}$ ) are compiled in Appendix 2. There are limitations to this approach, however. Primarily, conditions that are lethal to 50 percent of a population are extreme, and are not likely to occur often. Also, the toxicity of concentrations that are an order of magnitude or more less than the  $LC_{50}$  for a species of interest cannot be predicted from the  $LC_{50}$  values alone; such prediction would require species-specific dose/response curves, which are not available. Furthermore, the toxicity of mixtures of compounds and the effect of a combination of stressors, such as elevated toxicant concentrations with temperature or pH perturbations, are poorly understood. Finally,  $LC_{50}$ s can vary widely depending on the species of interest and may be more than an order of magnitude less for some invertebrates species than for such species as rainbow trout, depending on the pesticide. Considering that insecticides tend to be more toxic than herbicides, it would be appropriate to evaluate the toxicity of Phase III pesticide concentrations by comparison with  $LC_{50}$ s for an aquatic invertebrate species; however, there is no such species for which  $LC_{50}$ s are consistently available. For that reason, and because they are relatively sensitive, rainbow trout were selected as the target animal. Also, trout, including both rainbow and cutthroat varieties, inhabit many of the streams sampled in this study.

No pesticides were detected at concentrations higher than their respective  $LC_{50}$ s for rainbow trout. The highest chlorpyrifos concentration detected (WF Palmer, 3.3  $\mu\text{g/L}$ ) was nearly one-half of the 96 hour rainbow trout  $LC_{50}$  for chlorpyrifos, and three concentrations of chlorpyrifos at WF Palmer were up to an order of magnitude higher than the  $LC_{50}$  for the freshwater amphipod *Gammarus lacustris*. However, it is doubtful that chlorpyrifos was present at such high concentrations for the full 96 hours at a time in WF Palmer considering that samples were collected during the changing conditions accompanying storm runoff. Maximum concentrations

for 10 other compounds (atrazine, bromacil, bromoxynil, diazinon, diuron, fonofos, metolachlor, oryzalin, prometon, and trifluralin) were within approximately a factor of 1,000–5,000 of their respective rainbow trout  $LC_{50}$ s.

## RELATION OF PESTICIDE OCCURRENCE TO LAND USE

No single site or group of sites had a substantially larger number of pesticide detections and higher concentrations than all the others. Although the maximum number of pesticides detected in any single water sample (18, from the 2nd spring sampling) and the largest total number of pesticides detected at any one site (24) were both at WF Palmer, 18 pesticides were detected at two sites (UT Oak and Deer), and 14 of the 20 sites sampled had from 11 to 18 pesticides detected. The occurrence of pesticides detected in the Phase III samples was spread across sites draining varied land uses, but some patterns in the data were apparent.

Sites and compounds were ordered by a cluster analysis based on the detection of pesticides and the crop types in the study basins (table 15). The cluster analysis generated a matrix of sites and compounds in which the most frequently detected pesticides in each group of sites were closest together. A rectangle has been drawn around pesticides detected in samples from at least one-half of the sites in the group, defining a set of pesticides “associated” with each group of sites. The fact that a pesticide was not “associated” with a group of sites does not mean that the pesticide was not detected at any of the sites in that group; similarly, a pesticide not “associated” with a group of sites could have been detected at one or more sites in that group. The clustering of the sites and pesticides as in table 15 does, however, capture the more salient features of the occurrence patterns, and provides a way of organizing the data for discussion. Note that these site groupings were determined independently of the groupings that were based on the intensity and diversity of upstream land uses (table 6) discussed previously

Group I (with one exception) comprises agricultural sites that are moderately varied in the types of crops grown in their drainage basins (table 7) and generally have a low percentage of upstream agricultural land use—Baker, Chicken, Shafer, SF Ash, Simpson, and UT Ash Swale. With the exception of Simpson, this grouping is the same as the “nonintensive diverse” group defined on the basis of land use alone (table 6). Shafer is the only site in the group located in the southern part of the Willamette Valley. These subbasins also have the highest percentage of forested land; again, the exception is Simpson, which was included in the “intensive, nondiverse” grouping of sites (table 6, fig. 5) on the basis of cropping patterns. In terms of pesticide occurrence, Simpson is, nonetheless, more similar to Group I subbasins than to the subbasins in any other group. The explanation for the anomalous pesticide associations at this site is not apparent but could be due to a combination of factors such as soil type or slope (it is the northernmost subbasin dominated by grass seed in the study), irrigation practices, or other local influences that were beyond the scope of this study to explore. Only the frequently detected pesticides were associated with the Group I sites.

Group II subbasins are the most diverse in the study in terms of the crops grown, and have a high percentage of agricultural land (“intensive, diverse,” table 6). Group II sites—Deer, Senecal, W Champoeg, WF Palmer, and UT S Yamhill—are all located in the northern part of the Willamette Valley. Group II sites are associated with the largest variety of both herbicides (9) and insecticides (4), in addition to the frequently detected pesticides.

Group III includes the five subbasins that have the highest percentage of agricultural land and the least diverse crop types in the study (“intensive, nondiverse”, table 6), all of which are in the southern part of the Willamette Valley—Lake, Truax, UT Flat, UT Oak, and UT Shedd. Grass grown for seed is the dominant crop type in the Group III sites. In addition to the frequently detected pesticides, nine occasionally detected pesticides (eight herbicides and one insecticide) were associated with this group.

Group IV comprises the urban sites—Beaverton, Dixon, Clagget, and Pringle. Six occasionally detected pesticides (three herbicides and three insecticides) were associated with these sites.

Table 15 provides a valuable, but not complete, summary of pesticide occurrence in the Phase III streams. In order to gain additional insight into the distribution of compound concentrations across sites, a method of comparison was used that combines frequency of occurrence and concentration. The concentration distribution of each pesticide was rank-transformed, and the ranks were adjusted such that the maximum concentration had a ranked value of 100 regardless of the number of samples. The ranks of detections in the upper quartile of the distribution were then summed over each sampling site (table 16).

As an example of how the calculations were done, consider MCPA, which had 9 detections out of 94 samples. When scaled from 1 to 100, the ranks of those detections were 100, 98.94, 97.87, 96.81, 95.21, 95.21, 93.09, 93.09, and 91.49. The fifth and sixth values in the list were the same, so the ranks are tied; the same is true for the seventh and eighth values in the list. The third and fourth values in the list occurred at the same site, so their sum (194.68) is reported in table 16 under UT Oak. Note that all entries in table 16 are rounded.

Because entries in table 16 are based on the rank-transformed data, values that are similar in magnitude indicate a similar contribution to the upper quartile of the distribution. This remains true even when comparing two compounds with very different absolute concentration distributions. For example, the contribution of SF Ash to the ranked distributions of triclopyr and diuron was about the same (rank sums 164 and 162, respectively), even though the concentrations of the two compounds were quite different. Similarly, the contributions of SF Ash and UT Ash to the distribution of triclopyr was about the same (rank sums 164 and 165, respectively). Note that a pesticide can be associated with more than one group of sites by occurrence (table 15), but that the concentrations of that compound might be high primarily or exclusively at the sites in only one group (table 16). The results of this analysis are explored in greater detail in the following discussions.



**Table 16.** Summed ranks of detections in the upper quartile of pesticide concentrations, by sampling site, for Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996 [See table 6 for complete listing of site names. Five samples were collected at each site except at SF Ash, Lake, UT Oak, UT Shedd, and UT S Yamhill, where no summer sample was collected (4 samples at those sites). “—”, no contribution to the upper quartile of the pesticide concentration from that site. (\*) indicates that 1 or 2 nondetected values at a high method detection limit (MDL) for that compound have been dropped in order to accurately rank the remaining data. Data have been normalized such that the rank of each pesticide’s maximum concentration is 100. Shading as follows: ≤100 , >100 to 200 , >200 to 300 , >300 to 400 , >400  □

Site name	Alachlor	Oryzalin	Carbofuran	Norflurazon	Propanil	Malathion	Bromoxynil	Dinoseb	Trifluralin	Propachlor	DCPA	Bentazon	Fonofos	Triallate	Napropamide	EPTC	Chlorpyrifos	MCPA	Carbaryl (*)	Diazinon	Dichlobenil	Tebuthiuron (*)	Prometon	Triclopyr	Bromacil	Metolachlor	Atrazine (*)	Deethyl Atrazine	Simazine	Diuron (*)	Pronamide	Metribuzin	2,4-D	Ethoprop	Terbacil	Dicamba		
<b>Group I: Predominantly sites with a large percentage of nonagricultural land uses and moderately varied crop types upstream</b>																																						
Baker	—	—	—	—	—	—	100	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	95	—	—	—	—	—	—	—	91	—		
Chicken	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
Shafer	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	184	—	337	436	—	78	—	—	—	173	—	—	—		
Simpson	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	88	93	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
SF Ash	—	—	—	—	—	—	—	—	—	—	—	—	—	181	—	—	—	—	—	—	—	—	—	164	—	84	—	—	—	162	197	178	—	88	—	96		
UT Ash	—	—	—	—	—	—	—	—	—	—	—	—	—	381	—	—	—	93	—	—	—	—	—	165	89	—	—	—	82	—	88	89	—	—	—			
<b>Group II: Sites in the northern Willamette River Basin with intensive agriculture and highly varied crop types upstream</b>																																						
Senecal	—	—	—	—	—	—	—	—	—	—	—	—	—	—	100	281	—	95	97	79	—	95	—	—	—	—	80	158	444	88	335	78	86	81	183			
UT S Yamhill	—	—	—	—	—	—	—	—	—	—	—	—	—	382	—	161	87	91	—	—	—	80	—	—	—	179	78	—	—	—	258	252	82	86	85			
W Champoeg	—	—	—	—	—	—	100	—	—	—	—	—	199	—	96	376	91	99	—	177	—	—	—	—	—	77	—	254	271	—	257	87	374	274				
WF Palmer	100	394	296	—	—	—	—	—	394	—	—	—	—	186	98	181	489	100	379	263	182	173	—	—	—	246	88	81	99	—	89	165	84	83	—	99		
Deer	—	—	98	—	—	—	—	—	—	—	—	—	—	—	196	86	178	95	—	168	—	256	—	—	—	180	—	78	440	80	—	—	—	—	—			
<b>Group III: Sites in the southern Willamette River Basin with intensive agriculture and dominated by grass seed crops upstream</b>																																						
Lake	—	—	—	—	—	—	—	96	—	—	100	—	—	—	—	—	—	—	—	—	—	—	—	—	96	274	367	382	—	373	374	271	97	—	—	98		
Truax	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	274	95	—	—	—	—	—	—	—	—	—	285	454	333	256	339	—	175	256	183	268	278	100
UT Flat	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	169	92	93	—	—	—	175	93	185	187	77	—	—	—	163	157	92	95	—	89	97		
UT Oak	—	—	—	—	—	—	—	—	—	—	—	98	—	—	—	—	195	—	98	100	—	—	—	—	187	276	98	363	374	363	268	360	172	278	287	355	281	100
UT Shedd	—	—	—	—	100	—	—	—	—	—	—	99	—	—	—	—	—	—	—	—	—	—	—	78	91	99	294	374	373	272	77	197	273	268	100	164	287	
<b>Group IV: Sites with predominantly urban land use upstream</b>																																						
Beaverton	—	—	—	—	—	100	—	—	95	99	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	270	—	—	
Dixon	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Claggett	—	—	—	—	—	—	—	—	—	100	100	—	—	—	—	94	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	269	—
Pringle	—	—	—	—	—	—	—	—	—	—	—	98	—	—	—	169	94	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	81	100	—	

## **Pesticide Occurrence Relative to Urban and Agricultural Land Uses**

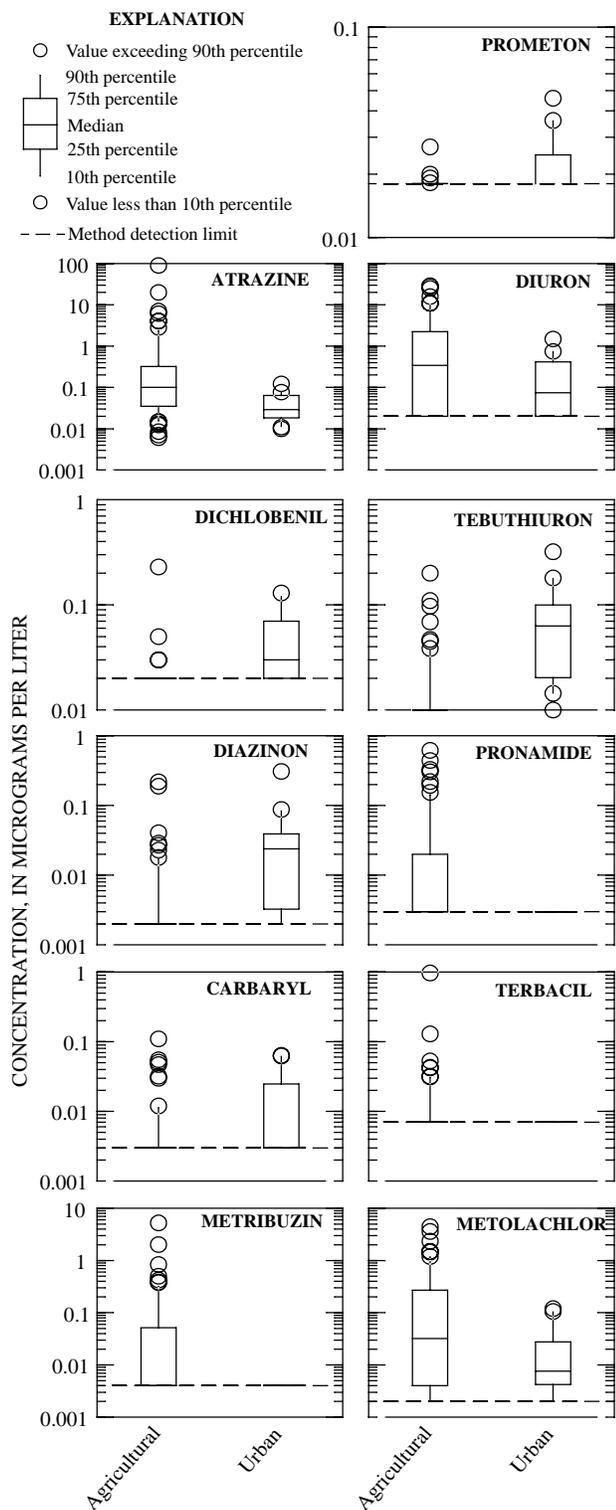
The urban sites were included in the study primarily to identify (1) those compounds that had an urban signature, that is, compounds that were found primarily or in higher concentrations at urban sites, and (2) compounds with a high frequency of detection and (or) high concentration in the agricultural basins, but that also have urban (noncropland) applications. In the first category are the compounds carbaryl, diazinon, dichlobenil, and tebuthiuron. In the second category are the compounds prometon, triclopyr, metolachlor, atrazine, simazine, and diuron.

Carbaryl, diazinon, dichlobenil, and tebuthiuron are associated with both Group IV (urban) and Group II (intensive agriculture, diverse crop types) sites, but each of these compounds had a significantly higher median concentration at the urban sites ( $p < 0.05$ , fig. 6). The rank-transformed data show that the urban sites contribute particularly heavily to the upper quartile of diazinon, dichlobenil, and tebuthiuron (table 16). Recommended uses of tebuthiuron include control of broadleaf weeds and woody brush on rangeland and pasture, but otherwise they are restricted to noncropland uses, such as under asphalt, in railroad rights-of-way, and in industrial settings (American Crop Protection Association, 1996). Carbaryl (Sevin), diazinon, and dichlobenil (Casoron) are readily available through retail sales to homeowners and are used by commercial landscapers; therefore their occurrence at higher concentrations in streams draining large areas of commercial and residential development (Group IV sites) is not unexpected. They are also used, however, by growers on a variety of fruit and vegetable crops (William and others, 1996), many of which are grown in the Group II subbasins (table 7). This use explains their appearance, although at a lower concentration than at the urban sites, at those agricultural sites. These compounds were not associated with the Group III subbasins, which is not surprising because few fruit and vegetable crops are grown in those subbasins. However, these compounds can also be used on many of

the fruit and vegetable crops that are grown in the Group I sites, but they were not associated with those subbasins either. It is likely that riparian growth or runoff from the relatively large forested fraction of the Group I subbasins helps reduce the stream concentrations of these compounds and several others found at higher concentrations at Group II and III agricultural sites.

Prometon and triclopyr were associated with both the Group III agricultural sites and the Group IV urban sites, but only prometon had significantly different median concentrations between urban and agricultural sites. The rank-transformed data show that Group IV urban sites contributed most heavily to the upper quartile of these compounds, but Group III agricultural sites contributed heavily as well (table 16). Because neither of these compounds is used on croplands, noncropland applications probably dominate, even in the agricultural basins. Each has recommended uses in landscaping, rights-of-way, and industrial settings (American Crop Protection Association, 1996), but prometon and triclopyr are also widely used by homeowners where complete vegetation control is desired; some formulations of these compounds are marketed heavily through the mail to homeowners as all-purpose herbicides. Prometon can be used under asphalt, but in the Willamette Valley is not used by government agencies in roadside applications. The use of triclopyr (Garlon) along primary and secondary roads in the Willamette Valley by the State or counties has decreased in recent years (Bill Manning, Steve Hande, Bette Coste, Oregon Department of Transportation, oral commun., 1997), and is currently limited to spot spraying of problem areas in some districts (Neil Michael, Linn County, oral commun., 1997); thus, right-of-way spraying by local transportation agencies was probably not the biggest contributor to the association of triclopyr with either the Group III or Group IV sites.

Bromacil has recommended uses similar to those of prometon and triclopyr. Bromacil did not have significantly different median concentration between agricultural or urban sites, but it was most strongly associated with the Group III agricultural sites (table 15). Given that bromacil has no uses on cropland, it is unclear why the upper quartile of its



**Figure 6.** Concentrations of all compounds detected with 10% or greater frequency in the Willamette Valley during 1996 that had significant differences in concentration between urban and agricultural land uses, on the basis of a Wilcoxon test ( $p < 0.05$ , except for metolachlor for which  $p = 0.08$ ).  $N = 74$  or  $75$  and  $19$  or  $20$  for the agricultural and urban basins, respectively.

