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

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Prepared in cooperation with
OREGON DEPARTMENT OF ENVIRONMENTAL QUALITY,
WILLAMETTE RIVER TECHNICAL ADVISORY STEERING COMMITTEE, and
NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Cover photograph. Looking upstream at the Willamette River with Mt. Hood and Portland Harbor in the background, February 7, 1993. *(Photograph by Dennis A. Wentz, U.S. Geological Survey.)*

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CONVERSION FACTORS

Multiply	By	To obtain
A. Factors for converting International System (SI) metric units to inch/pound units		
	Length	
meter (m)	3.281	foot
meter	1.094	yard
kilometer (km)	1.609	mile
	Volume	
milliliter (mL)	0.001057	quart
liter (L)	1.057	quart
liter	0.2642	gallon
	Mass	
gram (g)	0.03527	ounce avoirdupois
kilogram (kg)	2.205	pound avoirdupois
B. Factors for converting inch/pound units to SI metric units		
	Flow (volume per unit time)	
cubic feet per second (ft^3/s)	0.02832	cubic meter per second
C. Factors for converting SI metric units to other miscellaneous units		
	Concentration in Water	
milligrams per liter (mg/L)	1	parts per million
micrograms per liter (µg/L)	1	parts per billion

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Abstract

Between 1992 and 1994, the U.S.Geological Survey conducted a study of trace elements and organic compounds in the Willamette River Basin, Oregon, as part of the Willamette River Basin Water Quality Study. Low-level analyses were performed for trace elements, volatile organic compounds, organochlorine compounds, and pesticides. Overall, 94 water samples were collected from 40 sites, during predominantly high-flow conditions, representing urban, agricultural, mixed, and forested land uses. Although most observed concentrations were relatively low, some exceedances of water-quality criteria for acute and chronic toxicity and for the protection of human health were observed.

Concentrations of chromium, copper, lead, and zinc in unfiltered water were well correlated with concentrations of suspended sediment. The highest trace-element concentrations generally were found at urban sites that receive a large portion of their runoff from industrial areas, particularly at high suspended-sediment concentrations. In contrast, concentrations of trace elements in some urban streams draining primarily residential areas appeared to approach a maximum as sediment concentrations increased. Whether this difference was due to a difference in the nature of the suspended sediments or to different concentrations in the aqueous phases from the two site types was not addressed.

Eight organochlorine compounds were detected at 14 sites. Lindane, dieldrin, and DDT or its metabolites were each detected in about 30 percent of the samples, predominantly in samples collected from agricultural and urban areas. Polychlorinated biphenyl (PCB) compounds were detected in samples from two urban sites. For samples in which DDT and its metabolites were examined for partitioning, the largest proportion of the mass of DDT and its metabolites was associated with suspended sediment. In contrast, dieldrin and lindane were almost completely (greater than 99 percent) associated with the dissolved phase.

Sixty-one of the 94 pesticides analyzed in filtered water were documented to have been used in the basin in 1987; 43 of these were detected at least once during 1992–94. An additional five were detected that were not documented in the 1987 estimates. Although a comparison between the frequency of detected pesticides and 1987 estimates of pesticide usage in the basin showed generally little correlation, some patterns of detections did appear to reflect land use in the basin. Of the 25 most frequently detected pesticides, 3 were found primarily at urban sites, 6 were found primarily at agricultural sites, and 7 were found at all types of sites except forested. The four most commonly detected pesticides in the basin, observed at all except forested site

types, were atrazine, metolachlor, simazine, and diuron. A greater variety of compounds was detected at sites in the northern portion of the basin than in the southern portion of the basin probably because the northern portion has more diverse agricultural practices and a larger urban component. Possible reasons for the lack of agreement between pesticide detections and pesticide usage estimates include (1) uncertainty in the usage estimates due to spatial and temporal variability or due to changes in agricultural practices since the 1987 estimates were compiled, (2) chemical or biological transformations in the compounds after application, (3) variable hydrologic conditions among sites at the time of sampling, or (4) the ability of laboratory analytical procedures to detect low concentrations of some analytes.

Results from repeated samplings at two sites during sequential storms in the fall of 1994 indicated that concentrations and loads of several constituents, including suspended sediment, suspended organic carbon, DDT, metolachlor, and atrazine were highest during peak flows of the first or second significant storms of the fall. Samplings during subsequent storms indicated that instantaneous concentrations and loads were generally reduced; however, data were not sufficient to compare overall transport during sequential storms.

INTRODUCTION

In the 1930s and 1940s, discharges of organic wastes to the Willamette River, Oregon, and its tributaries produced severe water-quality problems that significantly degraded the river’s habitat, aesthetic value, and recreational uses (Gleeson, 1972). By 1972, basinwide efforts to improve the water quality of the Willamette River had proven quite successful, but some problems remained (Hines and others, 1977; Rickert, Peterson and others, 1977; Rickert, Kennedy, and others, 1977; F.A. Rinella and others, 1981; Fuhrer, 1989). In its biannual water-quality assessment report for 1990, the Oregon Department of Environmental Quality (ODEQ) listed dozens of stream reaches in the Willamette River Basin as not supporting or only partially supporting their designated beneficial uses (Oregon Department of Environmental Quality, 1990a). These remaining problems, as well as the 1987 Federal Clean Water Act amendments and a 1990 review of State water-quality standards, prompted the Oregon Legislature to establish the Willamette River Technical Advisory Steering Committee (WRTASC). Formed in 1990, this committee was created to work with ODEQ to establish priorities for and oversee the completion of a multiphase Willamette River Basin Water Quality Study (WRBWQS, also referred to herein as the Willamette Study).

Composed of representatives from ODEQ, State and local agencies, Federal agencies, industries, and environmental groups, the WRTASC established a broad range of scientific and educational goals for the Willamette Study (Oregon Department of Environmental Quality, 1990b). The overall objective of the study was:

> to develop a complete database for the river basin that is coupled with operative water-quality models that will enable Federal, State, and local agencies to cooperatively ensure the preservation and the beneficial uses of the Willamette River Basin and its associated biota (Tetra Tech, Inc., 1993a).

Specific work items included (1) development of predictive models of water quality, hydrology, and sediment transport; (2) calibration of these models using field-collected data; and (3) application of biological-community-assessment methods and other biological indices to assist ODEQ in future development of numerical biological criteria (Tetra Tech, Inc., 1993a).

Phase I of the Willamette Study included assessments, by a variety of investigators, of dissolved oxygen, nutrients, algae, trace elements and organic compounds, bacteria, point and nonpoint sources, sediment, flow, and ecological health. The U.S. Geological Survey (USGS) participated in Phase I through a cooperative project with ODEQ focusing on the trace elements and organic compounds, sediment, and flow components of the Willamette Study (Laenen, 1995; Lee, 1995; Laenen and Risley, in press). A summary of the other work was published in a series of technical reports that characterize the water quality and sources of pollution in the basin as well as the models that were developed in Phase I (Tetra Tech, Inc., 1992a, 1992b, 1993a, 1993b).

Phase II built upon the knowledge gained and the models developed during Phase I. The components of Phase II conducted by the USGS included (1) additional, basinwide investigations of the occurrence of trace elements and organic chemicals and their relation to land use, (2) measurement of sediment oxygen demand in the lower portion of the main-stem Willamette River (river miles 3.1 to 50.5) (Caldwell and Doyle, 1995), and (3) quantification of the factors controlling dissolved oxygen in the upper main-stem Willamette River and selected tributaries (Pogue and Anderson, 1995). As in Phase I, this work was part of a cooperative agreement with ODEQ. Other Phase II study components, conducted by Tetra Tech, Inc., included steady-state model calibration and data acquisition, nonpoint-source pollution studies, ecological monitoring, and a final report integrating results from the entire Willamette Study (Tetra Tech, Inc., 1994).

The USGS investigation of trace elements and organic compounds in Phases I and II was actively coordinated with two other concurrent USGS studies: the USGS National Water-Quality Assessment (NAWQA) Program (Wentz and McKenzie, 1991) and the Columbia River Bi-State Study (Fuhrer and others, 1996; Tetra Tech, Inc., 1993c). Relevant data from these studies also are included in this report.

Scope and Objectives

This report describes an investigation of the occurrence of trace elements and organic compounds in surface waters of the Willamette River Basin. The purposes of this report are to:

1. Document exceedances of State and/or Federal water-quality standards for trace elements and organic compounds in water.
2. Relate concentrations and (or) calculated instantaneous loads of trace elements and pesticides to land-use activities, streamflow conditions, and, for pesticides, agricultural practices and pesticide applications.
3. Assess the partitioning of selected trace elements and hydrophobic pesticides between the dissolved and suspended phases.

Table 1 shows the constituents and media that are discussed in this report. The primary focus is on Phase II; those constituents or media that were sampled exclusively in Phase I of the Willamette Study are not considered. All data from the Phase I and Phase II trace element and organic compound investigations, in addition to relevant data from the Willamette NAWQA and Columbia River Bi-State programs, were published by Harrison and others (1995).

Table 1. Constituent groups and sample media analyzed in Phases I and II of the Willamette River Basin Water Quality Study, Oregon, and discussed in this report
[✔, combination was analyzed; PCBs, polychlorinated biphenyls]

Constituent group	Unfiltered water	Filtered water	Suspended sediment
Trace elements	✔	✔	
Volatile organic compounds	✔		
Pesticides and PCBs	✔	✔	✔

Acknowledgments

The authors express their gratitude to the following individuals and organizations: the Oregon Department of Environmental Quality, for cooperative funding and logistical assistance; Ivan Blenderman, City of Portland Bureau of Environmental Services, for assistance in finding and gaining access to underground sampling locations, regardless of weather conditions or the time of day; the City of Corvallis Department of Public Works, for access to their sampling site at the Rock Creek Water Treatment Plant; Michael Fowler and Christa Reining of Woodward-Clyde Consultants, for access to flow data, maps, and water-quality information for underground sampling locations; and George Taylor, Oregon State Climatologist, for kindly supplying precipitation data. The WRTASC, the Association of Clean Water Agencies, and Northwest Pulp and Paper are gratefully acknowledged for their support and their contributions to the design of the Phase I and Phase II studies.

DESCRIPTION OF STUDY AREA

The Willamette River Basin, located in northwestern Oregon, is bounded on the north by the Columbia River and on the west, south, and east by the Coast Range, the Calapooya Mountains, and the Cascade Range, respectively (fig. 3). From the confluence of its

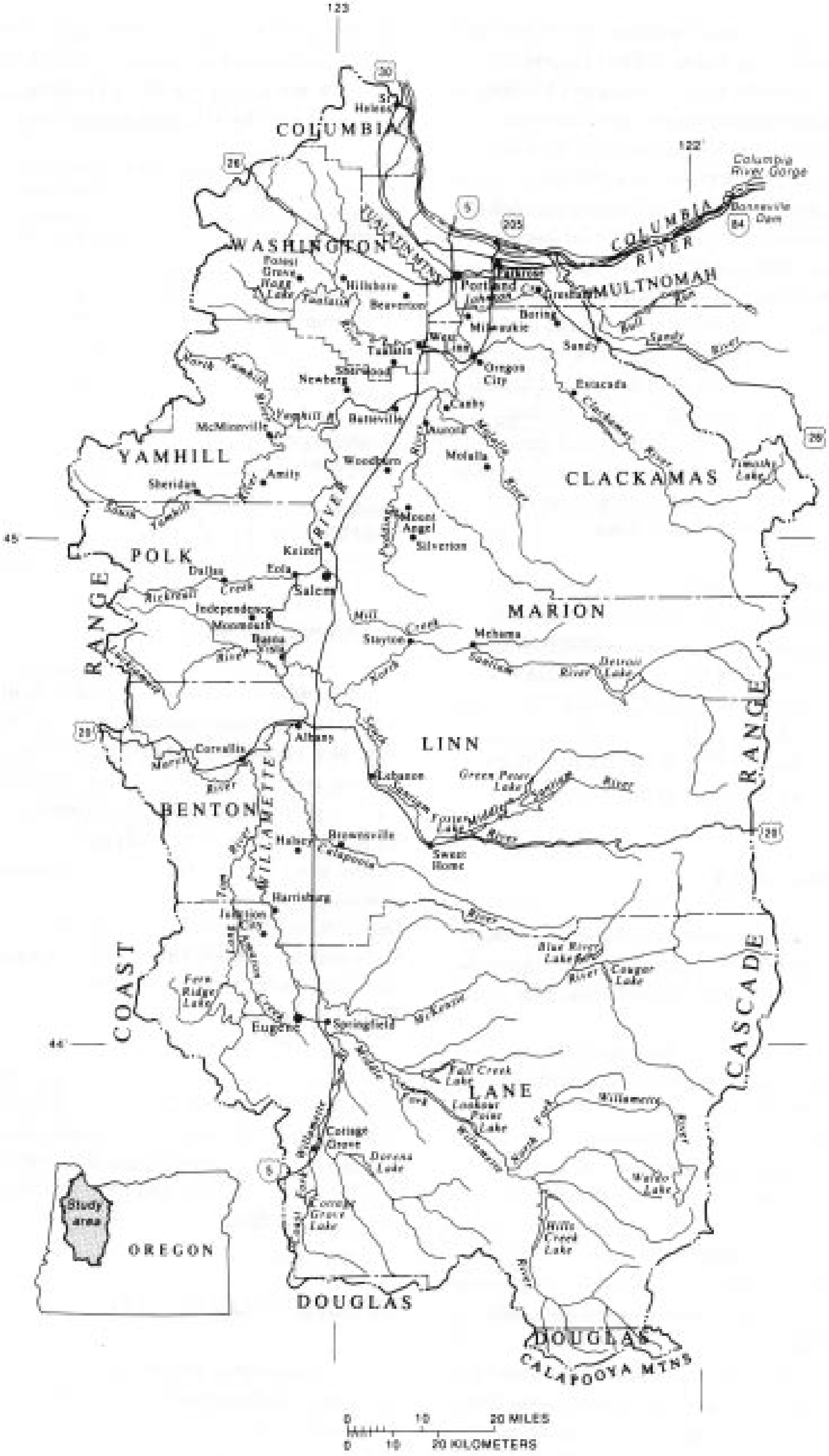


Figure 1. Willamette River Basin, Oregon.