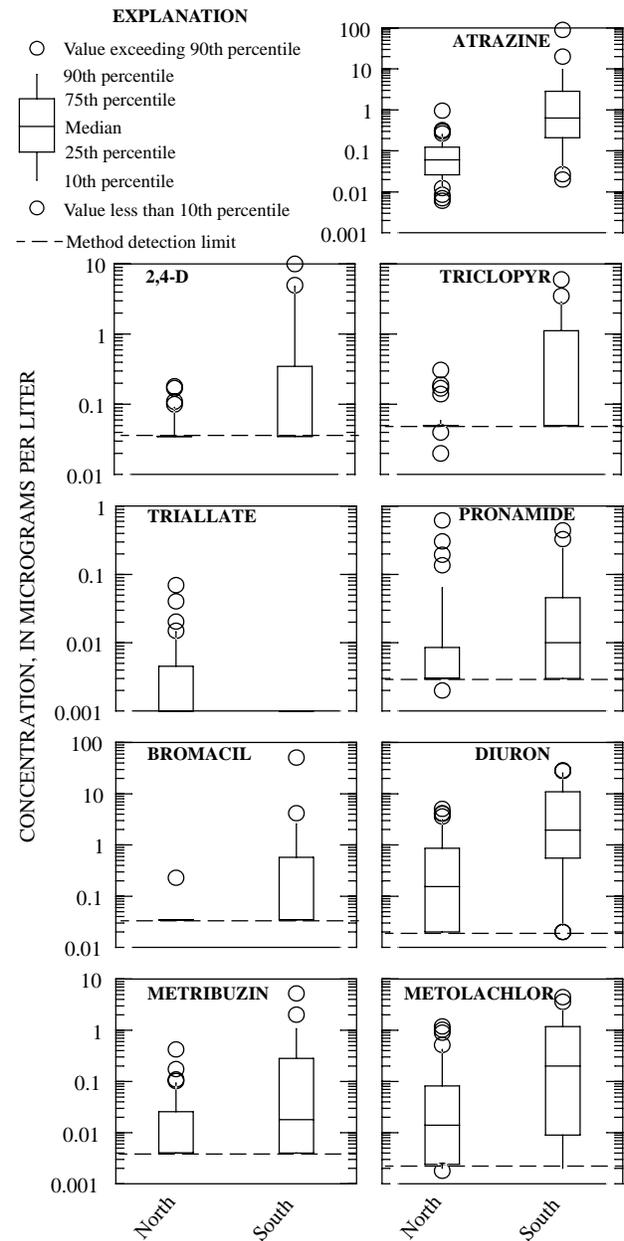
concentration distribution contained values predominantly from these sites. Custom analysis by the NWQL of two samples (from UT Oak and UT Shedd), for which considerable analytical interferences had been indicated initially, indicated the presence of bromacil and a breakdown product of diuron (Mark Sandstrom, U.S. Geological Survey, written commun., 1996). Concentrations of these compounds were high enough to saturate the electronics of the analytical equipment, making direct quantification impossible. The presence of these compounds at such high concentrations indicates a possible application of Krovar, a formulation of bromacil and diuron that is sometimes used during the spring for vegetation control along rights-of-way, including railroads (Rinehold and Witt, 1989; Thomas Mayer, Asplundh Corp. Railroad Division, written commun., 1997) and roadways. However, roadside application of bromacil by ODOT and Linn County is limited to problem areas (Bill Manning, Steve Hande, Bette Coste, ODOT, oral commun., 1997; Neil Michael, Linn County, oral commun., 1997) and was apparently not done at all in these watersheds during 1996. This is a case where the local cultural practices of homeowners and growers, practices that include spraying along fence rows and around the edges of fields, may be playing an important and unquantifiable role.

Noncropland applications also are indicated for the frequently detected compounds—metolachlor, atrazine, simazine, and diuron. These compounds were detected with greater than 70 percent frequency at the 20 sampling sites, regardless of land use (table 11). These compounds are used on a wide variety of crops, but they were consistently detected in the streams draining urban land as well as streams draining agricultural land, indicating a high rate of noncropland application. Median concentrations of atrazine and diuron were significantly higher at the agricultural sites than at the urban sites ( $p < 0.05$ , fig. 6), but median concentrations of simazine were not significantly different between the two land uses. Metolachlor, which had no contribution to its upper quartile from the urban sites (table 16), had a higher median concentration in the agricultural basins, albeit with lower statistical significance ( $p < 0.08$ ).

## Pesticide Occurrence Relative to Different Types of Agricultural Land Uses

Atrazine, metolachlor, and diuron had higher median concentrations at agricultural sites in the southern part of the basin than at agricultural sites in the northern part (fig. 7). The highest concentrations were measured at the Group III sites (table 16), which is probably indicative of the high percentage of cropland in those subbasins. Grass seed crops dominate in Group III subbasins; metolachlor and diuron are registered for use on those crops and diuron may be applied more than once in a year (Rinehold and Jenkins, 1994). The use of atrazine is more difficult to quantify, in part because of recent restrictions on its sale. Current usage guidelines indicate that it is not applied in large amounts on grass seed crops (Rinehold and Jenkins, 1994; William and others, 1996). Nonetheless, the fact that it is detected at all sites in this study, often at concentrations well into the microgram per liter (part per billion) range, indicates that it is still a widely used herbicide. The high concentrations of atrazine in Shafer Creek, a Group I site, are probably indicative of the large acreage of Christmas tree plantations there (table 7).

The compounds pronamide, metribuzin, 2,4-D, ethoprop, and terbacil were associated with the agricultural subbasins in Groups II and III, but were much less prevalent at Group I sites (table 15). This may again indicate that runoff from the large amount of forested land in the Group I subbasins was diluting concentrations in the streams, because each of these compounds is used on some crops that are grown in the Group I subbasins. None (except 2,4-D, which is used on lawns in many different formulations) is indicated as having heavy use in home or commercial landscapes, however, which is consistent with the lack of association of these compounds with the Group IV (urban) sites. Pronamide, metribuzin, 2,4-D, and terbacil are used on grass seed crops (William and others, 1996; also special registration under section 24c of FIFRA [U.S. Environmental Protection Agency, 1972]), which may explain why Group III sites contribute heavily to the upper quartile of these compounds (table 16), and why each of these except terbacil had a



**Figure 7.** Concentrations of compounds detected with 10% or greater frequency at 16 agricultural sites in the Willamette Basin during 1996 that had significant differences in concentration between the northern and southern sites, on the basis of a Wilcoxon test ( $p < 0.05$ ).

(For this purpose, the divide between the northern and southern basin is north of Albany, Oregon.  $N=48$  and 26 for the northern and southern basins, respectively. Dashed line is the method detection limit, when different from the x axis).

higher median concentration at the southern sites than at the northern sites (fig 7). Compounds applied to grass seed crops even at low rates could contribute heavily to the overall load to the basin because of the large acreages involved.

The association of several other compounds with the Group II agricultural sites but not the Group I and III sites (tables 15 and 16) is likely an indication of the greater variety of crops grown in the group II subbasins. Snap beans, broccoli, caneberries, nursery plants, corn, hops, mustard, peaches, prunes, sod, squash, strawberries, and wheat are crops that were grown exclusively or predominantly in the Group II subbasins (table 7). The herbicides EPTC, napropamide, and dichlobenil, and the insecticides chlorpyrifos, carbaryl, and diazinon are indicated for use on several of these crops. MCPA is an herbicide that is sometimes substituted for 2,4-D on grass seed crops in Marion and Yamhill counties if drift onto nurseries could be a problem (Rinehold and Jenkins, 1994), which could explain its preferential occurrence in the Group II sites.

The association of tebuthiuron with the Group II sites is more difficult to interpret, because this compound is not indicated for use on cropland. Tebuthiuron is used along railroad rights-of-way (Thomas Mayer, Asplundh Corp. Railroad Division, written commun., 1996), and railroads cross three of the Group II subbasins—Senecal, UT S Yamhill, and Deer as well as two Group III sites (UT Flat and UT Shedd) where tebuthiuron was also detected. It is also used to control woody plants in pasture and rangeland (William and others, 1996), a land use that is more prevalent among the Group II sites (table 7); this type of use may be on an as-needed basis, however, and is difficult to quantify on the basis of acreage.

Only one compound, triallate, had a significantly higher median concentration at the northern agricultural sites (fig. 7). Triallate is used on small grains such as wheat and barley; two of the four sites at which it was detected (UT S Yamhill and WF Palmer) had relatively large acreages of wheat (table 7), but the other two had much less (UT Ash Swale) or no (SF Ash) acreages of small grains. It is possible that some of the small acreages that had not yet been planted (table 7) at the time of the crop surveys were eventually planted in small grains, and that pesticides applied to those acreages, including triallate, may have been transported to the streams by the time of sampling.

## Correlations with Estimated Application Rates

A comparison of the ranked pesticide application estimates, combined over all agricultural study basins (table 10), and the ranking of pesticides by the number of detections (table 11) reveals little obvious agreement except with diuron, which is applied heavily and detected frequently in high concentrations. The most striking discrepancies are for 2,4-D, MCPA, and EPTC, which were estimated to be among the four most used compounds but which were detected only occasionally or rarely, and for atrazine, metolachlor, and simazine, which were estimated to be moderately little used but which were detected with high frequencies. Other discrepancies include compounds that were thought to have been applied but were not detected, and conversely, pesticides that were detected for which there were no estimated applications (table 17).

**Table 17.** Compounds whose detection or nondetection in Phase III of the Willamette River Basin Water Quality Study did not agree with estimated application in 1996

Compounds detected in Phase III but for which no usage was estimated during 1996	Compounds not detected in Phase III but having a nonzero estimated application rate in 1996
Bromacil	Azinphos-methyl <sup>a</sup>
DCPA	Butylate <sup>a</sup>
Dinoseb	Clopyralid
Prometon	2,4-DB
Propachlor	Disulfoton
Propanil	Methomyl
Tebuthiuron	Methyl parathion
	Oxamyl <sup>a</sup>
	Parathion
	Pendimethalin <sup>a</sup>
	Phorate
	Propargite <sup>a</sup>

<sup>a</sup> Detected in previous studies (Anderson and others, 1996; Rinella and Janet, in press) but at less than 10 percent frequency.

Several factors contribute to these discrepancies. First, the estimates of application rates on cropland may not be accurate, as they are not completely up-to-date and do not necessarily reflect local agricultural practices. Second, non-

cropland applications of some compounds (to residential or commercial landscaping or rights-of-way, for example) may contribute equally or more than cropland applications to stream concentrations, which may explain the detections of bromacil, prometon, and tebuthiuron, for which there were no estimated applications during Phase III. Most importantly, however, detections of pesticides are likely to be influenced by a host of site- and compound-specific factors—including geology and soils, topography, local hydrological patterns, runoff conditions during sampling, proximity of compound use to streambanks, and the compounds' chemical characteristics—that were beyond the scope of this study to address.

One of the objectives of this study was to determine the feasibility of quantifying the relation between concentrations of individual pesticides in streams draining agricultural land and estimates of the application of the compounds to land in the drainage basin. To that end, stream concentrations and loads (only for the frequently detected compounds) were correlated with the estimates of pesticide application to the Phase III study basins. Loads were not calculated for occasionally detected compounds because the large number of nondetections would have resulted in a dataset dominated by loads that could be defined only by their upper limit and that therefore could not reasonably be ranked with respect to each other. The correlations were done in two ways—first, by pairing each sample with the estimated application of pesticide over the appropriate time interval preceding sample collection, and second, by summing the application rates of each pesticide over the entire year to get a yearly rate of application of each pesticide in each basin. In the latter case, the application rates (one per basin) were correlated with the median values (of the five samples collected from each basin) of pesticide load and concentration (table 18). In light of the above-mentioned limitations, this analysis was expected to find only relations strong enough to stand out from substantial background variability.

Two frequently detected compounds (simazine and diuron) and five occasionally detected compounds (chlorpyrifos, 2,4-D, EPTC, metribuzin, and triallate) were significantly correlated with the application estimates on a yearly and (or) seasonal basis (table 18). The Spearman's  $\rho$  values were generally small, however, indicating that even though the correlation was significant, the amount of variability in concentration explained by the estimated application rates was small. The small Spearman  $\rho$  values, even for highly significant correlations, simply confirms that (1) there were many unmeasured factors that helped to determine pesticide stream concentrations, and (2) the estimated applications may not have been accurate. The best attempt at correlating pesticide concentrations with application estimates could be made for frequently detected compounds that had many data points above the MDL. In that regard, it is notable that atrazine and metolachlor did not correlate with their respective estimated application rates, indicating that either the concentration of those two compounds is little influenced by applications within the year, that their estimated application rates are highly inaccurate, or both.

Three compounds that were significantly correlated with application rate estimates, as well as five that were not, were significantly correlated with two basin characteristics—the fraction of the basin in agricultural land use and the fraction of the basin devoted to grass seed crops (table 18). Those basin characteristics are themselves correlated (fig. 5) because so much of the cropland in the most intensively agricultural basins is devoted to grass seed crops, and it is probable that application to grass seed crops resulted in correlations with both basin characteristics. Indeed, all but two of the compounds whose concentrations were correlated with at least one of the basin characteristics were indicated to have some application to grass seed crops, the exceptions being ethoprop and atrazine. The dataset generated for this study included estimates of diuron, metribuzin and 2,4-D to grass seed crops (table 8) based on data from Rinehold and Jenkins (1994). No estimates for terbacil on grass seed crops were included in the dataset, but a special registration exists for this use of terbacil under section 24(c) of FIFRA (U.S. Environmental Protection Agency, 1972). In 1996 there were also

**Table 18.** Correlations of pesticide concentrations, loads, and estimated application rates with several independent variables at agricultural sites for Phase III of the Willamette River Basin Water Quality Study, Oregon, 1996

[Correlations that are significant with at least 95% confidence are in bold. Only compounds with 10 or more detections and for which there were estimated application rates were included. Correlations were computed using rank-transformed data, and the Spearman correlation coefficient is reported. Spearman's  $\rho$  is analogous to Pearson's  $r$  calculated using the ranks of data; Spearman's  $\rho$  can range from -1 to 1 to indicate negative or positive relationships, respectively, with an absolute value of 1 indicating a perfect correlation. Median concentrations and loads at each site were used in correlations with the yearly estimated application rates, the percent agriculture, and the percent grass seed. The upper number is the correlation coefficient ( $\rho$ ) and the lower number is the probability that the null hypothesis of no correlation is true ( $p$ ). Values of  $p$  less than 0.005 are reported as 0.00.—, loads were not calculated for the compound because there were too many censored values]

Independent variable	Frequently detected compounds				Occasionally or rarely detected compounds									
	Atrazine	Diuron	Metolachlor	Simazine	Chlorpyrifos	2,4-D	Diazinon	EPTC	Ethoprop	Metribuzin	Pronamide	Terbacil	Triallate	Triclopyr
<b>Concentrations</b>														
Seasonal application rates	0.16	<b>0.29</b>	-0.01	<b>0.27</b>	<b>0.23</b>	<b>0.25</b>	0.12	<b>0.29</b>	0.19	<b>0.24</b>	0.13	-0.05	<b>0.31</b>	0.08
	0.16	<b>0.01</b>	0.93	<b>0.02</b>	<b>0.05</b>	<b>0.03</b>	0.32	<b>0.01</b>	0.10	<b>0.04</b>	0.25	0.68	<b>0.01</b>	0.47
Yearly application rates	0.11	<b>0.74</b>	-0.03	0.09	0.36	<b>0.50</b>	0.20	<b>0.52</b>	0.19	0.42	0.27	-0.20	0.25	-0.50
	0.68	<b>0.00</b>	0.91	0.73	0.17	<b>0.05</b>	0.46	<b>0.04</b>	0.48	0.10	0.31	0.45	0.36	0.05
Percentage of agricultural land	<b>0.68</b>	<b>0.75</b>	<b>0.74</b>	0.42	0.20	0.34	0.20	0.02	0.49	<b>0.62</b>	0.38	<b>0.51</b>	-0.45	0.17
	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	0.11	0.47	0.20	0.47	0.95	0.06	<b>0.00</b>	0.14	<b>0.04</b>	0.08	0.53
Percentage of land in grass seed crops	<b>0.64</b>	<b>0.82</b>	<b>0.70</b>	0.39	-0.25	<b>0.50</b>	-0.25	0.11	<b>0.57</b>	<b>0.67</b>	<b>0.56</b>	<b>0.52</b>	-0.33	0.40
	<b>0.01</b>	<b>0.00</b>	<b>0.00</b>	0.13	0.35	<b>0.05</b>	0.35	0.70	<b>0.02</b>	<b>0.00</b>	<b>0.03</b>	<b>0.04</b>	0.21	0.12
<b>Loads</b>														
Seasonal application rates	0.14	<b>0.39</b>	0.05	<b>0.39</b>	—	—	—	—	—	—	—	—	—	—
	0.24	<b>0.00</b>	0.66	<b>0.00</b>	—	—	—	—	—	—	—	—	—	—
Yearly application rates	0.17	<b>0.62</b>	0.06	0.25	—	—	—	—	—	—	—	—	—	—
	0.53	<b>0.01</b>	0.81	0.36	—	—	—	—	—	—	—	—	—	—
Percentage of agricultural land	<b>0.65</b>	<b>0.75</b>	<b>0.66</b>	0.29	—	—	—	—	—	—	—	—	—	—
	<b>0.01</b>	<b>0.00</b>	<b>0.01</b>	0.28	—	—	—	—	—	—	—	—	—	—
Percentage of land in grass seed crops	<b>0.52</b>	<b>0.68</b>	<b>0.53</b>	0.19	—	—	—	—	—	—	—	—	—	—
	<b>0.04</b>	<b>0.00</b>	<b>0.03</b>	0.47	—	—	—	—	—	—	—	—	—	—
<b>Yearly estimated application rates</b>														
Percentage of agricultural land	0.01	<b>0.85</b>	-0.06	-0.65	-0.36	0.45	-0.55	-0.03	0.13	0.48	0.11	0.15	0.04	-0.71
	0.96	<b>0.00</b>	0.83	0.01	0.17	0.08	0.03	0.92	0.63	0.06	0.69	0.57	0.87	0.00
Percentage of land in grass seed crops	-0.18	<b>0.92</b>	-0.27	-0.79	-0.54	0.41	-0.67	-0.20	-0.06	0.35	-0.12	-0.07	-0.13	-0.75
	0.51	<b>0.00</b>	0.30	0.00	0.03	0.11	0.00	0.45	0.83	0.18	0.65	0.79	0.64	0.00

emergency exemptions for the application of metolachlor and pronamide on grass seed crops

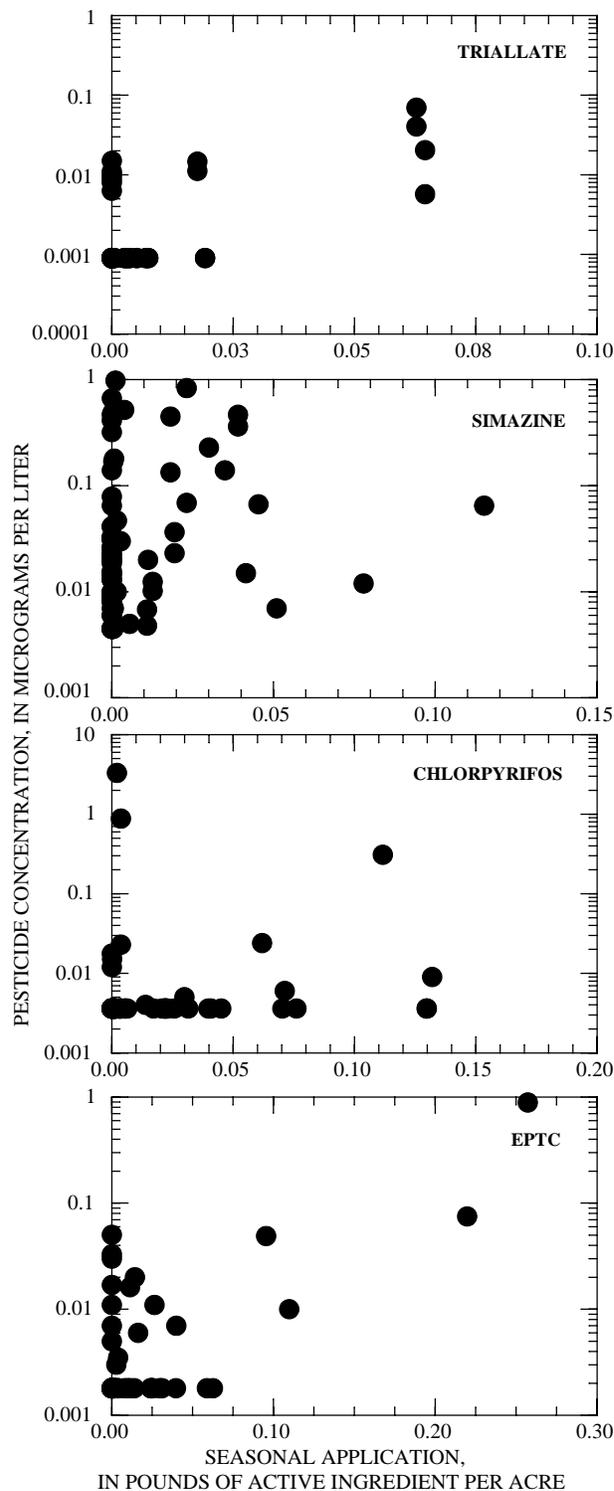
under section 18 of FIFRA (U.S. Environmental Protection Agency, 1972).

A significant correlation ( $p < 0.05$ ) between both atrazine and metolachlor and the percentage of the basin planted in grass seed crops was also found using the immunoassay data (Spearman's  $\rho = 0.46$  and  $0.57$ , respectively). Notably, however, there were no indications in the literature that atrazine is still used on grass seed crops, and the correlation of atrazine with the

percentage of the basin devoted to grass seed is probably a consequence of the correlation of atrazine with the percentage of agricultural land in the basin, or some other basin characteristic. The high concentrations of atrazine found in the most intensive agricultural basins was unexpected, and may be an indication that the cultural practices of growers are a matter of individual preference and are not necessarily determined by generalized guidelines.

In general, compounds that were applied to grass seed crops—2,4-D, diuron, metribuzin, pronamide, terbacil, and metolachlor—were more highly correlated (higher Spearman  $\rho$  values) with the acreage of grass seed crops in the basin than with their respective estimated application rates (table 18). (Diuron is highly correlated with the yearly estimated application rates, but that correlation is spurious because those rates are themselves highly correlated with the basin characteristics.) The acreages of grass seed crops are so large that they dominate all other crops in several of the basins. Even for Group II sites, where grass seed crops constitute less than 50% of the basin, the acreages of grass seed crops can be large compared to other single crop types. Because grass seed is the single most important crop in many of the basins, the per-acre rate of application of a compound to grass seed probably does not have to be large to result in a discernible correlation between that compound's stream concentration and the percentage of the basin in grass seed. The implication is that general predictions of pesticide impacts on stream quality that are based on the extent of a particular land use may be successful, but only in watersheds where that land use is dominant.

In contrast, compounds applied to a variety of fruit, vegetable, and small grain crops did not, in general, correlate with the percentage of agriculture in the basins or with acreages of specific crop types, because several of the crops are grown in the same basins and the acreages of individual crops are a small percentage of the basin as a whole. Estimating the application of those compounds to the basin on the basis of the crops grown, as attempted in this report, may be a more successful way to predict stream pesticide impacts than to base such predictions on the acreages of the individual crop types alone. However, as discussed above, success depends on having accurate application information. Even with more accurate application information, the amount of variability explained by the correlation is likely to be small (table 18 and fig. 8). Compounds that fall into this category and that were correlated with their estimated application rates are chlorpyrifos, EPTC, simazine, and triallate.



**Figure 8.** Relation between the concentration of four pesticides and their estimated seasonal application to 16 agricultural subbasins in the Willamette River Basin during 1996. (Nondetections are plotted at 0.9xMDL but can be interpreted as any value less than the MDL, including zero. Spearman's  $\rho$  values are generally less than or equal to 0.3; all correlations are significant ( $p < 0.05$ .)

It is revealing that the two most rapidly

degraded compounds (EPTC, half-life approximately 6 days, and 2,4-D, half-life approximately 10 days [Ahrens, 1994]) were detected with over 20% frequency, and that they were correlated with the estimated application rates when many other compounds that persist much longer in the soil were not. Essentially, they were not likely to be detected if they were not recently applied. Other compounds, such as atrazine and metolachlor (half-lives in the range of 1 to 3 months) that degrade more slowly, may build up in the soil and be carried into streams with every storm, even if they were applied much earlier in the year. This possibility may, in fact, be part of the explanation for the ubiquitous nature of atrazine and metolachlor.

### Other Correlations

Several of the compounds measured during the Phase III study, especially the most frequently detected ones, were significantly correlated with each other. It is likely that the environmental factors that control the mobility of large amounts of one compound, such as soil/water partitioning, the organic carbon content of the soil, and water solubility, also control the mobility of large amounts of several others simultaneously. For most pairs of compounds, however, the Spearman's  $\rho$  values were low ( $<0.4$ ), even when the correlation was significant (table 19).

Correlations with atrazine are potentially useful, because atrazine was detected with nearly 100% frequency. If atrazine concentration were highly correlated with the concentration of other pesticides, then it might be a useful indicator that other compounds are likely to be present (or absent). The correlation between atrazine and metolachlor has one of the highest Spearman's  $\rho$  values in table 19 (0.63), but there is still much unexplained variability in the data (fig. 9). Correlations between atrazine and metolachlor based on the immunoassay data also were highly significant, and with a comparable Spearman's  $\rho$  (0.64). Atrazine also was significantly correlated with several occasionally detected compounds, including bromacil and pronamide (fig. 9); those correlations have lower Spearman's  $\rho$  values and

consequently even more unexplained variability. In particular, there were nondetections of both bromacil and pronamide at some of the highest atrazine concentrations (see the highlighted sample points at UT Oak in fig. 9, for example), showing that atrazine is an imperfect indicator for the presence of those compounds. The UT Oak values are highlighted to demonstrate that the nondetections of bromacil and pronamide at high atrazine concentration came from sites at which those two compounds were sometimes detected.

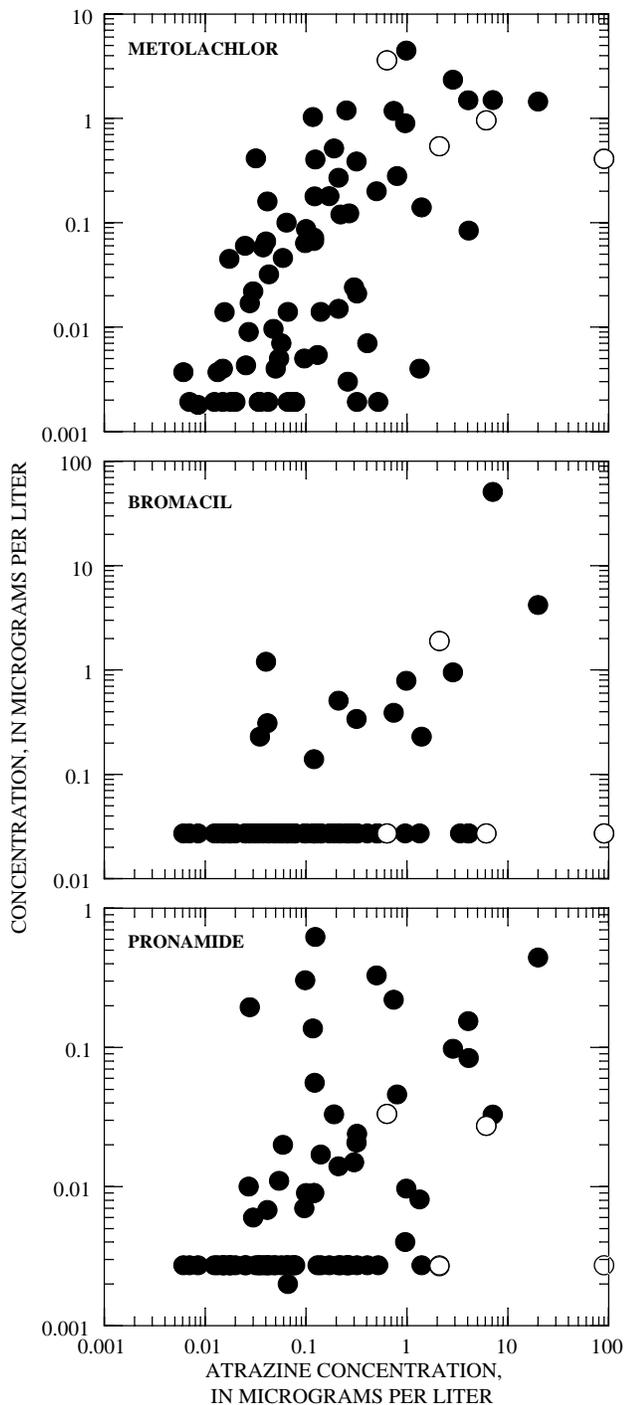
Nonetheless, several compounds, including diazinon, ethoprop, metolachlor, pronamide, terbacil, and triclopyr, were significantly correlated with the most frequently detected pesticides (atrazine, metolachlor, and [or] diuron) and not with their respective estimated application rates (compare tables 18 and 19). These correlations suggest that (1) when atrazine, diuron, or metolachlor are transported from the fields to the streams, many other compounds may be as well, and (2) monitoring environmental factors (suspended sediment and discharge, for example) that indicate the transport of one pesticide such as atrazine might be as fruitful as monitoring the specific amount and timing of application of several different pesticides to the fields, if the goal is to identify the conditions during which high stream loads are transported. Compounds that are commonly used and have moderate to long persistence in soil, like atrazine, may build up in the soil. Reservoirs of such compounds would make them available for transport to the streams with any storm that produced enough runoff, even if the compound was last applied much earlier in the year.

Correlations between pesticide and suspended sediment concentrations support this hypothesis. Suspended sediment concentration is an indication of the amount of soil that is being transported from the surrounding fields to the stream or resuspended from the streambed. Even the relatively hydrophilic compounds targeted in this study are largely sorbed onto soil particles in the fields, where there is little water into which they can dissolve. When the soil particles become suspended in water, most of these compounds

**Table 19.** Correlation statistics for pesticide concentrations, unit discharge, and suspended sediment concentrations at agricultural sites, Willamette River Basin, Oregon, 1996

[Correlations that are significant with at least 95% confidence are in bold. Only pesticides having 10 or more detections at agricultural sites were included. Unit discharge is discharge normalized by the size of the basin. Correlations were computed using rank-transformed data with nondetections included, and the Spearman correlation coefficient is reported. Spearman's  $\rho$  is analogous to Pearson's  $r$  calculated using the ranks of data; Spearman's  $\rho$  can range from -1 to 1 to indicate negative or positive relationships, respectively, with an absolute value of 1 indicating a perfect correlation. Upper number is the correlation coefficient ( $r$ ) and lower number is the probability that the null hypothesis of no correlation is true ( $p$ ). Values of  $p$  less than 0.005 are reported as 0.00]

	Bromacil	Chlorpyrifos	2,4-D	Diazinon	Diuron	EPTC	Ethoprop	Metolachlor	Metribuzin	Prometon	Pronamide	Simazine	Tebuthiuron	Terbacil	Triallate	Triclopyr	Discharge	Suspended sediment
Atrazine	<b>0.34</b> <b>0.00</b>	0.01 0.95	<b>0.33</b> <b>0.00</b>	<b>0.25</b> <b>0.03</b>	<b>0.58</b> <b>0.00</b>	0.14 0.23	<b>0.43</b> <b>0.00</b>	<b>0.63</b> <b>0.00</b>	<b>0.47</b> <b>0.00</b>	0.19 0.10	<b>0.47</b> <b>0.00</b>	0.21 0.07	-0.01 0.90	<b>0.38</b> <b>0.00</b>	-0.07 0.58	<b>0.25</b> <b>0.03</b>	0.05 0.66	<b>0.42</b> <b>0.00</b>
Bromacil	1.00 0.00	-0.11 0.36	<b>0.39</b> <b>0.00</b>	0.05 0.69	<b>0.40</b> <b>0.00</b>	-0.03 0.80	<b>0.27</b> <b>0.02</b>	<b>0.44</b> <b>0.00</b>	<b>0.28</b> <b>0.01</b>	0.22 0.06	<b>0.24</b> <b>0.04</b>	-0.05 0.69	-0.05 0.69	0.21 0.07	-0.12 0.32	<b>0.48</b> <b>0.00</b>	-0.13 0.28	<b>0.32</b> <b>0.02</b>
Chlorpyrifos		1.00 0.00	-0.08 0.50	<b>0.38</b> <b>0.00</b>	-0.01 0.91	<b>0.31</b> <b>0.01</b>	0.03 0.77	0.11 0.34	-0.09 0.47	0.05 0.65	0.05 0.68	0.17 0.14	<b>0.39</b> <b>0.00</b>	0.04 0.71	.09 0.42	-0.22 0.06	-0.01 0.94	-0.03 0.80
2,4-D			1.00 0.00	0.00 0.98	<b>0.29</b> <b>0.01</b>	0.00 11.00	<b>0.27</b> <b>0.02</b>	0.21 0.07	0.05 0.69	0.05 0.69	0.03 0.81	-0.09 0.46	0.04 0.73	0.15 0.21	-0.08 0.51	<b>0.46</b> <b>0.00</b>	-0.20 0.09	0.01 0.95
Diazinon				1.00 0.00	0.21 0.07	<b>0.35</b> <b>0.00</b>	0.22 0.06	<b>0.24</b> <b>0.04</b>	-0.04 0.72	0.10 0.37	0.00 0.97	<b>0.41</b> <b>0.00</b>	<b>0.31</b> <b>0.01</b>	<b>0.29</b> <b>0.01</b>	-0.17 0.15	-0.09 0.46	0.06 0.60	0.17 0.22
Diuron					1.00 0.00	0.13 0.27	<b>0.43</b> <b>0.00</b>	<b>0.73</b> <b>0.00</b>	<b>0.59</b> <b>0.00</b>	0.20 0.08	<b>0.57</b> <b>0.00</b>	<b>0.33</b> <b>0.00</b>	0.05 0.67	<b>0.34</b> <b>0.00</b>	-0.09 0.43	<b>0.27</b> <b>0.02</b>	0.00 0.99	<b>0.52</b> <b>0.00</b>
EPTC						1.00 0.00	<b>0.37</b> <b>0.00</b>	0.07 0.58	-0.18 0.12	-0.01 0.95	0.05 0.67	0.18 0.12	<b>0.23</b> <b>0.05</b>	0.18 0.12	-0.11 0.36	-0.11 0.35	-0.12 0.30	-0.25 0.06
Ethoprop							1.00 0.00	<b>0.44</b> <b>0.00</b>	<b>0.31</b> <b>0.01</b>	<b>0.30</b> <b>0.01</b>	0.12 0.30	0.22 0.06	-0.09 0.44	<b>0.39</b> <b>0.00</b>	-0.06 0.63	<b>0.32</b> <b>0.01</b>	-0.20 0.08	0.06 0.66
Metolachlor								1.00 0.00	<b>0.66</b> <b>0.00</b>	<b>0.27</b> <b>0.02</b>	<b>0.59</b> <b>0.00</b>	<b>0.33</b> <b>0.00</b>	0.08 0.52	<b>0.26</b> <b>0.02</b>	0.05 0.69	<b>0.26</b> <b>0.03</b>	-0.03 0.83	<b>0.43</b> <b>0.00</b>
Metribuzin									1.00 0.00	0.12 0.31	<b>0.61</b> <b>0.00</b>	0.18 0.13	-0.18 0.11	<b>0.28</b> <b>0.02</b>	0.19 0.10	0.14 0.23	<b>0.24</b> <b>0.04</b>	<b>0.36</b> <b>0.01</b>
Prometon										1.00 0.00	0.12 0.31	0.14 0.24	0.18 0.12	0.19 0.10	-0.10 0.38	0.19 0.10	-0.20 0.09	<b>0.30</b> <b>0.02</b>
Pronamide											1.00 0.00	0.12 0.31	0.10 0.39	<b>0.22</b> <b>0.05</b>	0.18 0.12	0.16 0.19	0.08 0.50	0.15 0.28
Simazine												1.00 0.00	<b>0.26</b> <b>0.03</b>	<b>0.29</b> <b>0.01</b>	-0.41 0.00	-0.19 0.10	0.18 0.12	<b>0.34</b> <b>0.01</b>
Tebuthiuron													1.00 0.00	-0.01 0.92	-0.12 0.30	-0.14 0.23	0.10 0.38	0.01 0.93
Terbacil														1.00 0.00	-0.15 0.21	0.04 0.76	0.13 0.28	<b>0.31</b> <b>0.02</b>
Triallate															1.00 0.00	0.08 0.51	0.08 0.52	-0.16 0.24
Triclopyr																1.00 0.00	-0.23 0.05	0.11 0.41
Discharge																	1.00 0.00	0.25 0.06