Coast and Middle Forks near Eugene, the main stem Willamette River flows 187 miles northward to the Columbia River and drains an area of approximately 11,500 square miles. The basin includes some of the most productive agricultural and forest lands in the State, as well as the most heavily populated urban areas. The three largest cities in Oregon (Portland, Eugene, and Salem) and 68 percent of the State's population are located in the basin. Previous reports have described the basin's general characteristics (Bonn and others, 1995) and hydrogeology (McFarland, 1983; Gonthier, 1985).

Climate and Hydrology

A temperate marine climate provides the Willamette River Basin with characteristically cool, wet winters and warm, dry summers. Annual precipitation ranges from about 37 inches in parts of the valley bottom to about 175 inches on the slopes of the Coast Range and Cascade Range mountains (Taylor, 1993). Most of the precipitation falls between November and April; the driest months are July, August, and September. Although the higher elevations of the Cascade Range receive a substantial amount of snowfall in the winter, only about 35 percent of the annual runoff is from snowmelt (Laenen and Risley, in press). Streamflow throughout the Willamette River Basin, with the exception of some flow regulation from the basin's 11 major reservoirs, is dominated by the seasonal patterns of rainfall (fig. 2). The low-flow period, generally from July through September, typically accounts for 2 to 5 percent of streamflow for unregulated streams in the basin. In contrast, the high-flow period from November to April generally accounts for 80 to 90 percent of the annual flow in streams unaffected by reservoir regulation, and 60 to 80 percent in regulated streams (Moffatt and others, 1990).

Hydrologic processes often are very important in determining a stream's water quality. Runoff from storms can transport large quantities of pollutants, including trace elements and organic chemicals, into streams. In urban areas, numerous impermeable roads and parking lots and extensive storm drainage systems tend to route even small amounts of precipitation to streams quickly. In contrast, agricultural and forested

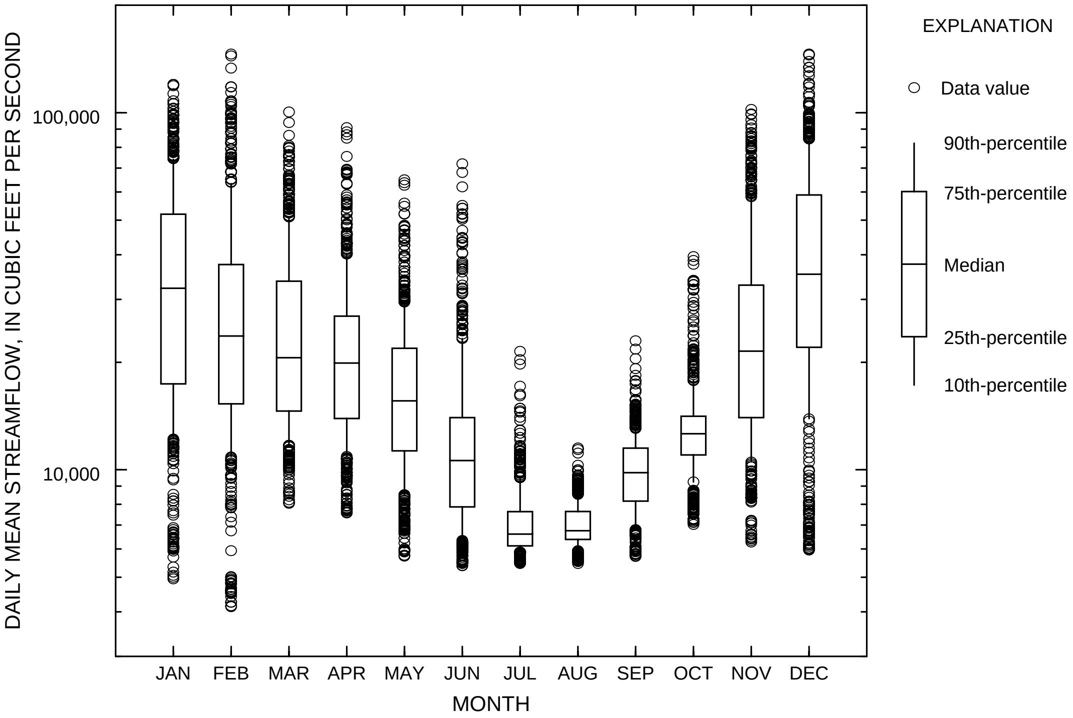


Figure 2. Monthly distribution of daily mean streamflow in the Willamette River at Salem, Oregon, 1975–94 water years.

areas allow more opportunities for precipitation to infiltrate into the ground rather than flow overland to a stream. All types of landscapes, however, produce runoff in response to moderate and strong rainfall; soils and contaminants from those landscapes are transported to streams with the runoff.

In streams, trace elements and organic compounds may be either dissolved or associated with particulate matter. The predominant phase depends on the contaminants chemical properties and other factors including the concentration of suspended sediment. The mobility and ultimate fate of pollutants that associate strongly with particulate matter depend in part on the mobility of the particulate matter. These pollutants may be transported, deposited, and resuspended with or disassociated from the particles in response to different hydrologic conditions.

During the low-flow, summer period, Willamette River Basin streams typically are characterized by low suspended-sediment concentrations; the occurrence and magnitude of high suspended-sediment concentrations is generally governed by precipitation runoff (Laenen, 1995). The highest concentrations of suspended sediments, and possibly of the pollutants that associate with those sediments, typically occur during storms.

Land Use, Crop Types, and Pesticide Use

Approximately 70 percent of the Willamette River Basin is forested, 22 percent is agricultural, and 5 percent is urban (Bonn and others, 1995). Land use in the basin is generally correlated with the basin's topographic characteristics. Elevations in the basin range from less than 10 feet near the Columbia River to more than 10,000 feet for the peaks of the Cascade Range. The higher elevations have shorter summers, harsher winters, steeper slopes, and poorer soils than the lower elevations, making them unsuitable for agriculture. The Willamette Valley bottom has a more hospitable climate and better soils for agriculture, and most major transportation hubs and industrial centers have been located near the rivers.