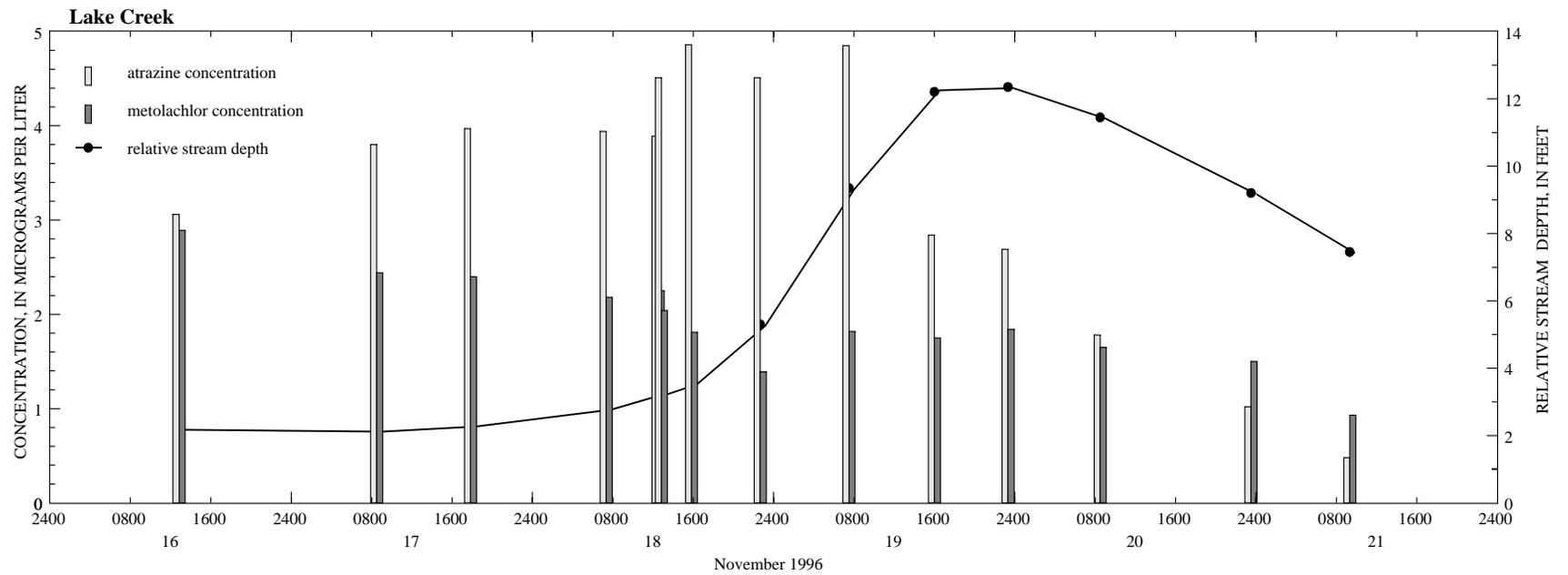
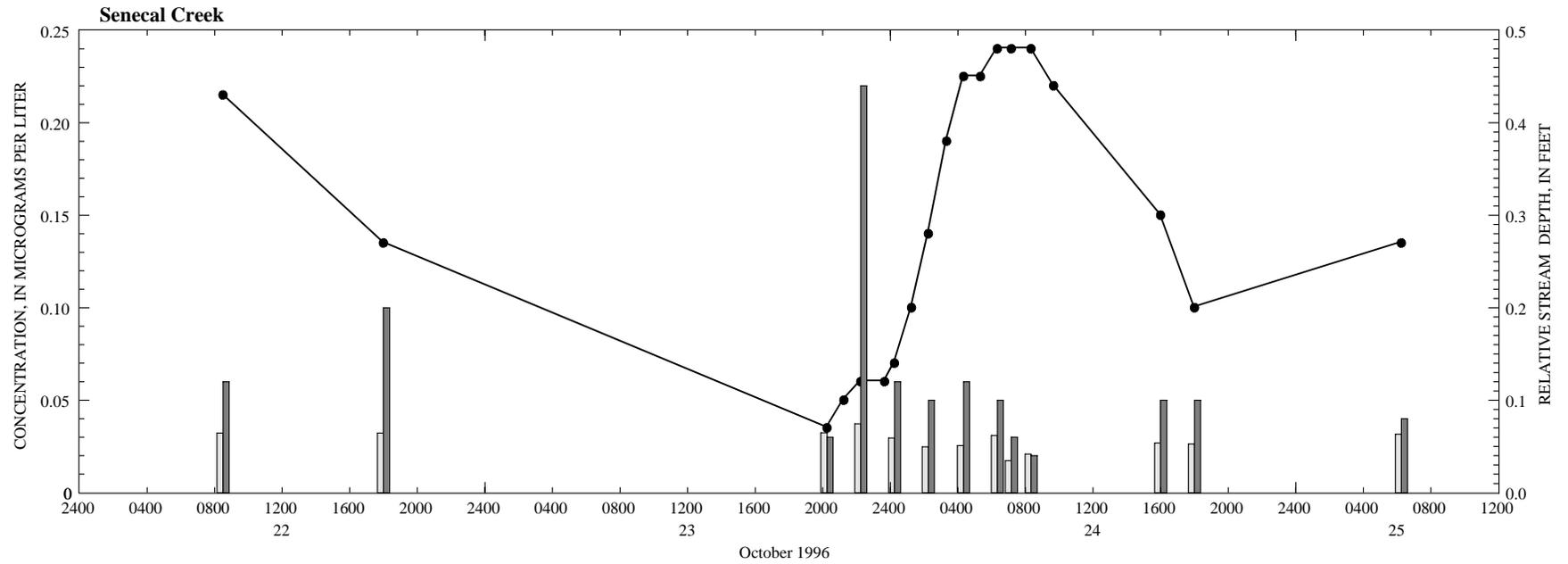


**Figure 9.** Comparison of atrazine concentrations with concentrations of metolachlor, bromacil, and pronamide in samples collected from 16 agricultural sites in the Willamette Basin during 1996. (Open circles are UT Oak samples; samples from all other sites are plotted as closed circles. Nondetections of the y-axis compound are plotted at 0.9xMDL, but can be interpreted as being any concentration less than the MDL. Spearman's  $\rho$  values are 0.63, 0.34, and 0.47 for correlations of the atrazine with metolachlor, bromacil, and pronamide, respectively.)

will largely desorb to achieve equilibrium, but the correlation between dissolved pesticide concentration and suspended sediment concentration will have been established; therefore, elevated suspended sediment concentration is often an indication of elevated pesticide concentration. It is also possible, however, that mobilized colloidal particles with sorbed pesticides (Larson and others, 1997) could have passed through the glass fiber filters in a few cases. Atrazine, bromacil, diuron, metolachlor, metribuzin, prometon, simazine, and terbacil were all positively and significantly correlated with suspended sediment concentration (table 19).

Suspended sediment concentration was not, however, significantly correlated with unit discharge (that is, discharge normalized for subbasin area), and the only pesticide whose concentrations were correlated with discharge was metribuzin (see table 19). This lack of correlation may not be surprising even if hydrologic conditions were an important factor in determining the amount of transport to the streams. Hydrographs in the small streams sampled in this study rise and fall rapidly in response to storms, and it was anticipated that the resulting dataset would contain variability due to the collection of samples at different points over the hydrographs during each of the spring and fall storm sampling cycles.

In order to investigate the magnitude of this variability, immunoassays were used to analyze samples collected over the hydrograph at single sites during two fall storms. The two storms resulted in much different hydrologic conditions. The first set of samples was collected at Senecal Creek during a small storm in October, when compound concentrations were low (in the 0.05 µg/L range). The second set was collected at Lake Creek in November, when compound concentrations were much higher (in the 1-5 µg/L range), and covered the period leading up to and during a rain event that resulted in heavy flooding in many Willamette Valley streams, including Lake Creek (fig. 10). In spite of the differences in the conditions represented, both of these immunoassay datasets show that large relative variations in pesticide concentration can occur over time periods that are short in comparison to the duration of a hydrologic event.



**Figure 10.** Short-term temporal variability of atrazine and metolachlor concentration at Senecal Creek in October 1996 and Lake Creek in November 1996. (Stream depth is referenced to an arbitrary datum.)

**Senecal Creek**—On October 23rd and 24th, 1996, Senecal Creek was monitored for the response of atrazine and metolachlor concentrations as the streamflow increased moderately over the course of a small storm (fig. 10). Prior to the storm, the stream had not risen much compared to summer low-flow conditions, despite several moderate rainstorms. A DO concentration of 3.1 mg/L on October 24, and a near-zero DO concentration together with precipitation of iron from the suspended-sediment sample collected on October 19, were indications that the streamflow at this time was probably still dominated more by ground water contributions than by surface runoff. Given that, it is notable that the both atrazine and metolachlor were detected throughout the sampling, providing supporting evidence for “reservoirs” of these compounds that build up in the subsurface and may be contributed by ground water. Second, large relative variability is apparent over the short times between samples (as little as 2 hours). Concentrations observed are near the MDLs determined for the immunoassay technique, and uncertainty in the method contributes to the variability in concentration; nonetheless, some of the variability in concentration over the hydrograph suggests a dilution effect, particularly for metolachlor at peak flow, with subsequent concentrations increasing somewhat as flows decreased.

**Lake Creek**—Storm sampling in November provided an opportunity to examine the response of the atrazine and metolachlor concentrations to streamflow at Lake Creek. A series of storms produced more than 6 inches of rain in 6 days (Oregon Climate Service, 1997), resulting in localized flooding. The creek’s response and flooding was monitored as the water level rose more than 10 feet and then slowly receded (fig. 10). Despite no streamflow for months prior to the storm (the site was visited on November 13th and had no flow then), discharge at peak flow was measured at approximately 2,600 ft<sup>3</sup>/s underneath the bridge, with a large additional amount of water going around the bridge and through adjacent fields. Although atrazine and metolachlor concentrations were both approximately 3 µg/L at the beginning of the storm, the atrazine concentration increased to 4.8

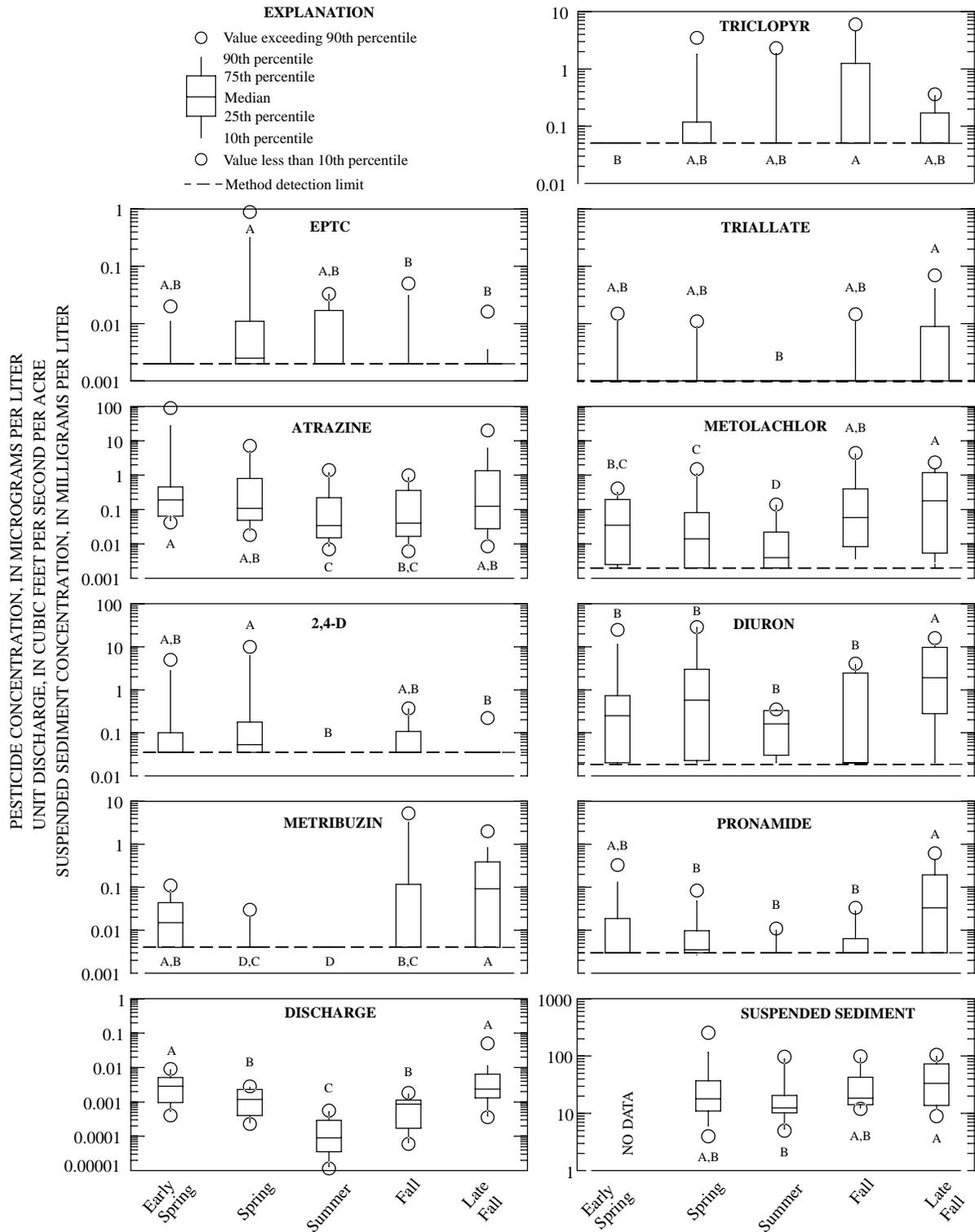
µg/L just prior to peak flow, whereas the metolachlor concentration dropped by almost one-half in the same period. The atrazine concentration decreased due to dilution, to 2.8 µg/L during peak flow, and continued to decrease as the water level declined (fig. 10). In contrast, the metolachlor concentrations remained fairly constant after the initial drop.

The concentrations when the storm began were approximately two orders of magnitude higher than they were during the Senecal Creek experiment. When streamflow began on about November 16th after having previously been dry, both compounds appear to have been mobilized from the soils. The hydrograph in figure 10 clearly shows the rapid response of the stream to the storm, and the concurrent dilution of both compounds is evident. However, although the metolachlor concentration shows dilution occurring from the time that streamflow began to increase, the atrazine concentration first increased with streamflow, and then started to decrease at some point before the stream reached peak depth. Apparently, the surface runoff that contributed to the rising limb of the hydrograph was depleted of metolachlor, but enriched in atrazine, compared to concentrations already in the stream. This may indicate a difference in the relative mobility of the two compounds, and (or) the relative amounts of the compounds applied to, and subsequently stored in, soils in the basins.

### Seasonal distribution of pesticides

Discharge, sediment concentration, and the concentration of a few of the frequently and occasionally detected compounds showed a statistically significant seasonal pattern (fig. 11). Less frequently detected compounds may have similar seasonal patterns that are not quantifiable because the concentrations of those compounds were often below the MDL. Consistencies in the patterns of discharge, sediment concentration, and pesticide concentration are more apparent in this context than they were in the correlations between those variables.

The clearest seasonal pattern was displayed by unit discharge—highest in early spring and late fall, lower in spring and fall, and lowest in summer



**Figure 11.** Seasonal patterns of pesticide concentrations, unit discharge, and suspended sediment concentrations measured at 16 agricultural sites in the Willamette Valley during 1996 that were detected with 10% or greater frequency and had significant differences in concentration between sampling dates on the basis of a 2-way ANOVA test on the ranks ( $p < 0.05$ ). (Suspended sediment was not collected in early spring. Boxes with the same letter are not significantly different. Number of values = 15 or 16, 16, 11, 13, and 19 for early spring, spring, summer, fall and late fall, respectively, except for suspended sediment, for which the number of values = 16, 10, 12, and 18 for spring, summer, fall, and late fall, respectively. Dashed line is the method detection limit when different from the x axis.)

(fig. 11), as is typical for streams west of the Cascades. The patterns in pesticide concentration and sus-

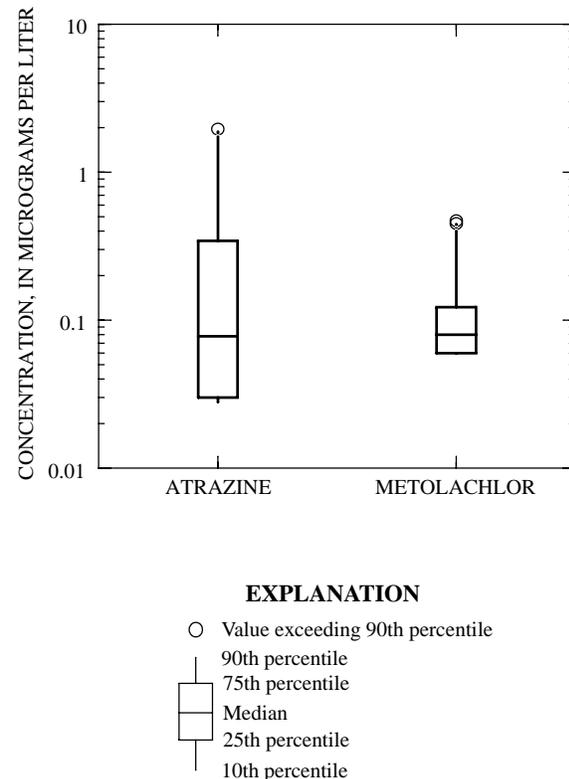
pended sediment are not as clear as the discharge pattern, but most variables had distributions of their values in the summer that were lower and statistically distinguishable from the highest distribution in the fall or the spring. The patterns in atrazine, metolachlor, and metribuzin were most similar to that of discharge in that the summer low distribution was distinguishable from distributions in both the spring and the fall. In general, the seasonal patterns indicate that the concentrations of most compounds were lowest in the summer during low-flow conditions and were highest in either the spring or the fall, coincident with higher stream flows. The exceptions in figure 11 were EPTC and triclopyr, with the lowest distributions in the late fall and early spring, respectively.