The slopes and foothills of the Cascade and Coast Ranges make up more than 50 and 20 percent of the basin's area, respectively. These areas are predominantly forested, with some smaller areas of agriculture at the lower elevations and no large urban centers. The Willamette Valley, generally considered to be the portion of the basin below an elevation of 500 feet, encompasses the remaining 30 percent of the basin's area. Land use within the Willamette Valley is varied, but taken as a whole, it is predominantly agricultural. The valley is also home to all of the basin's large urban areas, including the Portland metropolitan area (population approximately 1.5 million) at the northern end.

To understand what factors affect a stream's water quality, it is important to consider the land use upstream of each site of interest. The percentages of forested, agricultural, and urban lands upstream of several sites representing the valley's various land uses are listed in table 2. These data show some general patterns regarding the distribution of land uses throughout the Willamette River Basin. For example, many of the large tributaries that drain the Cascade Range and the Calapooya Mountains, including the Clackamas, McKenzie, Santiam, and the Coast and Middle Fork Willamette Rivers, have heavily forested basins, particularly in their headwater areas. The Coast Range tributaries, including the Long Tom, Luckiamute, Tualatin, and Yamhill Rivers, originate at lower elevations than those draining the Cascade Range and generally have larger percentages of agricultural land in their basins. The Calapooia River, Pudding River, and Muddy Creek Basins incorporate even larger percentages of agricultural land, originating and flowing predominantly through agricultural areas of the valley bottom.

Each site was classified as either "Forested," "Agricultural," "Urban," or "Mixed-use," on the basis of an areal assessment of the upstream land uses. The guidelines used here are the same as the preliminary scheme used by the Willamette NAWQA study and are summarized in table 3. These guidelines were selected with the recognition that water-quality impacts from agricultural and urban areas are typically stronger than those that result from forested areas. It was also recognized that strong point or nonpoint sources upstream from a sampling site could mask the influence of predominant land uses; sites were chosen to minimize these interferences.

Because agricultural practices and pesticide uses vary with crop type, the impact of agriculture on stream water quality often is related to the crops grown. The agricultural land in the Willamette River Basin supports a wide variety of crops (table 4). In terms of planted acreage, grass seed, wheat, and hay are by far the most important crops grown in the basin (Rinehold and Witt, 1989). Other important crops

Table 2. Percentages of forested, agricultural, and urban land upstream of selected locations in the Willamette River Basin
[Modified from Fegeas and others, 1983; not all locations listed here were used as sampling sites]

Site	Percentage of land use upstream of site			Drainage area (square miles)
	Forested	Agricultural	Urban	
Calapooia River (at mouth)	50	47	3	371
Clackamas River (near mouth)	89	8	3	941
Coast Fork Willamette River (below Cottage Grove dam)	96	1	1	106
Long Tom River (at Monroe)	58	28	9	394
Luckiamute River (near Suver)	78	21	1	237
McKenzie River (near Coburg)	94	2	1	1,336
Middle Fork Willamette River (at Jasper)	96	1	1	1,344
Muddy Creek (near Peoria)	27	71	2	146
Pudding River (at Aurora)	37	59	4	480
Santiam River (at Jefferson)	86	11	1	1,786
Tualatin River (at West Linn)	49	38	13	714
Willamette River (at Linnton)	70	24	5	11,205
Yamhill River (at Dayton)	58	40	2	771
Zollner Creek (near Mt. Angel)	0	99	1	15

Table 3. Guidelines used to classify sampling sites according to upstream land use

Site Classification	Percent of land upstream of sampling site		
	Forest land	Agricultural land	Urban land
Forested	≥ 90	≤ 10	≤ 10
Agricultural	≤ 50	≥ 50	< 25
Urban	≤ 50	< 25	≥ 50
Mixed-use	< 90	< 50	< 50

include grains (oats, barley, corn, and hops), seed crops (clover, sugar beets, vegetables, and flowers), fruits and nuts (cherries, filberts, and walnuts), row crops (beans, broccoli, peas, and others), many types of berries, and Christmas trees.

Pesticide applications are extremely variable. Among other considerations, the type of pesticide used depends on the crop, and the timing of its use depends on weather and soil conditions. To further complicate matters, the most recently published basinwide crop and pesticide-use estimates for the State of Oregon (Rinehold and Witt, 1989), which are based on data from 1987, are neither current nor comprehensive. These estimates, based on surveys of pesticide dealers and reports from commercial applicators and county agents, represent usages associated with cultivated agriculture, forestry, rights-of-way, urban, and miscellaneous uses. Because they are compiled for counties rather than for drainage areas, they only provide a general estimate of potential pesticide loadings to individual streams. Nevertheless, these estimates are the best available and are needed to help interpret instream pesticide concentration data. In this report interpretation of pesticide data in streams is made with the understanding that current practices are potentially different in important ways from those during the time of the 1987 survey.

In 1992 statewide agricultural chemical uses associated with seed and specialty crops, which have grown in importance in Oregon since the 1987 survey, were estimated by Reinhold and Jenkins (1994). Other recent reports detailing statewide pesticide use estimates have been prepared for small fruits, tree fruits, and vegetable crops. As with the seed and specialty crop report, these data are available on a statewide rather than a basin or countywide basis. Furthermore, the reports document surveys from successive years, with the result that compiling a comprehensive and quantitative estimate of updated, basinwide, annual application practices by crop type cannot be readily done on the basis of available literature. Nonetheless, the statewide estimates do provide an important indication of overall changes in pesticide application practices. Indeed, because the Willamette Basin is the location for much of the State’s crop production for

Table 4. Acres of crops, by county, in the Willamette River Basin, Oregon, 1987
[Data are from 1987 county estimates (Rinehold and Witt, 1989); Ranks are based only upon the crops listed in this table; —, not available]