Some of the differences among compounds make sense in the context of application estimates. For example, both EPTC and 2,4-D were estimated to be applied much more heavily in the early spring than in the summer or fall, and both have a relatively short half-life. These application patterns are consistent with the higher concentrations found in the spring, followed by consistently lower concentrations in the summer and fall. In contrast, application estimates indicated that the application of triallate was heaviest in the fall on winter grain crops, and the highest distribution in triallate concentrations were measured during the late fall sampling.

However, as with the inconclusive results that were obtained when pesticide concentrations were correlated with the estimated rates, the seasonal pattern in most of the compounds in figure 11 cannot be explained in terms of the estimated application of the compound. Both atrazine and metolachlor were estimated to be applied in far greater amounts in the spring than in the fall, but compared with the summer low distributions, concentrations of these compounds were elevated in both the spring and the fall. The high frequency of occurrence of these two compounds throughout the summer and fall supports the hypothesis that they are relatively persistent in the soil. The seasonal patterns in discharge and compound concentrations indicate that for persistent compounds, the transport to the streams is determined in large part by the amount of runoff from the fields and to a lesser extent by

recent applications. That hypothesis, however, must be modified according to the characteristics of the specific compound being considered.

From the GC/MS and HPLC analytical data it is evident that concentrations of some pesticides were higher in the fall, particularly during initial runoff periods, than during summer low flow conditions. On the basis of these data alone, it would be unclear whether elevated concentrations would be maintained throughout the winter with high flow, implying a somewhat stable supply of pesticides in nonpoint runoff, or whether concentrations would drop to lower or perhaps non-detectable levels as the available supply of mobile pesticides was depleted. Using immunoassays, a basinwide sampling, with one sample from each study subbasin, was performed in a 2-day period in mid-January, 1997, to investigate winter “baseline” conditions in the streams (fig. 12). This sampling occurred during a quiescent period after



**Figure 12.** Concentrations of atrazine and metolachlor measured with enzyme immunoassays at 20 sites in the Willamette Basin in January 1997.

abnormally wet conditions in the fall and winter,

including regional flooding in the Willamette River Basin during both November and December, 1996. There is no documented use of either metolachlor or atrazine in the intervening time period. The stream and upland drainage areas, therefore, should have had ample opportunity to be purged of the most mobile pools of the immunoassay's target compounds, atrazine and metolachlor.

The median concentrations of atrazine and metolachlor in the study streams during the winter survey were comparable to or higher than the median concentrations during the preceding spring and fall, as determined with GC/MS. The median concentrations of atrazine and metolachlor during the winter sampling were both 0.08 µg/L, as compared to spring medians of 0.08 and 0.013 µg/L and fall medians of 0.05 and 0.07 µg/L, respectively. These results agree with the findings above that imply both atrazine and metolachlor are persistent in the environment. Furthermore, the consistency in concentrations among seasonal time periods during the year implies that there is a steady supply of both compounds, particularly atrazine, entering streams in the basin. The same cannot be said, however, for the more short lived compounds such as 2,4-D or EPTC, given the differences noted in the previous discussion.

## SUMMARY

Water quality samples were collected from sites in 16 randomly selected agricultural subbasins and 4 urban subbasins in Phase III of the Willamette River Basin Water Quality Study during 1996. About five samples were collected from each stream site—twice each during rainfall runoff periods in spring and fall and once during low flow conditions in summer. Samples were analyzed for suspended sediment, temperature, dissolved oxygen, pH, specific conductance, nutrients, biochemical oxygen demand, bacteria, and a suite of 86 dissolved pesticides. The data were collected to characterize the distribution of dissolved pesticides in small streams throughout the basin, to identify the relative importance of several land use categories and seasonality in

determining these distributions, and to document exceedances of water quality standards and guidelines. Estimates of pesticide applications, which were derived from discussions with local agricultural extension agents and from published estimates of application rates in Oregon, were made for the 16 agricultural subbasins. Estimates for selected pesticides were correlated with stream concentrations (and loads) to evaluate the feasibility of predicting concentrations (or loads) in small Willamette River Basin streams.

The 20 selected subbasins ranged in size from 2.6 to 13.0 square miles, with the 16 agricultural subbasins comprising 75% of the total study area. The percentage of agricultural land within the agricultural subbasins ranged from 31% to 95%. Thirty-nine crop types were identified during crop surveys of the study basins. Grass seed crops covered the largest acreage, by far, of any single crop type; grass seed crops comprised 39% of the total agricultural land, and some study subbasins had more than 85% of the agricultural land in grass seed production.

Eighteen pesticides were estimated to have been applied in a total of more than 1,000 pounds each to the agricultural areas in the study in 1996. In general, pesticides that are used on grass seed crops had the largest total application simply because of the large areas involved. Diuron, a herbicide that is used to control many types of broad-leaf weeds and grasses on a wide variety of crop types, had by far the greatest use in 1996 (over 38,000 pounds) in the study area. Furthermore, of the 10 most heavily used pesticides (7 herbicides, 3 insecticides), 6 were used to some extent on grass seed crops; these include, in descending order, diuron, 2,4-D, MCPA, chlorpyrifos, dicamba, and atrazine. EPTC, diazinon, simazine, and malathion complete the list of the 10 most abundantly applied target compounds in the study areas; these were estimated to be applied in a range from 5,000 down to 2,000 total pounds in 1996. The application estimates do not include uses along rights of way, industrial settings or landscaping, or any other non-cropland uses, so the total application of some compounds in the subbasins was underestimated. There were no application estimates for some compounds that were detected in the study but that had only noncropland uses indicated in the

literature.

The list of detected compounds is similar to those from previous studies. All of the compounds detected had been reported previously in Phases I and II of the Willamette River Basin Water Quality Study or the USGS's Willamette Basin NAWQA study. Thirty-six pesticides (29 herbicides and 7 insecticides) were detected basinwide. Five compounds were "frequently" detected, including atrazine (99% of samples), desethylatrazine (93%), simazine (85%), metolachlor (85%), and diuron (73%). Each of these except diuron was detected at every site, and diuron was detected at all but three sites. Fifteen compounds were detected "occasionally," in 10–37% of samples, and 16 compounds were detected "rarely," in 1–9% of samples.

The "frequently" detected compounds were detected in Phase III at rates similar to those in the previous studies, but detection rates for several of the "occasionally" or "rarely" detected pesticides were different. However, the principal difference in the datasets is the large number of high concentrations detected during Phase III, particularly when data from one site (Zollner Creek near Mount Angel) are excluded from the previous dataset. Zollner Creek drains a subbasin that has highly diverse crop types grown upstream from the sampling site and that has more than 80% agricultural land; in this sense it is similar to many subbasins studied sampled during Phase III. In particular, streams sampled in Phase III were in smaller subbasins, with more intensive agricultural uses upstream from sampling sites, than most of the streams sampled previously. As an artifact of sampling these small subbasins, highly concentrated pulses of pesticide runoff appear to have been sampled; these pulses were probably diminished somewhat by dilution, degradation, or dispersion at sites draining larger areas, such as those sampled during Phases I and II or by NAWQA.

Twelve compounds that were estimated to have been applied in one or more of the study subbasins were not detected in this study; five of these had been rarely detected in the previous studies, but the rest had not been. Eight com-

pounds, detected "occasionally" to "rarely," had no estimated applications. No organochlorine insecticides, such as p,p'-DDE (a derivative of DDT), dieldrin, or lindane, were detected. The lack of detections of organochlorine compounds in water, despite often high suspended sediment concentrations, supports conclusions from previous studies that the occurrence of these compounds is not necessarily a concern throughout the Willamette Basin, but rather is confined to specific streams in subbasins where their use was historically prevalent, and to larger streams downstream of those subbasins.

State of Oregon water quality standards were exceeded at all sites but one for the indicator bacterium *E. coli*; the previous standard, for fecal coliform bacteria, was exceeded at all sites. Bacterial concentrations tended to be higher during periods of storm runoff than during low flow. Both *E. coli* and fecal coliform bacteria counts were well over 1,000 colonies / 100 mL in many samples, much higher than the State's maximum-count standards. Nitrate concentrations exceeded the State standard of 10 mg/L at three sites, including four of five samples at one site and two samples at another. The temperature standard was exceeded at 10 sites, all during summer, and pH was higher than the State standard at one site during summer. The minimum DO (dissolved oxygen) standard was not met at four sites, one of which was an urban site. Pesticide concentrations exceeded State of Oregon or U.S. Environmental Protection Agency aquatic-life toxicity criteria only for chlorpyrifos, which was higher than both the acute and chronic toxicity criteria in three out of five samples from one site. State or Federal criteria have been established for only four other target compounds, two of which (2,4-D and malathion) were detected during the study but at concentrations well below the criteria values.

Thus, the conventional constituents examined in this study exceeded water quality standards or criteria more often than did the pesticides. However, the literature on toxicology of pesticides is not sufficiently developed to readily determine the impacts of the pesticide concentrations observed in this study on aquatic life or human health. Furthermore, the effects of combinations of multiple stressors, such as several pesticides in combination

with each other or with high temperatures, low dissolved oxygen, or high pH, remain largely unstudied.

The study subbasins fell naturally into four groups on the basis of upstream land uses: “nonintensive, diverse” agricultural subbasins had moderately varied crop types and a relatively high percentage of nonagricultural land (forests, residential, industrial); “intensive, nondiverse” subbasins had low crop diversity (primarily dominated by grass seed crops) and a high percentage of agricultural land; “intensive, diverse” subbasins had high crop diversity and a high percentage of agricultural land; and the “urban” subbasins had little or no agricultural or forested land upstream of the sampling sites. To a large extent, the site groupings also coincided with a division of the Willamette Basin by geographical area, with “intensive, nondiverse” subbasins located in the southern part of the basin and all but one of the more diverse subbasins (including both “intensive” and “nonintensive” groupings) located in the northern part of the basin. These site groupings were almost identical to subsequent groupings derived solely on the basis of pesticide occurrence patterns and were used to help explain associations of pesticides with different land uses.

Using cluster analysis, the sampling sites could be divided into four groups according to their association with detections of certain groups of pesticides. With the exception of one site, these groupings were identical to those made beforehand on the basis of the diversity and intensity of upstream land uses. The most frequently detected pesticides were associated with all four site groups; three of the pesticides—atrazine, metolachlor, and diuron—had significantly higher ( $p < 0.05$ ) median concentrations at agricultural sites than at urban sites. The “intensive, nondiverse” (grass seed) sites in particular were associated with high concentrations of these three compounds. The fact that atrazine, diuron, metolachlor, and simazine were found at urban sites, however, is an indication that they also were applied in noncropland settings. Four compounds—carbaryl, diazinon, dichlobenil, and tebuthiuron—were associated with both the “intensive, diverse” sites and urban sites, but had

significantly higher concentrations at the urban sites than at the agricultural sites. Carbaryl, diazinon, and dichlobenil are used on a variety of different crops, but in this study noncropland uses (home and commercial landscaping, for example) evidently contributed to higher stream concentrations in urban basins than either cropland or noncropland uses did in agricultural basins.

A few associations of compounds with agricultural subbasins are difficult to interpret because the compounds have few or no recommended uses on cropland. In particular, prometon, triclopyr, and bromacil were associated with the “intensive, nondiverse” subbasins. Each of these has uses in landscaping, rights-of-way, industrial settings, or under asphalt. None, however, was used in large quantities by State or county government agencies in roadside applications. The applications listed do not account for the occurrence of these compounds, sometimes at high concentrations, in the group of sites with largest percentage of agricultural land use. These compounds can, however, be used by landowners as all-purpose herbicides in many settings, especially where total vegetation control is desired. There, prometon, triclopyr, and bromacil may be examples of compounds for which localized use of favored compounds in noncropland settings can affect water quality. Quantifying that type of use was beyond the scope of this study.

Several compounds—pronamide, metribuzin, 2,4-D, ethoprop, terbacil, EPTC, napropamide, carbaryl, diazinon, and dichlobenil—were associated with the most intensive agricultural subbasins. They were much less prevalent at the less agriculturally intensive subbasins, despite estimated uses on one or more crops grown in those subbasins. Runoff from the large percentage of forested land in the “nonintensive, diverse” subbasins may have diluted the concentration of these compounds.

The high frequency of atrazine detections is in contrast to its apparent decline in use since it became a “restricted-use” pesticide in 1993. Similarly, the high frequency of detection of metolachlor and simazine are in contrast to their lower use compared to compounds such as 2,4-D and MCPA, which were detected only occasionally to rarely. Factors specific to certain compounds,

such as past use, persistence in the environment, water solubility, or even differences in the analytical method, can affect their prevalence in the streams. In this case, however, the disproportionately high detection frequency of atrazine, simazine, and metolachlor is apparently due in large part to uses that are not accounted for in published literature. Frequent detections of atrazine at well over 1 µg/L suggest that its use remains common despite current restrictions on its sale.

Concentrations of some pesticides differed depending on whether a sample was collected in the northern and southern Willamette Basin; for example atrazine, metolachlor, and diuron had significantly higher median concentrations at sites in the southern part of the basin than at those in the northern part. Because grass seed crops dominate the agricultural land in the study's southern subbasins, the occurrence of diuron at high concentrations in streams draining those subbasins might be expected. The occurrence of atrazine and metolachlor at very high concentrations in these streams is more difficult to explain, and supports the idea that these are more widely used herbicides than is generally recognized.

One of the objectives of this study was to determine the feasibility of quantifying the relation between concentrations of pesticides in streams in agricultural basins and land uses within those basins. This relation was investigated, for the 14 pesticides that were detected often enough to be suitable for statistical analysis (10% of samples) and for which there were non-zero application rates, by using correlation. The results differed between pesticides applied to a dominant crop type (in this case grass seed) and pesticides applied to a wide variety of crops such as fruits, vegetables, and small grains. Pesticides whose stream concentrations were significantly correlated with their estimated total upstream application were of the latter type, that is they were applied to a wide variety of crops. Even correlations with estimated use that were significant ( $p < 0.05$ ), however, were weak, with correlation coefficients in the range of 0.2 to 0.3. For compounds applied principally to grass seed crops, simple correlations between the stream concen-

trations (or loads) and percentage of agricultural land in the basin, or the percentage of the basin planted in grass seed crops, were more likely to be significant than correlations between stream concentrations (or loads) and estimated application rates. The variability in stream concentrations of those compounds was successfully explained in part by the proportion of land in the basin to which the compounds were applied, whereas small errors in the per-acre application rates may have been compounded when the acreages were large, preventing successful correlation with concentrations.

Several compounds were significantly, but weakly, correlated with each other, indicating that the environmental factors that mobilize large amounts of one compound can mobilize large amounts of several others simultaneously. Atrazine, metolachlor, and diuron, being the most frequently detected pesticides in the study, naturally had the most opportunity to correlate with other pesticides; indeed, each compound that was significantly correlated with atrazine concentrations was also significantly correlated with either diuron or metolachlor (if not both). In fact, several compounds, including diazinon, metolachlor, ethoprop, pronamide, terbacil, and triclopyr, were significantly correlated with atrazine and not with their respective estimated application rates. Thus it appears that the environmental conditions were as important as the specific amount and timing of application in determining the transport of many compounds to the streams.

Atrazine, metolachlor, and terbacil were also among several compounds significantly correlated with suspended sediment concentrations. Suspended sediment concentration was not, however, significantly correlated with unit discharge (discharge acre in the subbasin), and of the pesticides, only metribuzin was significantly correlated with discharge. In this dataset, therefore, there is no simple dependence of pesticide or suspended sediment concentration on flow in the streams. This lack of dependence was probably a consequence of collecting water samples from the various geographically separated sites at different points in the hydrograph during storms.

Even though correlations between discharge and pesticide concentration were poor when data were pooled for all sites, the seasonal pattern in both quantities is evidence that transport to the streams was related to discharge and consequently to the amount of runoff. Discharge data show that there were, in general, significantly higher flows in the streams in the spring and fall than in the summer, as was anticipated in the design of the study. Pesticide and suspended sediment concentrations tended to have similar patterns, though not as clear as for discharge, with low distributions in the summer that were statistically distinguishable from the highest distribution in the fall or the spring. Median concentrations of atrazine, metolachlor, diuron, metribuzin, pronamide, and suspended sediment were significantly higher in the late fall than in summer. Spring concentrations were in general higher, but the medians were often not statistically distinguishable from either the summer or fall medians. Median winter “baseline” concentrations of atrazine and metolachlor, as measured by immunoassay, were as high as those in the spring or fall, indicating that there remained a steady supply of these compounds long after they were applied.

The variation in pesticide concentrations with stream stage was investigated with 2 special immunoassay studies that involved the collection of, in one case, 8 samples over a 24-hour period during a small storm and, in another case, 14 samples over a 6-day period during a large storm that caused flooding. During the large storm, atrazine concentrations increased initially, peaking just prior to peak flow, and were diluted for the duration of the storm. This pattern is similar to what might be expected of a typical suspended sediment response to a storm and helps illustrate the potential importance of suspended sediment to concentrations of certain pesticides. The response of metolachlor during the large storm and both compounds during the small storm was not as marked, but nonetheless also indicated the importance of stream stage at the time of sample collection.

The future prospects for successfully correlating stream loads of certain pesticides with estimates of application rates are probably good in

select cases. However, current and locally specific rates of application to various crop types would be preferred. The compound must be applied in enough quantity and must have physical and chemical properties (for example high water solubility and moderate soil half-life) such that it can be detected but does not persist more than a few weeks past its use. The compound must also not be a “general-purpose” herbicide or insecticide that is used for multiple purposes by landowners, in addition to the specific recommended uses on cropland. EPTC, which probably meets these criteria, correlated well with its estimated application rates. In contrast, diazinon and dichlobenil are examples of compounds that have specific uses on cropland, but also are probably used extensively by landowners in many different noncropland settings. Furthermore, application estimates based on crop types cannot be correlated with the concentration of a compound like bromacil that has virtually no cropland uses.