Crop5	Acres in each Willamette River Basin county									Total acres	Rank
	Benton	Clackamas	Lane	Linn	Marion	Multnomah	Polk	Washington	Yamhill		
Alfalfa hay	1,400	3,800	1,500	2,200	5,000	600	2,600	5,000	4,300	26,400	7
Barley	800	700	2,000	2,500	1,000	300	2,400	800	2,500	13,000	13
Blackberries	60	930	135	75	2,720	270	470	495	600	5,755	17
Broccoli	20	365	—	140	1,700	90	30	300	250	2,895	24
Cabbage	—	345	—	—	90	490	—	—	—	925	27
Cauliflower	—	680	—	100	2,200	320	60	5	200	3,565	22
Cherries	60	95	475	65	1,500	10	2,400	480	1,500	6,585	16
Christmas trees	12,400	1,150	2,000	700	—	50	—	—	—	16,300	12
Clover and vetch seed	550	2,700	600	5,850	5,000	250	4,000	22,500	8,200	49,650	5
Cucumbers	—	695	10	10	340	340	—	500	40	1,935	26
Dry onions	—	140	—	—	2,500	—	50	500	250	3,440	23
Filberts	390	3,950	2,700	740	4,400	50	1,850	5,550	5,400	25,030	8
Grass seed	28,110	7,900	24,130	144,550	51,000	90	27,880	2,000	7,500	293,160	1
Green peas	1,440	455	100	130	4,800	285	—	—	—	7,210	14
Hops	—	50	—	—	4,500	—	800	—	—	5,350	18
Mint	2,000	—	5,400	4,000	4,500	—	1,120	—	—	17,020	10
Oats	3,000	4,600	3,000	5,000	7,000	500	15,600	9,900	13,600	62,200	4
Other hay	9,000	26,500	28,000	24,500	14,000	3,500	12,500	17,000	17,000	152,000	3
Pumpkins and squash	70	480	20	75	500	350	170	45	290	2,000	25
Raspberries	25	2,160	70	220	300	825	55	930	130	4,715	21
Silage corn	800	2,300	1,500	1,200	3,800	—	1,300	3,500	2,400	16,800	11
Snap beans	1,515	305	1,925	1,900	12,860	60	520	770	1,500	21,355	9
Strawberries	90	750	145	200	2,200	330	260	2,450	500	6,925	15
Sugarbeet seed	1,070	140	645	540	2,130	—	200	—	145	4,870	20
Sweet corn	2,780	1,860	2,600	3,250	15,960	1,010	1,670	3,060	3,270	35,460	6
Vegetable and flower seed	700	200	320	600	2,600	—	150	50	370	4,990	19
Wheat	19,500	10,000	10,500	26,000	23,000	1,800	30,600	16,000	36,000	173,400	2

certain crops, many of the changes may be largely attributed to the basin.

One example of a change in agricultural practices is the increased prominence of nurseries, a crop which in the 1987 estimates accounted for only 70 acres of land in the basin, yet by 1992 had become the second-largest crop in the State on a monetary basis, covering approximately 24,000 acres statewide (Reinhold and Jenkins, 1994). As nursery crops have increased in importance, so has the use of chemicals associated with them. For example, the use of chlorothalonil, metolachlor, napropamide, oryzalin, pendimethalin, and chlorpyrifos, all of which were analyzed as part of this study, each increased by amounts ranging from 1,000 to as much as 18,000 pounds statewide on nursery crops alone. Grass seed growing, which is more predominant in the Willamette Valley than any other place in the United States, has undergone major changes associated with a reduction in field burning since the late 1980's. As a result herbicide use for grass seed has changed; reductions in atrazine usage, a nationwide trend, were offset by equivalent increases in diuron usage and registration of the herbicide oxyflurfen to aid in removal of nuisance grasses. Other notable changes in chemical applications to seed and speciality crops include significant increases in the statewide usage of terbufos, glyphosate, terbacil, cycloate, and bentazon. Meanwhile other chemicals, including fonofos, dinoseb, simazine, and dicamba, have decreased in usage since 1987 (Reinhold and Jenkins, 1994).

Selected 1987 pesticide-use estimates for counties in the Willamette River Basin (Rinehold and Witt, 1989) are listed in table 5. The main section of the table lists the 30 most used pesticides in the basin, some of which were not analyzed as part of this study. The second section of the table lists 10 other chemicals of interest. These 10 were not among the 30 most used pesticides in the basin, but all were detected frequently in this study; therefore, their usage estimates are relevant. Several other pesticides, most notably prometon, ethoprop, and tebuthiuron, also were detected frequently, but were not included in table 5 because no usage rates were available. Note that although the pesticide-use surveys were focussed on agricultural areas, the estimates were not restricted to those areas; urban areas also were represented. For example, usage estimates for both malathion and glyphosate, chemicals used extensively in urban areas, are much higher in predominantly urban Multnomah County than in mostly rural Benton County.

STUDY DESIGN AND METHODS

Objectives

The streamflow and precipitation patterns of the Willamette River Basin were critical factors in the design of the Phase I and Phase II studies. An objective of Phase I was to examine trace-element and organic-compound concentrations to determine whether the concentrations are larger during summer low flow, when river dilution is minimal and when point sources may have their largest impact; or during intense rainstorms. The results indicated that high concentrations of trace elements and organic compounds were more likely during high-flow conditions.

The Phase II toxics study built on the results of Phase I. Concentrating on the runoff and resuspension during storms, Phase II was designed to examine relations between the timing of pesticide applications, streamflow, and concentrations of trace metals and organic compounds. Specific objectives included:

1. To examine the temporal variability of trace element and pesticide concentrations and loads in a sequence of major periods of storm runoff following pesticide application.

2. To relate concentrations and, where relevant, instantaneous loads of trace elements and pesticides to land use activities, pesticide applications, and streamflow conditions.

1. To measure the partitioning of selected trace elements and hydrophobic pesticides between the dissolved and suspended phases for selected samples.

The locations of sites sampled during Phases I and II are shown in figure 3. Selected sites were sampled at high flow in the spring shortly after pesticides were applied, and in the fall during the first major storms following summer low-flows. In addition, the fall sampling included several samples taken during the rise and fall of successive storm hydrographs.

Sampling Locations, Dates, and Constituents

Phase I sampling was done at only 11 sites (table 6); however, the number of constituents analyzed was extensive. In addition to both filtered and unfiltered water samples, samples of suspended and bed sediment were also collected. These samples were analyzed for a wide range of toxic constituents, including trace elements, organochlorine and organophosphorus compounds (OCs and OPs), volatile organic compounds (VOCs), semivolatile organic compounds, polychlorinated dibenzo-*p*-dioxins, and polychlorinated dibenzofurans. Filtered water samples were also analyzed for a set of 40 to 90 pesticides. Ancillary data included discharge, suspended-sediment concentrations, water hardness, and organic carbon and nutrient concentrations. The Phase I sites and analyses discussed in this report are listed in table 6.

Phase II sampling was performed at 32 sites during the spring of 1994 and at 16 sites during the fall of 1994 (tables 7 and 8, respectively). Several of the fall sites were sampled multiple times. Samples collected during Phase II were analyzed for organochlorine compounds in unfiltered water, triazine herbicides in filtered water, and a suite of 89 pesticides in filtered water. On selected samples, additional analyses were performed, including VOCs in unfiltered water, trace elements in unfiltered and (or) filtered water, and OCs in both filtered water and suspended sediment. Ancillary data, including discharge, suspended-sediment concentration, water hardness, and organic carbon and selected nutrient concentrations were also collected. A

Table 5. Annual usage rates of chemicals to control weeds and pests, by county, in the Willamette River Basin, Oregon, 1987

[Data are from 1987 county pesticide use estimates (Rinehold and Witt, 1989); *, analyzed as part of Phases I and II of the Willamette River Basin Water Quality Study; —, not available; 2,4-D, 2,4-dichlorophenoxyacetic acid; EPTC, S-ethyl dipropylthiocarbamate; MCPA, (4-chloro-2-methyl)phenoxyacetic acid; DCPA, dimethyl tetrachloroterephthalate]