Atrazine and metolachlor are examples of pesticides whose loads in streams cannot be predicted by reported application rates under current reporting methods. Both herbicides were detected more frequently and at higher concentrations than would be expected from published application estimates, probably indicating that there are both cropland and noncropland applications that are not generally reported. Although much of the detected atrazine and metolachlor may have been residual, this explanation does not account for the frequent detections at high concentrations (more than 1 µg/L) that indicate recent use. The cultural practices of growers may be influenced by intangibles such as individual preference, and they may not always be determined by generalized guidelines that do not take local conditions into account.

Although the largely unexplained prevalence of atrazine in the Willamette River Basin may make it a poor predictor of *concentrations* of other pesticides, the significant correlations of atrazine with concentrations of suspended sediment and several other pesticides suggest that periods of atrazine transport are at least a rough indicator for *conditions* that may move other compounds. It was demonstrated in this study that atrazine concentration can be

measured relatively cheaply, and with good accuracy and precision, with enzyme immunoassays. A future monitoring plan could make good use of this technique to develop relations between hydrology, suspended sediment concentration, and an indicator compound such as atrazine. This approach might be a viable alternative to that of correlating concentrations with estimated application rates, if the goal is to develop a screening mechanism for sampling based on the probability of measuring high stream loads.

## REFERENCES CITED

- Ahrens, W.H., (ed.), 1994, *Herbicide Handbook: Champaign, Illinois, Weed Science Society of America*, 352 p.
- American Crop Protection Association, 1996, *Crop Protection Reference*, 12th ed.: New York, C&P Press Inc., [variously paged].
- American Public Health Association, 1989, *Standard Methods for the Examination of Water and Wastewater* (17th ed.): Washington, D.C., American Public Health Association, 1136 p.
- Anderson, C.W., Rinella, F.A., and Rounds, S.A., 1996, Occurrence of selected trace elements and organic compounds and their relation to land use in the Willamette River Basin, Oregon, 1992–94: U.S. Geological Survey Water-Resources Investigations Report 96–4234, 68 p.
- Bonn, B.A., Hinkle, S.R., Wentz, D.A., and Uhrich, M.A., 1995, Analysis of nutrient and ancillary water-quality data for surface and ground water of the Willamette Basin, Oregon, 1980–90: U.S. Geological Survey Water-Resources Investigations Report 95–4036, 141 p.
- Bonn, B.A., Wentz, D.A., and Hinkle, S.R., 1996, Willamette Basin, Oregon—Nitrogen in streams and ground water, 1989–90: U.S. Geological Survey Open-File Report 96–227, 4 p.
- Caldwell, J.M., and Doyle, M.C., 1995, Sediment oxygen demand in the lower Willamette River, Oregon, 1994: U.S. Geological Survey Open-File Report 95–4196, 14 p.
- Canadian Council of Resources and Environment Ministers, 1996, *Canadian water quality guidelines: Ottawa, Ontario, prepared by the Task Force on Water Quality Guidelines, Canadian Council of Resource and Environment Ministers, originally published 1987, plus 21 appendices published through May 1996 [variously paged].*
- Edwards, T.K., and Glysson, D.G., 1988, *Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86–531*, 118 p.
- Edwards, T.K., 1994, *Assessment of surface-water quality and water-quality control alternatives, Johnson Creek Basin, Oregon: U.S. Geological Survey Water-Resources Investigations Report 93–4090*, 50 p.
- Fisher, G., DeAngelis, J., Baird, C., Stoltz, R., Sandvol, L., Antonellis, A., Beers, E., and Mayer, D., (comps.), 1996, *Pacific Northwest insect control handbook: Corvallis, Oregon State University*, 347 p.
- Fishman, M.J. (ed), 1993, *Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determinations of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125*, 217 p.
- Fishman, M.J., and Friedman, L.C., 1989, *Methods for the determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chapter A1*, 546 p.
- Fuhrer, G.J., Tanner, D.Q., Morace, J.L., McKenzie, S.W., and Skach, K.A., 1996, *Water quality of the lower Columbia River Basin: Analysis of current and historical water-quality data through 1994: U.S. Geological Survey Water-Resources Investigations Report 95–4294*, 157 p.
- Gonthier, J.B., 1985, *Oregon ground-water resources, in U. S. Geological Survey, National water summary 1984—Hydrologic events, selected water-quality trends, and ground-water resources: U. S. Geological Survey Water-Supply Paper 2275*, p. 355–360.
- Gregory, S.V., 1993, *Willamette River Basin—Periphyton algal dynamics [Final Report to the Oregon Department of Environmental Quality]: Corvallis, Oregon State University*, 112 p.
- Gruessner, B., Shambaugh, N.C., Watzin, M.C., 1995, *Comparison of an enzyme immunoassay and gas chromatography/mass spectrometry for the detection of atrazine in surface waters: Environmental Science and Technology, v. 29, p. 251-254.*
- Guy, H.P., 1969, *Laboratory theory and methods of sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chapter C1*, 58 p.
- Harrison, H.E., Anderson, C.W., Rinella, F.A., Gasser, T.M., and Pogue, T.R., Jr., 1995, *Analytical data from Phases I and II of the Willamette River Basin water quality study, 1992–94: U.S. Geological Survey Open-File Report 95–373*, 176 p. [Revised and reprinted 1997.]

- Helsel, D.R., and Cohn, T.A., 1988, Estimation of descriptive statistics for multiply censored water quality data: *Water Resources Research*, v. 24, no. 12, p. 1997–2004.
- Helsel, D.R., and Hirsch, R.M., 1992, *Statistical methods in water resources*: Amsterdam, Elsevier Publishers, 522 p.
- Hitt, K.J., 1994, Refining 1970's land-use data with 1990 population data to indicate new residential development: U.S. Geological Survey Water-Resources Investigations Report 94-4250, 15 p.
- Hines, W.G., Rickert, D.A., and McKenzie, S.W., 1976, Hydrologic analysis and river quality data programs: U.S. Geological Survey Circular 715-D, 20 p.
- Hinkle, S. R., 1997, Quality of shallow ground water in alluvial aquifers of the Willamette Basin, Oregon, 1993–95: U.S. Geological Survey Water-Resources Investigations Report 97-4082-B, 48 p.
- Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.M., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.
- Hottenstein, C.S., Rubio, F.M., Herzog, D.P., Fleeker, J.R., Lawruk, T.S., 1996, Determination of trace atrazine levels in water by sensitive magnetic particle-based enzyme immunoassay: *Journal of Agricultural and Food Chemistry*, v. 44, p. 3576–3581.
- Laenen, Antonius, and Risley, J. C., 1997, Precipitation-runoff and streamflow-routing modeling as a foundation for water-quality simulation in the Willamette River Basin, Oregon: *In* Laenen, Antonius, and Dunnette, D. A., eds., *River Quality—Dynamics and Restoration—Proceedings of the Poland-USA International River Quality Symposium, March 21–25, 1994, Portland, Oregon*: New York, CRC Press, p. 117–130.
- Larson, S. J., Capel, P.D., and Majewski, M.S., 1997, Pesticides in surface waters—distribution, trends, and governing factors: Chelsea Michigan, Ann Arbor Press, 373 p.
- Lawruk, T.S., Lachman, C.E., Jourdan, S.W., Fleeker, J.R., Herzog, D.P., Rubio, F.M., 1993, Determination of metolachlor in water and soil by a rapid magnetic particle-based ELISA: *Journal of Agricultural and Food Chemistry*, v. 41, p. 1426–1431.
- Leland, D., Anderson, S., and Sterling, D., 1997, The Willamette—A river in peril: *Journal of the American Water Works Association*, v. 89, no. 11, p. 73–83.
- Lee, K.L., 1995, Stream velocity and dispersion characteristics determined by dye-tracer studies on selected stream reaches in the Willamette River Basin, Oregon: U.S. Geological Survey Water-Resources Investigations Report 95-4078, 39 p.
- Lydy, M.J., Carter, D.S., Crawford, C.G., 1996, Comparison of gas chromatography/mass spectrometry and immunoassay techniques on concentrations of atrazine in storm runoff: *Archives of Environmental Contamination and Toxicology*, v. 31, p. 378–385.
- Markle, D.F., 1995, Evaluation of fish identifications for the Willamette River Basin Water Quality Study Phase II, Skeletal deformities in northern squawfish—Final report to Oregon Department of Environmental Quality: Corvallis, Oregon State University, 17 p.
- McFarland, W.D., 1983, A description of aquifer units in Western Oregon: U. S. Geological Survey Open-File Report 82-165, 35 p.
- Meister, R.T., (ed.), 1995, *Farm Chemicals Handbook*: Willoughby, Ohio, Meister Publishing, [variously paged].
- National Academy of Sciences and National Academy of Engineering, 1973, *Water quality criteria 1972*: U.S. Environmental Protection Agency Ecological Research Series EPA-R3-73-033, 594 p.
- Oregon Climate Service, 1997, Climate data—Daily precipitation for Corvallis St Univ station: Internet World Wide Web page, URL <<http://ocs.ats.orst.edu/>>, accessed May 20, 1997.
- Oregon Department of Environmental Quality, 1994, *Willamette River Toxics Study, 1998/1991*: Portland, Oregon Department of Environmental Quality, [variously paged].
- 1996, *Oregon Draft 1994/1996 List of Water Quality Limited Water Bodies—303(d)(1)*: Portland, Oregon Department of Environmental Quality, [variously paged].
- Ohmicron Environmental Diagnostics, Inc. 1992, *RPA-I™ RaPID Photometric Analyzer*: Newtown, Pennsylvania, 26 p.
- Page, B.G., and Thomson, W.T., 1997, *The insecticide, herbicide, fungicide quick guide*: Fresno, Thomson Publications, 198 p.
- Pogue, T.R., and Anderson, C.W., 1995, Processes controlling dissolved oxygen and pH in the Upper Willamette River Basin, Oregon, 1994: U.S. Geological Survey Water-Resources Investigations Report 95-4205, 71 p.

- Pscheidt, J. (ed.), 1996, Pacific Northwest plant disease control handbook: Corvallis, Oregon State University, 384 p.
- Rantz, S.E., and others, 1982, Measurement and computation of streamflow: U.S. Geological Survey Water Supply Paper 2175, 2 v., 631 p.
- Rinehold, J.W., and Witt, J.M., 1989, County pesticide use estimates for 1987—National Pesticide Impact Assessment Program, Supplement to special report 843: Corvallis, Oregon State University, Department of Agricultural Chemistry, Extension Service, [variously paged].
- Rinehold, J.W., and Jenkins, J.J., 1993a, Oregon pesticide use estimates for small fruits, 1990: Corvallis, Oregon State University, Department of Agricultural Chemistry, Extension Service, 32 p.
- 1993b, Oregon pesticide use estimates for tree fruits, 1990: Corvallis, Oregon State University, Department of Agricultural Chemistry, Extension Service, 38 p.
- 1994, Oregon pesticide use estimates for seed and specialty crops, 1992: Corvallis, Oregon State University, Department of Agricultural Chemistry, Extension Service, 93 p.
- 1996, Oregon pesticide use estimates for vegetable crops, 1993: Corvallis, Oregon State University, Department of Agricultural Chemistry, Extension Service, 127 p.
- 1997, Oregon pesticide use estimates for small grains, forage, and livestock, 1994: Corvallis, Oregon State University, Department of Agricultural Chemistry, Extension Service, 76 p.
- Rinella, F.A., 1993, Evaluation of organic compounds and trace elements in Amazon Creek Basin, Oregon, September 1990: U.S. Geological Survey Water-Resources Investigations Report 93-4941, 41 p.
- Rinella, F.A., and Janet, M.L., in press, Seasonal and spatial variability of nutrients and pesticides in streams of the Willamette Basin, Oregon: U.S. Geological Survey Water-Resources Investigations Report 97-4082-C.
- Sandstrom, M.W., 1989, Field method for isolation of herbicides in surface and ground water using solid-phase extraction, *in* Pederson, G.L., and Smith, M.M., eds., U.S. Geological Survey second national symposium on water quality—Abstracts of the technical sessions, Orlando, Florida, November 12-17, 1989: U.S. Geological Survey Open-File Report 89-409, p. 82.
- She, N., 1997, Analyzing censored water quality data using a non-parametric approach: Journal of the American Water Works Association, v. 33, no. 3, p. 615-624.
- Tetra Tech, Inc., 1992, Willamette River Basin water quality study—Component 7—Point source discharges and waste loading to the Willamette River Basin during 1991—Final report: Redmond, Washington, 61 p. plus appendices.
- 1993a, Willamette River Basin bacteria component report—Final report: Redmond, Washington, 55 p.
- 1993b, Willamette River Basin toxics component report—Final report: Redmond, Washington, 24 p.
- 1993c, Willamette River Basin Water Quality Study, Component 2: Toxic chemical model application report. Submitted by Limno-Tech, Inc. to Tetra Tech: Redmond, Washington, 33 p.
- 1995a, Willamette River Basin Water Quality Study, Phase II—Ecological monitoring component—Habitat assessment report—Final report: Redmond, Washington, 62 p. plus appendices.
- 1995b, Willamette River Basin Water Quality Study, Phase II—Ecological monitoring component, Assessment of aquatic communities and biological indices—Final report: Redmond, Washington, 128 p. plus appendices.
- 1995c, Willamette River Basin Water Quality Study, Phase II—Steady state model refinement component, QUAL2E-UNCAS dissolved oxygen model calibration and verification: Redmond, Washington, 55 p. plus appendices.
- 1995d, Willamette River Basin Water Quality Study—Summary and synthesis of study findings: Bellevue, Washington, Tetra Tech Report TC9925-04, [variously paged].
- Tetra Tech, Inc., and E&S Environmental Chemistry, 1993a, Willamette River Basin Water Quality Study—Willamette River Basin nonpoint source component report—Final report: Redmond, Washington, 34 p.
- 1993b, Willamette River Basin Water Quality Study, Component 8—Nonpoint source pollution model application—Final report: Redmond, Washington, 147 p., plus appendices.
- 1995, Willamette River Basin Water Quality Study, Phase II—Nonpoint source pollution in the Pudding River subbasin of the Willamette River: Redmond, Washington, [variously paged].

- Thurman, E.M., Meyer, M., Pomes, M., Perry, C.A., Schwab, A.P., 1990, Enzyme linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of triazine herbicides in water: *Analytical Chemistry*, v. 62, p. 2043–2048.
- Timme, P.J., 1994, National Water Quality Laboratory 1994 Analytical Services Catalog: U.S. Geological Survey Open-File Report 94–304, 103 p.
- U.S. Environmental Protection Agency, 1972, Federal Insecticide, Fungicide, and Rodenticide Act, parts 152–186, Sections 18, 24(c): Code of Federal Regulations, Title 40, parts 150–189.
- 1983, Methods for chemical analysis of water and waste: EPA 600/4-79-020, revised edition, [variously paged]
- 1986, Quality criteria for water: EPA-440/5-86-001, [variously paged].
- U.S. Geological Survey, 1990, Land use and land cover digital data from 1:250,000- and 1:100,000-scale maps: Data user guide, Reston, Virginia, 25 p.
- Water Providers of the Portland Metropolitan Area, 1996, Regional Water Supply Plan, Final Report: Portland, Oregon, [variously paged]. [Available from Portland Water Bureau, 1120 SW Fifth Avenue, Portland, Oregon, 97204].
- Wentz, D.A., Waite, I.W., and Rinella, F.A., in press, Comparison of streambed sediment and aquatic biota as media for characterizing occurrence of trace elements and organochlorine compounds in the Willamette River Basin, Oregon: *Environmental Monitoring and Assessment*.
- Werner, S.L., Burkhardt, M.R., and DeRusseau, S.N., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96–216, 42 p.
- Wetzel, R.G., 1983, *Limnology*: Philadelphia, Saunders College Publishing, 767 p., plus appendixes.
- William, R.D., Ball, D., Miller, T.L., Parker, R., Al-Khatib, K., Callihan, R.H., Eberlein, C., and Morishita, D., (comps.), 1996, *Pacific Northwest Weed Control Handbook*: Corvallis, Oregon State University, 378 p.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95–181, 45 p.