Compound	Usage rate in each Willamette River Basin county (pounds/year)									Total usage (pounds/year)	Rank
	Benton	Clackamas	Lane	Linn	Marion	Multnomah	Polk	Washington	Yamhill		
Chemicals with the 30 highest usage rates											
2,4-D*	19,000	5,700	47,000	79,000	57,000	45,000	28,000	13,000	37,000	330,700	4
Alachlor*	7,300	3,700	3,900	8,300	30,000	440	3,000	2,400	4,500	63,540	25
Atrazine*	35,000	12,000	34,000	140,000	110,000	17,000	39,000	6,400	16,000	409,400	2
Benomyl	2,500	1,000	2,900	4,500	9,500	3,000	2,200	1,500	10,000	37,100	30
Calcium polysulfide	1,800	100,000	23,000	2,100	53,000	60,000	52,000	72,000	38,000	401,900	3
Captan	960	3,400	12,000	1,700	9,000	9,000	5,400	6,200	4,300	51,960	27
Carbaryl*	3,500	17,000	18,000	4,500	26,000	20,000	6,800	6,700	17,000	119,500	14
Chlorothalonil*	25,000	1,300	6,400	21,000	26,000	8,300	14,000	4,500	5,500	112,000	16
Chlorpyrifos*	8,100	2,900	13,000	25,000	28,000	30,000	4,300	610	8,800	120,710	13
Copper*	3,800	25,000	5,300	7,200	90,000	23,000	56,000	13,000	93,000	316,300	6
Diazinon*	2,000	4,900	15,000	5,500	23,000	46,000	12,000	2,000	12,000	122,400	12
Dicamba*	4,000	530	5,500	21,000	16,000	2,500	16,000	1,800	4,900	72,230	22
Dichlobenil*	580	3,000	3,500	1,600	7,500	17,000	6,000	2,300	4,600	46,080	28
Dichloropropene	—	13,000	—	—	2,500	11,000	—	29,000	—	55,500	26
Diclofop	13,000	580	9,000	16,000	13,000	1,800	19,000	15,000	21,000	108,380	18
Dinoseb*	15,000	9,400	9,400	16,000	40,000	4,000	4,600	1,900	8,500	108,800	17
Diuron*	44,000	7,500	36,000	160,000	82,000	18,000	100,000	47,000	58,000	552,500	1
EPTC*	14,000	2,400	8,000	17,000	25,000	1,600	1,800	4,300	4,500	78,600	20
Ethofumesate	7,500	200	6,000	45,000	7,500	—	2,600	50	190	69,040	24
Fonofos*	3,600	6,300	20,000	11,000	56,000	2,600	6,200	2,100	6,300	114,100	15
Glyphosate	4,700	4,700	19,000	17,000	27,000	61,000	7,500	8,900	8,500	158,300	10
MCPA*	12,000	2,500	12,000	19,000	24,000	1,400	30,000	13,000	20,000	133,900	11
Malathion*	360	2,100	350	370	5,600	50,000	2,600	3,400	6,900	71,680	23
Maneb	32,000	1,400	41,000	80,000	100,000	5,000	4,000	9,000	6,800	279,200	7
Metaldehyde	400	2,900	3,900	340	27,000	20,000	4,000	1,600	20,000	80,140	19
Metolachlor*	12,000	1,400	2,600	9,500	12,000	350	1,200	1,900	1,500	42,450	29
Napropamide*	890	12,000	3,000	1,600	16,000	15,000	5,800	14,000	6,500	74,790	21
Oil	1,300	23,000	40,000	1,500	120,000	27,000	16,000	17,000	74,000	319,800	5
Simazine*	7,700	5,400	18,000	40,000	42,000	23,000	15,000	11,000	4,500	166,600	9
Sulfur	4,000	1,700	12,000	5,000	61,000	3,500	96,000	8,200	49,000	240,400	8
Additional chemicals of interest—basinwide usage rates ranked lower than 30th											
Carbofuran*	—	1,400	1,200	—	760	1,300	180	5,400	500	10,740	54
Cycloate*	4,300	140	2,700	2,200	250	42	540	—	1,700	11,872	53
DCPA*	45	—	—	320	—	—	—	—	—	365	122
Hexazinone*	5,700	1,000	530	1,400	570	2,800	4,000	1,400	1,600	19,000	47
Lindane*	—	—	—	—	110	—	230	—	75	415	121
Metribuzin*	—	610	—	—	710	300	370	580	1,000	3,570	80
Pronamide*	1,300	2,800	970	2,100	6,300	1,100	3,700	1,400	2,100	21,770	42
Terbacil*	2,100	160	6,000	6,000	3,700	160	750	300	—	19,170	46
Triclopyr*	2,800	1,200	2,400	3,400	1,100	6,400	240	3,300	140	20,980	43
Trifluralin*	2,800	280	2,300	2,300	13,000	350	590	690	1,100	23,410	39

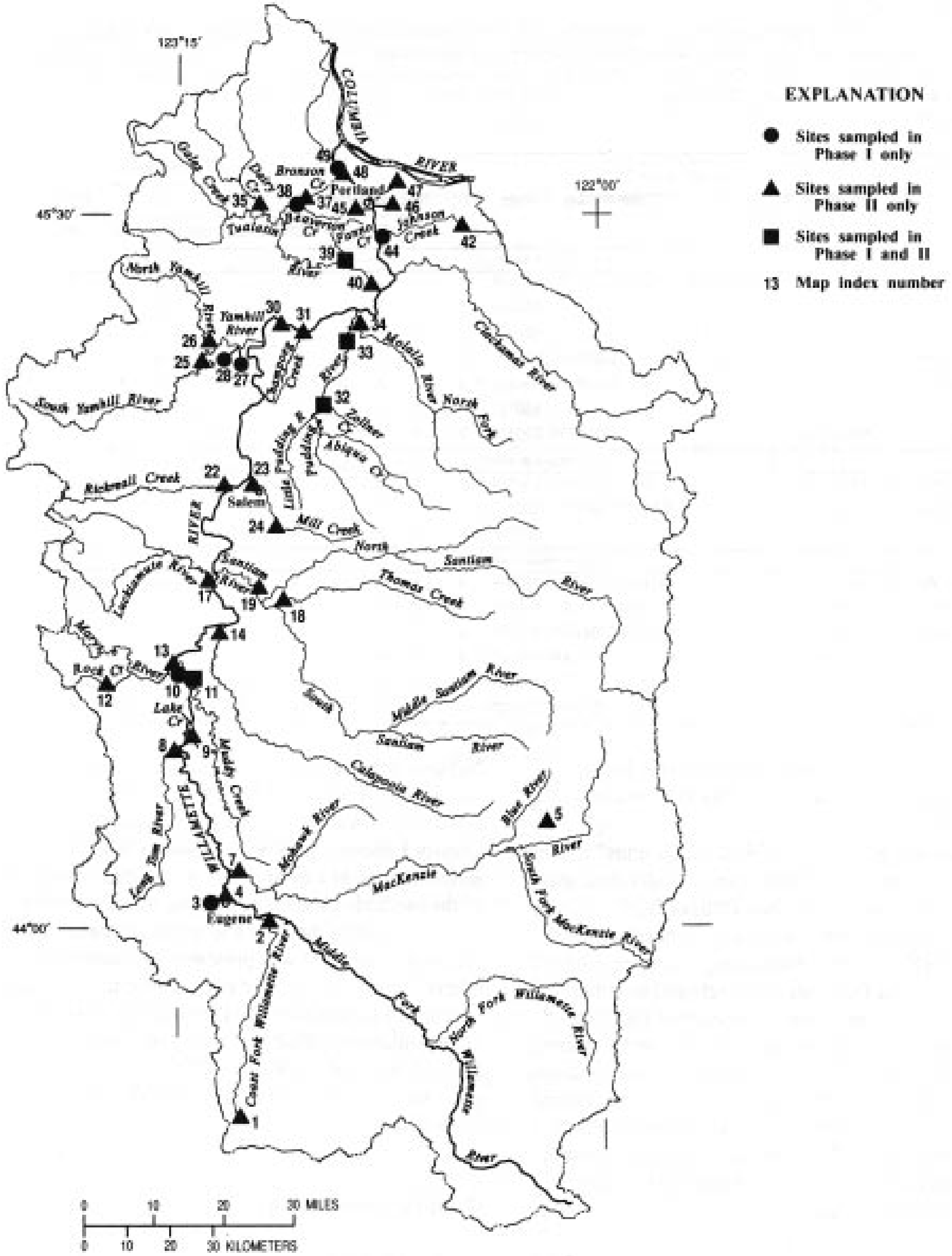


Figure 3. Sampling sites for Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94. (Index numbers on the map refer to specific sites listed in tables 6, 7, and 8.)

Table 6. Sampling plan for data used in this report and collected during Phase I of the Willamette River Basin Water Quality Study, Oregon, 1992–93

[Sites are listed in downstream order by site type and can be located in figure 3 by map index number; Basic, basic analyses, including flow, water temperature, specific conductance, pH, dissolved oxygen, suspended sediment, and dissolved and suspended organic carbon; UW, unfiltered water; FW, filtered water; SS, suspended sediment; GCMS, analysis of filtered water by gas chromatography/mass spectrometry; HPLC, analysis of filtered water by high-performance liquid chromatography; OC, organochlorine compounds; VOCs, volatile organic compounds; for a list of specific constituents refer to Harrison and others, 1995]

Map index number	Station name	Station number	Date	Basic	Trace elements			Organic compounds					
								Pesticides		OC			VOCs
					UW	FW	SS	GCMS	HPLC	UW	FW	SS	UW
	Urban sites												
3	A-3 Channel at Wallis and 5th St., Eugene	440313123091100	920416	X				X			X	X	X
			921016	X	X	X		X			X	X	X
			921029	X	X	X	X	X					
38	Beaverton Cr at 216th Ave. nr Orenco	453115122535500	930331	X	X	X		X	X		X	X	X
39	Fanno Cr at Durham	14206950	930301	X	X	X	X	X			X	X	X
			930722	X	X	X		X	X	X			X
44	Johnson Cr at Milwaukie	14211550	930314	X	X	X	X	X			X	X	X
	Mixed-use sites												
10	Willamette R nr Corvallis	443207123145500	930824	X	X	X		X	X	X			X
49	Willamette R at Linnton	453547122463000	920418	X	X	X	X						
			921026	X	X	X		X				X	X
	Agricultural sites												
11	Muddy Cr nr Peoria	443138123120901	930824	X	X	X		X	X	X			X
27	Palmer Cr at Dayton	451309123041501	930907	X	X	X		X	X	X			X
28	Yamhill R at Dayton	451320123041100	930907	X				X	X	X			
32	Zollner Cr nr Mt Angel	14201300	930601	X	X	X	X	X	X		X	X	X
			930727	X	X	X		X	X	X			X
33	Pudding R at Aurora	14202000	930427	X	X	X	X	X	X		X	X	X

complete list of the constituents analyzed during Phases I and II was documented by Harrison and others (1995).

In this report, the term “DDX compounds” is used to refer to undefined combinations of individual species of DDT or its metabolites, DDE or DDD, whereas “ΣDDX” refers to the sum of their concentrations (DDT + DDD + DDE). From a regulatory standpoint, DDT, DDE, and DDD are often referred to either interchangeably (to indicate presence of DDX compounds) or in summation (to indicate a total concentration). When tallying ΣDDX, individual concentrations of DDT, DDD, or DDE were set to zero if the individual species was not detected. DDX compounds and ΣDDX generally refer to just one sampling medium (unfiltered or filtered water or suspended sediment) unless otherwise noted.

Methods

Data for this report were published by Harrison and others (1995). These data are from the USGS’s National Water Information Storage system (NWIS) and were current as of May 1995. Owing to periodic updates to NWIS from the USGS National Water Quality Laboratory (NWQL), data in NWIS are subject to change at a future date. A detailed description of the methods used for collecting and processing samples (both in the field and in the laboratory) and cleaning equipment was provided by Harrison and others (1995). Sampling methods used in this study conformed to standard USGS procedures except where otherwise noted. For safety reasons, water from storm drains and manholes was collected as grab samples. Samples were analyzed at the NWQL in Arvada, Colorado.

Quality Assurance

The NWQL maintains an extensive and continuous quality-assurance/quality-control program. In addition, the USGS Branch of Technical Development and Quality Systems routinely administers nationwide laboratory intercomparison studies for analysis of

Table 7. Sampling plan for Phase II of the Willamette River Basin Water Quality Study, Oregon, spring 1994

[Sites are listed in downstream order and can be located in figure 3 by map index number; Basic, basic analyses, including flow, water temperature, specific conductance, pH, dissolved oxygen, suspended sediment, and dissolved and suspended organic carbon; UW, unfiltered water; FW, filtered water; Pesticides, selected pesticides in filtered water by solid phase extraction and gas chromatography/mass spectrometry or high-performance liquid chromatography; Triazines, low-level triazine herbicides in filtered water; OCs-UW, organochlorine compounds in unfiltered water; VOCs, volatile organic compounds; for a list of specific constituents see Harrison and others, 1995]