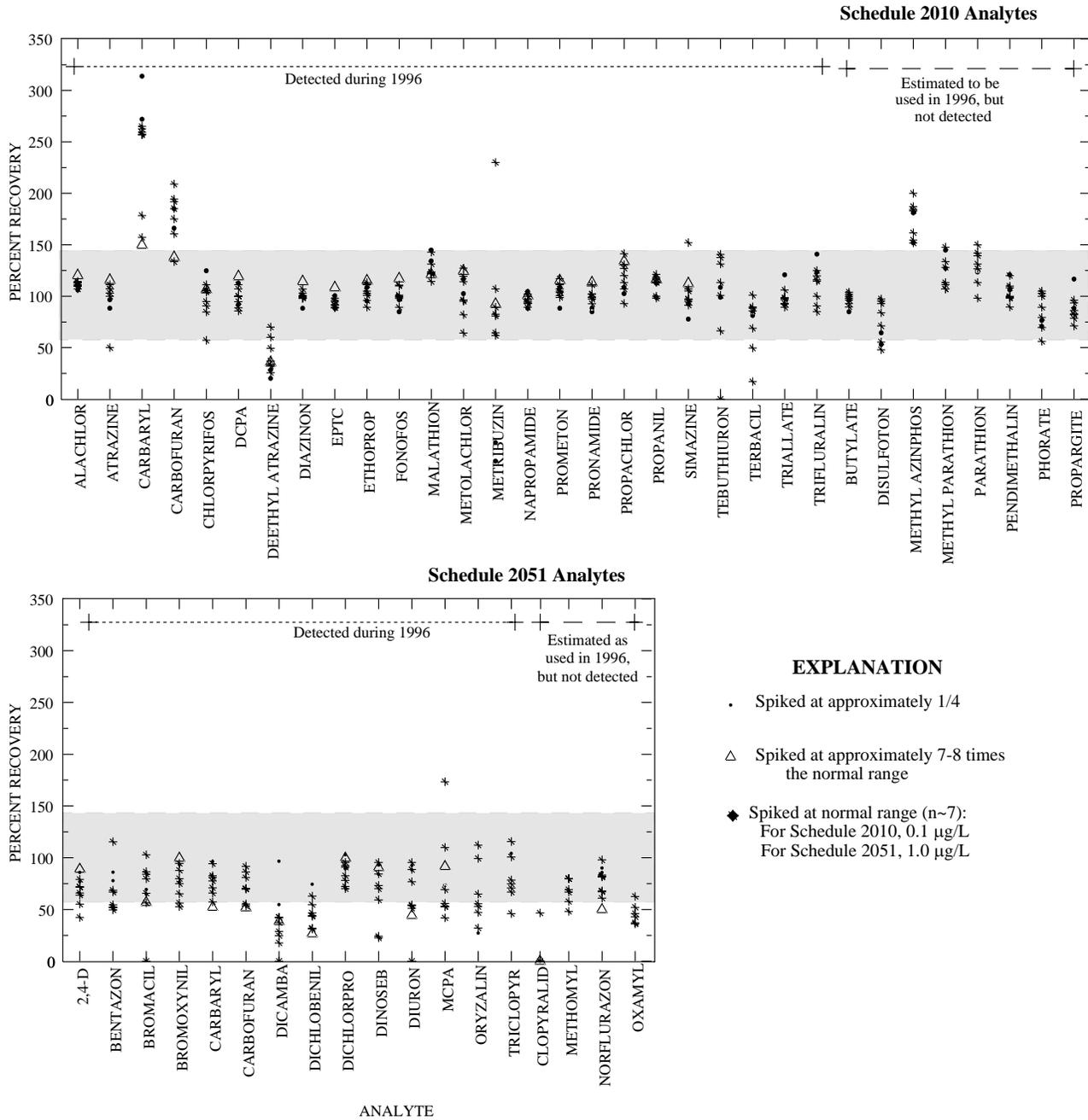
---

## APPENDIX 1

---



# APPENDIX 1. QUALITY ASSURANCE DATA AND FIGURES



**Figure 1-1.** Recovery of pesticides spiked into native water for compounds detected or estimated to be applied during Phase III of the Willamette River Basin Water Quality Study, 1996. Recoveries are calculated as  $100 * [(concentration\ in\ the\ spiked\ solution\ (in\ \mu g/L)) - (concentration\ in\ native\ water\ (in\ \mu g/L))] / (expected\ concentration\ (in\ \mu g/L))$ , where the expected concentration is determined as the  $[(Concentration\ of\ analyte\ in\ the\ spike\ solution\ (in\ \mu g/L)) * (amount\ of\ spike\ added\ (in\ mL))] / (sample\ volume\ (in\ mL))$ .

**APPENDIX 1. QUALITY ASSURANCE DATA AND FIGURES—Continued**

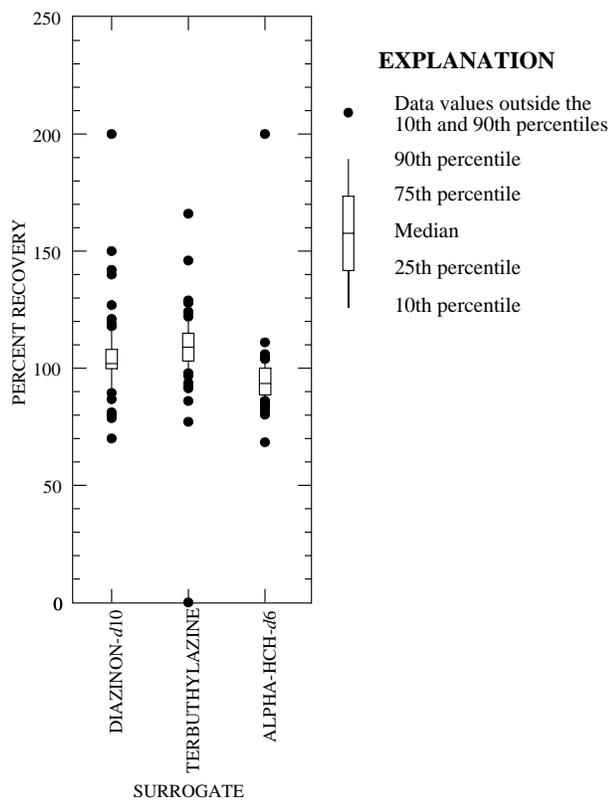
**Table 1-1.** Results of analyses of replicate grab samples and depth and width integrated samples for pesticides detected in the Willamette River Basin, Oregon, during 1996

[Values are in micrograms per liter (µg/L), except surrogate recoveries, which are in percent. Schedule 2010 compounds are analyzed at the U.S. Geological Survey’s National Water Quality Laboratory (NWQL) by gas chromatography/mass spectrometry, and Schedule 2051 compounds are analyzed by high performance liquid chromatography. Replicate samples for Schedule 2051 were not submitted for the sample from Oak Creek on 4/18/96. UT, Unnamed tributary; Cr, Creek; WF, West Fork; R1, first replicate (grab); R2, second replicate (grab); W, depth and width integrated sample; Rel. Diff, Relative difference, calculated as the range divided by the mean, in percent; E, Concentration is considered an estimate only; ND, not detected at the method detection limit (see table 3) for that compound; —, not applicable; NSA, no surrogate added. In all cases R1 is the primary value that is used for data analysis]

Compound	UT Oak Cr, 4/18/96			UT Ash Cr, 4/19/96			WF Palmer Cr, 5/14/96			Truax Cr, 10/24/96			UT Oak Cr, 11/17/96			
	R1 (µg/L)	R2 (µg/L)	Rel. Diff (%)	R1 (µg/L)	R2 (µg/L)	Rel. Diff (%)	R1 (µg/L)	R2 (µg/L)	Rel. Diff (%)	R1 (µg/L)	R2 (µg/L)	Rel. Diff (%)	R1 (µg/L)	R2 (µg/L)	W (µg/L)	Rel. Diff (%)
<b>Schedule 2010 Compounds</b>																
Alachlor	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Atrazine	90	90	0	0.05	0.048	4.1	0.96	0.93	3.2	0.317	0.314	1	6.11	6.09	6.13	0.6
Carbaryl (E)	ND	ND	—	ND	ND	—	.03	.027	11	ND	ND	—	ND	ND	ND	—
Carbofuran (E)	ND	ND	—	ND	ND	—	.043 <sup>a</sup>	.048	11	ND	ND	—	ND	ND	ND	—
Chlorpyrifos	ND	ND	—	ND	ND	—	.31	.26	18	ND	ND	—	ND	ND	ND	—
DCCA	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Desethyl atrazine (E)	.2	.33	49	.015	.015	0	.022	.022	0	.050	.053	5.8	.14	.151	.146	7.5
Diazinon	ND	ND	—	ND	ND	—	.22	.21	4.7	ND	ND	—	ND	ND	ND	—
EPTC	ND	ND	—	ND	ND	—	.075	.074	1.3	ND	ND	—	ND	ND	ND	—
Ethoprop	E.003	<.003	100	ND	ND	—	.006	.005	18	.012	.013	8	.007	.006	.006	16
Fonofos	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Malathion	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Metolachlor	.41	.4	2.5	.004	.004	0	.9	.89	1.0	.387	.382	1.3	.958	.914	.94	4.3
Metribuzin	.044	.038	16	.11	.091	19	ND	ND	—	.144	.142	1.4	.84	.889	.903	7.2
Napropamide	ND	ND	—	ND	ND	—	.007	.006 <sup>a</sup>	15	ND	ND	—	ND	ND	ND	—
Prometon (E)	.009	.011	20	ND	ND	—	.009	.009	0	ND	ND	—	ND	ND	ND	—
Pronamide	ND	ND	—	ND	ND	—	.004 <sup>a</sup>	.003	29	.021	.016	27	.027	.023	.024	16
Propachlor	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Propanil	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Simazine	.01	.34	190	.006	.006	0	.067	.064	4.6	.009	.01	1.1	.667	.682	.675	2.2
Triallate	ND	ND	—	.015	.016	6.5	ND	ND	—	ND	ND	—	ND	ND	ND	—
Tebuthiuron	ND	ND	—	ND	ND	—	.047	.049	4.2	ND	ND	—	ND	ND	ND	—
Terbacil (E)	.043	.033	26	ND	ND	—	ND	ND	—	ND	ND	—	.009	.009	.01	11
Trifluralin	ND	ND	—	ND	ND	—	.021	.017	21	ND	ND	—	ND	ND	ND	—
Diazinon Surrogate	100	100	0	100	90	10	89.4	84.4	5.8	106	102	3.8	100	85.7	NSA	15
Terbutylazine Surrogate	NSA	NSA	—	112	104	7.4	119	120	.8	107	106	1	102	92.1	NSA	10
Alpha HCH Surrogate	90	90	0	100	90	10	86.9	82.5	5.2	93.5	96.1	2.7	87.1	72.9	NSA	18
<b>Schedule 2051 Compounds</b>																
Bentazon	ND	—	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Bromacil	ND	—	—	ND	ND	—	ND	ND	—	E.34	E.46 <sup>a</sup>	29	ND	ND	ND	—
Bromoxynil	ND	—	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
2,4-D	E5	—	—	ND	ND	—	ND	ND	—	.18	.15	18	.22	.32	<.035 <sup>b</sup>	120
Dicamba	E14	—	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Dichlobenil (E)	ND	—	—	ND	ND	—	.05	.05	0	ND	ND	—	ND	ND	ND	—
Dinoseb	ND	—	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Diuron	E2.5	—	—	.11	.1	9.5	.52	.53	2.9	E2.2	E2.5	13	E11	E12	E10	18
MCPA	.71	—	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Norflurazon	ND	—	—	ND	ND	—	ND	ND	—	ND	ND	—	ND	ND	ND	—
Oryzalin	ND	—	—	ND	ND	—	.86	.87 <sup>a</sup>	1.2	ND	ND	—	ND	ND	ND	—
Triclopyr	ND	—	—	ND	ND	—	ND	ND	—	E2.6	E2.6	0	.34	.51 <sup>a</sup>	.48	36
BDMC Surrogate	103	—	—	101	109	7.6	99	102	2.9	38	86	77	97	106	84	23

<sup>a</sup> Not detected initially. Revised upon verification request to NWQL.

<sup>b</sup> Verification attempted but chemical interferences rendered results inconclusive.



**Figure 1-2.** Recoveries for surrogate compounds added to environmental samples during 1996 to evaluate performance of analysis of pesticides by gas chromatography/mass spectroscopy. Diazinon-*d*10 and alpha-HCH-*d*6 are similar in structure and behavior to an orthophosphate insecticide (diazinon) and a chlorinated organic compound (alpha-HCH, or lindane) from the U.S. Geological Surveys schedule 2010, respectively, but are labelled with deuterium. Terbutylazine is a triazine herbicide and behaves similarly to other triazines in schedule 2010.



---

## APPENDIX 2

---



## APPENDIX 2. TOXICOLOGICAL REFERENCE DATA

**Table 2-1.** Toxicological reference values (LC<sub>50</sub>s) for compounds detected at study sites during 1996

[The target animal was rainbow trout, and LC<sub>50</sub> values are given for other animals only if data for rainbow trout were unavailable. Where sources disagree, the lower value was shown. Data Sources: 1, EXTNET (World Wide Web Page, <http://ace.orst.edu/info/extnet/pips/ghindex.html> 1997) 2, Meister, 1995; 3, William and others, 1996; 4, U.S. Environmental Protection Agency, 1986; 5, Rhône-Poulenc Ag Company, written commun.1997; —, not available; Exp. time, exposure time; µg/L, micrograms per liter, equivalent to parts per billion]

LC <sub>50</sub> values for aquatic organisms					
Compound	Animal	Exp. time	Concentration (µg/L)	Data sources	Remarks
Alachlor	Rainbow trout	96	2,400	1,4	Only moderately toxic to aquatic invertebrates and to fish (1)
Atrazine	Rainbow trout	96	9,900	3	Only slightly toxic to fish and other pond life (1)
Bentazon	Rainbow trout	—	>100,000	2	Practically nontoxic to both cold-water and warm-water fish (1)
Bromacil	Rainbow trout	48	56,000–75,000	1,3	Not toxic to aquatic invertebrates (1)
Bromoxynil	Rainbow trout	—	150 (**)	1	(** octanoate); (***) pure formulation)
	Rainbow trout	—	50 (***)	2	
Carbaryl	Goldfish	24	28,000	2	Moderately toxic to aquatic organisms (1)
Carbofuran	Rainbow trout	96	380	2	Very toxic to, coho salmon, perch, bluegills, catfish (1)
Chlorpyrifos	Rainbow trout	96	7.1–51	1	(* different temperatures); very highly toxic to freshwater fish, aquatic invertebrates (1)
	*				
2,4-D	Rainbow trout	96	377,000	3	Some formulations highly toxic to fish (1)
DCPA	—	—	—	—	Nontoxic to bluegill or sunfish, slightly toxic to rainbow trout (1), nontoxic to fish (2)
Desethylatrazine	—	—	—	—	
Diazinon	Rainbow trout	—	90–140	1	Most fish are very sensitive (1), toxic to fish (2)
Dicamba	Rainbow trout	96	135,400	1,3	Low toxicity to fish (1)
	Rainbow trout	48	35,000	1,2	
Dichlobenil	Rainbow trout	96	4,930–6,260	3	
Dinoseb (DNBP)			—	1,2	Highly toxic to fish (1,2)
Diuron	Rainbow trout	96	3,500	2	Moderately toxic to fish and highly toxic to aquatic invertebrates (1)
EPTC	Rainbow trout	96	19,000	1,2,3	Slightly toxic to fish (1)
Ethoprop	Rainbow trout	96	2,100	2,5	Moderately to highly toxic to rainbow trout; highly toxic to bluegill (2)
Fonofos	Rainbow trout	96	50	1,2	Highly toxic to freshwater fish (1)
Malathion	Rainbow trout	—	200	2	Fish have a wide range of toxicities (1)
MCPA	Rainbow trout	96	117,000	3	
Metolachlor	Rainbow trout	96	2,000	1	Moderately toxic to both cold and warm-water fish (1)
Metribuzin	Rainbow trout	96	64,000–76,000	1,2,3	Slightly toxic to fish, moderately toxic to invertebrates(1)
Napropamide	Rainbow trout	—	9,400–13,300	1	Moderately toxic to freshwater fish (1); slight hazard to fish (2)
	Rainbow trout	96	16,600	3	
Norflurazon	—	—	—	—	
Oryzalin	Rainbow trout	96	3,260	1,3	Moderately toxic to fish (1)
Prometon	Rainbow trout	96	19,600	3	
Pronamide	Rainbow trout	96	72,000	1,2,3	Practically nontoxic to warm-water fish; slightly toxic to cold-water fish (1)
Propachlor	Rainbow trout	96	170	3	Toxic to fish (2)
Propanil	Rainbow trout	96	2,300	1	Toxic to aquatic invertebrates and fish (1)
	Rainbow trout	—	1,300	2	
Simazine	Rainbow trout	48	56,000	1,2	Low toxicity to all aquatic species reviewed (1)
	Rainbow trout	96	2,800	1	
Tebuthiuron	Rainbow trout	96	87,000	3	Not hazardous to aquatic organisms (1)
Terbacil	Rainbow trout	—	46,200	1	Not toxic to fish (1)
Triallate	Rainbow trout	96	1,200	1,2,3	Highly toxic to fish and other aquatic organisms(1)
Triclopyr	Rainbow trout	96	117,000	1,3	Practically nontoxic to fish and aquatic invertebrates (1)
Trifluralin	Rainbow trout	96	41	3	Toxic to fish and other aquatic organisms, toxic to <i>Daphnia</i> (1); toxic to fish (2)



---

## APPENDIX 3

---



## APPENDIX 3. DATA PRESENTATION

The information presented in this appendix is designed to be used with the CD-ROM included in this report. The CD-ROM contains data collected during the Phase III study for organic compound concentrations determined by gas chromatography/mass spectrometry (GC/MS) and high pressure liquid chromatography (HPLC), atrazine and metolachlor concentrations determined by immunoassay, field water quality data (water temperature, barometric pressure, streamflow, gage height, specific conductance, dissolved oxygen, pH, and suspended sediment), data for conventional constituents (nutrients, biochemical oxygen demand, and bacteria) and quality assurance (blank and replicate) data. Both here and on the CD-ROM are header files for each data file that explain the format and give an example line of the data file. Complete quality assurance data are not included on this CD-ROM because of the complexity involved in interpreting the data, but they are available upon request. GIS data for each of the subbasins sampled are also available upon request. Data on the CD-ROM are not aligned on decimal points and trailing zeros to the right of the decimal points were not removed. Text and data alignment in the electronic files may be font dependent; if alignment appears incorrectly, try changing to a nonproportional font such as courier.

### Header Files and Information

Header files are provided to facilitate data retrieval from the CD-ROM. There are seven subject-specific subdirectories each containing the data file (.dat) and accompanying header file (.hdr) that explains how the data are arranged. At the end of each header file is an example of how a line of data appears in the data file. A “-” is used as a placeholder when a field is blank. See table 3-1 for a list of remark codes used in the data files.

**Table 3-1.** Remark codes used in data files

Remark Code	Code Definition
E	Estimated value
<	Actual value is known to be less than value shown
>	Actual value is known to be greater than value shown
-	No remark

Because the data files included in these subdirectories are wide and are designed to be read into a spreadsheet for viewing, a printable data table of the field parameter and organic compound data has also been included on the CD-ROM. It is called “data.tab,” and is about 18 pages long, with 125 columns and 95 lines per page.

## APPENDIX 3. DATA PRESENTATION—Continued

### Header Information for Site Name and Location Data

The data file that contains the USGS station number, station name, date, time, latitude, and longitude is in the subdirectory “Sites.” The data file is called “sites.dat.” The header information for this data file is called “sites.hdr.” The data file is tab delimited and is arranged as follows:

USGS station number ..... columns 1–15;  
Map index number (see fig. 3) ..... columns 17–19;  
Station name ..... columns 25–94;  
Date ..... columns 97–104, yyyyymmdd;  
Time ..... columns 113–116, hhmm;  
Latitude ..... columns 121–126, in degrees minutes seconds (ddmmss);  
Longitude ..... columns 129–135, in dddmmss;  
Classification ..... columns 137–148, AGRICULTURAL or URBAN.

Below is an example of a line of data as it appears in the data file:

443239123072800 81 Lake Creek near Tangent 19960418 1310 443239 1230728 AGRICULTURAL

### Header Information for Organic Compound Data (GC/MS and HPLC)

The data files for the organic compound data are located in the subdirectory “Organics.” The data file that contains the organic compound data determined by GC/MS and HPLC is called “organics.dat.” The header information for this data file is called “organics.hdr.” The STORET codes used to identify the data values are listed in the data file called “organics.prm.” The data file is space delimited and is arranged as follows:

USGS station number ..... columns 1–15 (see “sites.dat” for full site names);  
Date ..... columns 17–24, yyyyymmdd;  
Time ..... columns 26–29, hhmm;  
Data values are listed as remark/value pairings in columns 31–821 listed by the STORET code, in micrograms per liter (see “organics.prm” or table 2 for interpretation of STORET codes; see table 3-1 for interpretation of remark codes).

Below is an example of a line of data as it appears in the data file:

441255123134300 19960513 1150 < 0.0070 < 0.0020 < 0.0350 - 0.0050 E 0.0070 E 0.0240 ...

## APPENDIX 3. DATA PRESENTATION—Continued

### Header Information for Atrazine and Metolachlor Data (Immunoassay)

The data files for the atrazine and metolachlor immunoassay data are located in the subdirectory “Organics.” The data file that contains the atrazine and metolachlor data determined by immunoassay is called “immuno.dat.” The header information for this data file is called “immuno.hdr.” The data file is space delimited and is arranged as follows:

USGS station number ..... columns 1–15 (see “sites.dat” for full site names);  
Date ..... columns 17–24, yyyyymmdd;  
Time..... columns 26–29, hhmm;  
Depth to water (DTW)..... columns 31–35, in feet, measured from a defined reference point to the water surface (an inverse measure of depth);  
Remark codes for atrazine ..... columns 37 (see table 3-1 for interpretation of remark codes);  
Atrazine concentration ..... columns 39–45, in micrograms per liter (µg/L);  
Remark codes for metolachlor ..... columns 47 (see table 3-1 for interpretation of remark codes);  
Metolachlor concentration ..... columns 49–53, in µg/L.

Below is an example of a line of data as it appears in the data file:

452204122521200 19960419 1210 0.83 - 0.052 < 0.06

### Header Information for Field Water Quality Data

The data file for the field water quality data (water temperature, barometric pressure, streamflow, gage height, specific conductance, dissolved oxygen, pH, and suspended sediment) is located in the subdirectory “Field.” The data file that contains the field water quality data is called “field.dat.” The header information for this data file is called “field.hdr.” The data file is space delimited and is arranged as follows:

USGS station number ..... columns 1–15 (see “sites.dat” for full site names);  
Date ..... columns 17–24, yyyyymmdd;  
Time..... columns 26–29, hhmm;  
Data values are listed as remark/value pair in columns 31–110, with a space between the remark and the value, in the order of the STORET code (see table 3-1 for interpretation of remark codes);  
P00010 (Water temperature) ..... columns 31–38, in degrees Celsius (°C);  
P00025 (Barometric pressure)..... columns 40–47, in millimeters of mercury;  
P00061 (Streamflow) ..... columns 49–56, in cubic feet per second;  
P00095 (Specific conductance) ..... columns 58–65, in microSiemens per centimeter at 25°C;  
P00300 (Dissolved oxygen) ..... columns 67–74, in milligrams per liter (mg/L);  
P00301 (Dissolved oxygen) ..... columns 76–83, in percent saturation;  
P00400 (pH) ..... columns 85–92, in standard units;  
P80154 (Suspended sediment concentration) ..... columns 94–101, in mg/L; and  
P70331 (Suspended sediment, finer than 62-micrometer sieve) ..... columns 103–110, in percent.

Below is an example of a line of data as it appears in the data file:

441255123134300 19960513 1150 - 17.760 - - - 1.3600 - 278.00 - 7.9500 - 83.400 - 7.4000 - 10 - 81

### APPENDIX 3. DATA PRESENTATION—Continued

#### Header Information for Data on Conventional Constituents

The data file for the conventional constituents (nutrients, biochemical oxygen demand, and bacteria) is located in the subdirectory “Cnventnl.” The file that contains the data for conventional constituents is called “cnventnl.dat.” The header information for this data file is called “cnventnl.hdr.” The data file is space delimited and is arranged as follows:

- USGS station number ..... columns 1–15 (see “sites.dat” for full site names);
- Date ..... columns 17–24, yyyyymmdd;
- Time..... columns 26–29, hhmm;
- Data values are listed as remark/value pair in columns 31–112, with a space between the remark and the value, and include an identifier for the lab that performed the analysis (see table 3-1 for interpretation of remark codes);
- Ammonium (NH4) ..... columns 31–37, filtered, in mg/L as nitrogen (N);
- Nitrite (NO2) ..... columns 39–45, filtered, in mg/L as N;
- Total kjeldahl nitrogen (TKN)..... columns 47–53, in mg/L as N;
- Nitrite plus nitrate (N2+3) ..... columns 55–61, filtered, in mg/L as N;
- Total phosphorus (TTP)..... columns 63–69, in mg/L as phosphorus (P);
- Orthophosphate (SRP) ..... columns 71–77, filtered, in mg/L as P;
- Agency lab used for nutrient analyses ..... columns 79–82, USGS = U.S. Geological Survey’s National Water Quality Lab, USA = Unified Sewerage Agency of Washington County (an ACWA member lab), ODEQ = Oregon Department of Environmental Quality;
- 5-day biochemical oxygen demand (BOD)..... columns 84–88, in mg/L of oxygen demand;
- Agency lab used for BOD analyses ..... columns 90–93, POR = City of Portland’s Water Pollution Control Facility (an ACWA member lab), ODEQ = Oregon Department of Environmental Quality;
- Escherichia coli* bacteria (ECOL) ..... columns 95–100, in colonies per 100 milliliters;
- Fecal coliform bacteria (FECAL)..... columns 102–108, in colonies per 100 milliliters; and
- Agency lab used for bacteria analyses ..... columns 110–112, EUG = Eugene/Springfield Water Pollution Control Facility (an ACWA member lab), OHD = Oregon Health Division (an ACWA member lab).

Below is an example of a line of data as it appears in the data file:

441255123134300 19960724 0950 E 0.039 < 0.005 - 2.94 - 0.03 - 0.894 - 0.119 USA < 2 POR...

### APPENDIX 3. DATA PRESENTATION—Continued

#### Header Information for Land Use Data

The data file for the land use data is located in the subdirectory “Landuse.” The data file that contains the land use data is called “landuse.dat.” The header information for this data file is called “landuse.hdr.” The map numbers and abbreviated station names (see “sites.dat” for full site names) are listed across the top of the data file in the first two lines. Land use data are only provided for those sites classified as “agricultural” (see table 6 or “sites.dat”). The data file is tab delimited and is arranged as follows:

- Crop type ..... columns 1–23;
- The land use data in columns 25–148 are listed by station as acreages in the subbasin.
  - 14206680 (Baker, 09) ..... columns 25–28;
  - 441255123134300 (Flat, 106) ..... columns 33–36;
  - 441842123174200 (Shafer, 104) ..... columns 41–44;
  - 442742123072300 (Shedd, 94)..... columns 49–52;
  - 443239123072800 (Lake, 81) ..... columns 57–60;
  - 443425123070700 (Oak, 80)..... columns 65–68;
  - 443856123012700 (Truax, 86) ..... columns 73–76;
  - 445032123144800 (SF Ash, 69) ..... columns 81–84;
  - 445146122505800 (Simpson, 61)..... columns 89–92;
  - 450419123191300 (Yamhill, 48)..... columns 97–100;
  - 450618123111600 (UT Ash Swale, 43) ..... columns 105–108;
  - 450947122564801 (Champoeg, 39)..... columns 113–116;
  - 451223122494500 (Senecal, 37) ..... columns 121–124;
  - 451244123050200 (Palmer, 40) ..... columns 129–132;
  - 451353122464700 (Deer, 27)..... columns 137–140;
  - 452204122521200 (Chicken, 10) ..... columns 145–148.

Below is an example of a line of data as it appears in the data file:

FESCUE SEED 24 606 224 155 1512 226 462 595 203 56 171 166 0 52 50

#### Header Information for Data from Extra Samples Not Included in Interpretation

The subdirectory “Extra” contains data from four extra samples that were collected during the study but were not included in the data sets (listed above) used for the interpretations presented in this report. These extra samples were excluded in order to make the number of samples consistent among sites. There is one extra sample from Shedd Slough at Bell Plain Drive near Shedd (452925123072303) that was collected during April 1996 before the site was moved to the location ultimately used for the study [Unnamed tributary to Shedd Slough at Fayetteville Road (442742123072300)]. There was an extra sample collected at Senecal Creek (451223122494500) during the October sampling period, and during some localized flooding in November 1996 there were two extra samples collected at West Champoeg Creek (450947122564801) and one at Lake Creek (443239123072800).

## APPENDIX 3. DATA PRESENTATION—Continued

### Header Information for Organic Compound Data (GC/MS and HPLC)

The data file for the organic compound data for the extra samples is located in the subdirectory “Extra.” The data file that contains the organic compound data for the extra samples determined by GC/MS and HPLC is called “extraorg.dat.” The header information for this data file is called “extraorg.hdr.” The STORET codes used to identify the data values are listed in the data file called “organics.prm” in the “Organics” directory. The data file is space delimited and is arranged as follows:

USGS station number ..... columns 1–15 (see “sites.dat” for full site names);

Date ..... columns 17–24, yyymmdd;

Time..... columns 26–29, hhmm;

Data values are listed as remark/value pair in columns 35–825, with a space between the remark and the value, in the order of the STORET code, in micrograms per liter (see “organics.prm” for interpretation of STORET codes; see table 3-1 for interpretation of remark codes).

Below is an example of a line of data as it appears in the data file:

442924123070303 19960418 1210 < 0.0070 < 0.0020 E 1.4000 - 0.0500 - 0.0390 E 0.0920 ...

### Header Information for Field Water Quality Data

The data file for the field water quality data (water temperature, barometric pressure, streamflow, specific conductance, dissolved oxygen, pH, and suspended sediment) for the extra samples is located in the subdirectory “Extra.” The data file that contains the field water quality data for the extra samples is called “extrafld.dat.” The header information for this data file is called “extrafld.hdr.” The data file is space delimited and is arranged as follows:

USGS station number ..... columns 1–15 (see “sites.dat” for full site names);

Date ..... columns 17–24, yyymmdd;

Time..... columns 26–29, hhmm;

Data values are listed as remark/value pair in columns 31–110m with a space between the remark and the value, in the order of the STORET code (see table 3-1 for interpretation of remark codes);

P00010 (Water temperature) ..... columns 31–38, in degrees Celsius (°C);

P00025 (Barometric pressure)..... columns 40–47, in millimeters of mercury;

P00061 (Streamflow) ..... columns 49–56, in cubic feet per second;

P00095 (Specific conductance) ..... columns 58–65, in microSiemens per centimeter at 25°C;

P00300 (Dissolved oxygen) ..... columns 67–74, in milligrams per liter (mg/L);

P00301 (Dissolved oxygen) ..... columns 76–83, in percent saturation;

P00400 (pH) ..... columns 85–92, in standard units.

P80154 (Suspended sediment concentration) ..... columns 94–101, in mg/L; and

P70331 (Suspended sediment, finer than 62-micrometer sieve) ..... columns 103–110, in percent.

Below is an example of a line of data as it appears in the data file:

451223122494500 19961024 0710 - 10.040 - 752.00 - 6.3800 - 492.00 - 3.0700 - 27,600 - 6.8100 - 12 - 74

### APPENDIX 3. DATA PRESENTATION—Continued

#### Header Information for Data on Conventional Constituents

The data file for the conventional water quality data (nutrients, biochemical oxygen demand, and bacteria) for the extra samples is located in the subdirectory “Extra.” The data file that contains the conventional water quality data for the extra samples is called “extracnv.dat.” The header information for this data file is called “extracnv.hdr.” The data file is space delimited and is arranged as follows:

- USGS station number ..... columns 1–15 (see “sites.dat” for full site names);
- Date ..... columns 17–24, yyymmdd;
- Time..... columns 26–29, hhmm;
- Data values are listed as remark/value pair in columns 31–112, with a space between the remark and the value, and include an identifier for the lab that performed the analysis (see table 3-1 for interpretation of remark codes);
- Ammonium (NH<sub>4</sub>) ..... columns 31–37, filtered, in mg/L as nitrogen (N);
- Nitrite (NO<sub>2</sub>) ..... columns 39–45, filtered, in mg/L as N;
- Total kjeldahl nitrogen (TKN)..... columns 47–53, in mg/L as N;
- Nitrite plus nitrate (N<sub>2</sub>+3) ..... columns 55–61, filtered, in mg/L as N;
- Total phosphorus (TOTP)..... columns 63–69, in mg/L as phosphorus (P);
- Orthophosphate (SRP) ..... columns 71–77, filtered, in mg/L as P;
- Agency lab used for nutrient analyses ..... columns 79–82, USGS = U.S. Geological Survey’s National Water Quality Lab, USA = Unified Sewerage Agency of Washington County (an ACWA member lab), ODEQ = Oregon Department of Environmental Quality;
- 5-day biochemical oxygen demand (BOD)..... columns 84–88, in mg/L of oxygen demand;
- Agency lab used for BOD analyses ..... columns 90–93, POR = City of Portland’s Water Pollution Control Facility (an ACWA member lab);
- Escherichia coli* bacteria (ECOL) ..... columns 95–100, in colonies per 100 milliliters;
- Fecal coliform bacteria (FECAL)..... columns 102–108, in colonies per 100 milliliters;
- Agency lab used for bacteria analyses..... columns 110–112, EUG = Eugene/Springfield Water Pollution Control Facility (an ACWA member lab).

Below is an example of a line of data as it appears in the data file:

450947122564801 19961117 1600 - 1.15 - - - 3.3 - 7.6 - 0.98 E 0.59 ODEQ - 3.8 POR - 900 - - EUG

## APPENDIX 3. DATA PRESENTATION—Continued

### Header Information for Quality Assurance Data

#### Header Information for Organic Compound Data (GC/MS and HPLC)

The quality assurance data file for the organic compound data is located in the subdirectory “QA.” The quality assurance data file that contains the organic compound data determined by GC/MS and HPLC is called “qa\_org.dat.” The header information for this data file is called “qa\_org.hdr.” The STORET codes used to identify the data values are listed in the data file called “organics.prm” in the “Organics” directory. The data file is space delimited and is arranged as follows:

USGS station number ..... columns 1–15 (see “sites.dat” for full site names);

Date ..... columns 17–24, yyyymmdd;

Time..... columns 26–29, hhmm;

Type ..... columns 31–33, NAT = native water sample, REP = replicate sample, BNK = field blank sample (see “Methods” section of report for explanation of sample types);

Data values are listed as remark/value pair in columns 35–825, with a space between the remark and the value, in the order of the STORET code, in micrograms per liter (see “organics.prm” for interpretation of STORET codes; see table 3-1 for interpretation of remark codes).

Below is an example of a line of data as it appears in the data file:

443426123070700 19960418 1520 NAT < 0.0070 < 0.0020 < 0.0350 - 0.0100 E 0.0090 E 0.200 ...

## APPENDIX 3. DATA PRESENTATION—Continued

### Header Information for Data on Conventional Constituents

The quality assurance data file for the conventional water quality data (nutrients, biochemical oxygen demand, and bacteria) is located in the subdirectory “QA.” The quality assurance data file that contains the conventional water quality data is called “qa\_conv.dat.” The header information for this data file is called “qa\_conv.hdr.” The data file is space delimited and is arranged as follows:

USGS station number ..... columns 1–15 (see “sites.dat” for full site names);  
Date ..... columns 17–24, yyymmdd;  
Time..... columns 26–29, hhmm;  
Type ..... columns 31–33, NAT = native water sample, REP = replicate sample, BNK = field blank sample (see “Methods” section of report for explanation of sample types);  
Data values are listed as remark/value pair in columns 31–112, with a space between the remark and the value, and include an identifier for the lab that performed the analysis (see table 3-1 for interpretation of remark codes);  
Ammonium (NH<sub>4</sub>) ..... columns 31–37, filtered, in mg/L as nitrogen (N);  
Nitrite (NO<sub>2</sub>) ..... columns 39–45, filtered, in mg/L as N;  
Total kjeldahl nitrogen (TKN)..... columns 47–53, in mg/L as N;  
Nitrite plus nitrate (N<sub>2</sub>+3) ..... columns 55–61, filtered, in mg/L as N;  
Total phosphorus (TOTP)..... columns 63–69, in mg/L as phosphorus (P);  
Orthophosphate (SRP) ..... columns 71–77, filtered, in mg/L as P;  
Agency lab used for nutrient analyses ..... columns 79–82, USGS = U.S. Geological Survey’s National Water Quality Lab, USA = Unified Sewerage Agency of Washington County (an ACWA member lab), ODEQ = Oregon Department of Environmental Quality;  
5-day biochemical oxygen demand (BOD)..... columns 84–88, in mg/L of oxygen demand;  
Agency lab used for BOD analyses ..... columns 90–93, POR = City of Portland’s Water Pollution Control Facility (an ACWA member lab), ODEQ = Oregon Department of Environmental Quality;  
*Escherichia coli* bacteria (ECOL) ..... columns 95–100, in colonies per 100 milliliters;  
Fecal coliform bacteria (FECAL)..... columns 102–108, in colonies per 100 milliliters;  
Agency lab used for bacteria analyses..... columns 110–112, EUG = Eugene/Springfield Water Pollution Control Facility (an ACWA member lab), OHD = Oregon Health Division (an ACWA member lab).

Below is an example of a line of data as it appears in the data file:

441353122464700 19960722 1241 REP < 0.02 < 0.005 - 0.469 - 1.78 - 0.368 - 0.252 USA ...