Map index number	Station name	Station number	Date	Basic	Trace elements		Organic compounds			
					UW	FW	Pesticides	Triazines	OCs-UW	VOCs
	Urban sites									
4	Urban outfall at Greenway Bicycle Bridge at Eugene	440402123063900	940613	X		X	X	X	X	X
37	Bronson Cr at 185th Ave nr Aloha	14206298	940527	X	X		X	X	X	
39	Fanno Cr at Durham	14206950	940524	X			X		X	
			940616	X			X			
45	Urban runoff at Harbor Way at Portland	453043122402200	940617	X	X	X	X	X	X	
47	Interstate 84 runoff at Portland	453154122394200	940531	X	X	X	X	X	X	X
	Forested sites									
1	Coast Fork Willamette R bl Big R nr London	433548123040600	940520	X	X		X	X	X	
5	Mack Cr nr Blue River	441310122095801	940527	X			X	X	X	
12	Rock Cr ab Griffith Cr nr Philomath	443045123273000	940518	X			X	X	X	
	Mixed-use sites									
2	Coast Fork Willamette R at Seavey Loop Rd nr Eugene	440045122585600	940519	X	X		X	X	X	
7	McKenzie R nr Eugene	440707123041300	940519	X			X	X	X	
13	Marys R at Corvallis	443321123155201	940518	X	X		X	X	X	
17	Luckiamute R nr Buena Vista	444349123094000	940516	X			X	X	X	
19	Santiam R at Jefferson	14189000	940517	X			X	X	X	
30	Willamette R at Hwy 219 nr Newberg	451602122564400	940531	X	X	X	X	X	X	
34	Molalla R nr Canby	451603122423301	940525	X			X	X	X	
40	Tualatin R at West Linn	14207500	940525	X	X		X	X	X	
46	Willamette R at Portland harbor	14211720	940510	X			X		X	
			940614	X			X			
48	Willamette R ab St John's Bridge at Portland	14211805	940523	X	X		X	X	X	
	Agricultural sites									
8	Long Tom R at Bundy Bridge nr Monroe	442223123153703	940519	X			X		X	
9	Lake Cr at Pine Grove Dr nr Harrisburg	442413123122500	940519	X			X		X	
14	Calapooia R at Albany	14173500	940526	X			X		X	
11	Muddy Cr nr Peoria	443138123120901	940526	X			X		X	
			940603	X			X		X	
			940620	X			X		X	
18	Thomas Cr at Kelly Rd nr Jefferson	444123122562200	940516	X			X	X	X	
22	Rickreall Cr nr mouth nr Salem	445547123065400	940526	X			X	X	X	
24	Mill Cr at Delaney Rd nr Turner	445037122573800	940614	X	X		X	X	X	
25	S. Yamhill R at McMinnville	14194150	940517	X	X		X	X	X	
26	N. Yamhill R nr McMinnville	451355123093600	940517	X			X	X	X	
31	Champoeg Cr bl Mission Cr nr Butteville	451502122524700	940526	X			X	X	X	
32	Zollner Cr nr Mt Angel	14201300	940525	X			X			
			940613	X			X			
33	Pudding R at Aurora	14202000	940412	X			X			
			940525	X			X			
			940615	X			X			
35	Dairy Cr at Rte 8 nr Hillsboro	14206200	940527	X			X	X	X	
42	Johnson Cr at Palmblad Rd nr Gresham	452823122240900	940524	X			X	X	X	

Table 8. Sampling plan for Phase II of the Willamette River Basin Water Quality Study, Oregon, fall 1994

[Sites are listed in downstream order by site type and can be located in figure 3 by map index number; Basic, basic analyses, including flow, water temperature, specific conductance, pH, dissolved oxygen, suspended sediment, and dissolved- and suspended-organic carbon; UW, unfiltered water; FW, filtered water; SS, suspended sediment; Pesticides, selected pesticides in filtered water by solid phase extraction and gas chromatography/mass spectrometry or high-performance liquid chromatography; Triazines, low-level triazine herbicides in filtered water; OC, organochlorine; VOCs, volatile organic compounds; for a list of specific constituents see Harrison and others, 1995]

Map index number	Station name	Station number	Date	Basic	Trace elements		Organic compounds					
					UW	FW	Pesticides	Triazines	OC compounds			VOCs
									UW	FW	SS	
			Urban sites									
23	Pringle Cr at Bush Park at Salem	14190970	941123	X	X	X	X	X	X			
			941130	X	X		X	X	X			
			941130	X	X		X	X	X			
37	Bronson Cr at 185th Ave nr Aloha	14206298	941123	X	X	X	X	X	X			X
39	Fanno Cr at Durham.	14206950	941027	X	X		X	X	X			
			941130	X			X					
47	Interstate 84 runoff at Portland	453154122394200	941108	X	X	X	X	X	X	X	X	X
			941108	X	X		X	X	X			
			941130	X	X		X	X	X			X
			941130	X	X		X	X	X			
			941202	X	X		X	X	X			
			Mixed-use sites									
40	Tualatin R at West Linn	14207500	941028	X	X		X	X	X			
			941205	X			X					
46	Willamette R at Portland harbor	14211720	941025	X		X	X					
			941029	X	X	X	X	X	X	X	X	
			941103	X		X	X	X	X			
			941202	X			X		X			
			Agricultural sites									
8	Long Tom R at Bundy Bridge nr Monroe	442223123153703	941101	X			X	X	X			
11	Muddy Cr nr Peoria	443138123120901	941102	X			X	X	X	X	X	
			941106	X			X	X	X	X	X	
			941109	X			X	X	X			
14	Calapooia R at Albany	14173500	941101	X			X	X	X			
24	Mill Cr at Delaney Rd nr Turner	445037122573800	941031	X			X	X	X			
			941104	X			X	X	X	X	X	
			941104	X			X	X	X			
25	S. Yamhill R at McMinnville	14194150	941102	X			X	X	X			
31	Champoeg Cr bl Mission Cr nr Butteville	451502122524700	941031	X			X	X	X			
32	Zollner Cr nr Mount Angel	14201300	941028	X			X	X	X			
			941128	X			X					
33	Pudding R at Aurora	14202000	941028	X			X	X	X	X	X	
			941029	X			X	X	X			
			941109	X			X	X	X			
			941129	X			X					
35	Dairy Cr at Rte 8 nr Hillsboro	14206200	941201	X	X		X	X	X			
42	Johnson Cr at Palmblad Rd nr Gresham	452823122240900	941027	X			X	X	X	X	X	
			941028	X			X	X	X	X	X	
			941101	X			X	X	X			
			941103	X	X		X	X	X			
			941123	X			X	X	X			

inorganic constituents to assess the performance of USGS and other laboratories using selected standard reference samples. The performance of the NWQL in these intercomparisons for the period of this study has been assessed and documented (laboratory #1 in Long and Farrar, 1994, 1995).

Quality-control samples accounted for approximately 15 percent of the Phase I and II samples sent to the NWQL; these samples were used to assess the quality of the data collected in this study. Several types of quality-control samples were submitted: laboratory, field, and equipment blanks were used to assess the potential for contamination; split samples were analyzed to estimate precision; spike solutions in native-water samples were used to test both accuracy and precision (when performed in duplicate). Specific results from the quality-control program were documented by Harrison and others (1995). Because of the variable nature of spike-recovery tests, use of quality assurance results to normalize native-water concentrations is not recommended. In this report data are presented as they were reported by the laboratory, with interpretations regarding quality control provided where appropriate. In general, the results of spike-recovery tests, blanks, and duplicate spike recoveries for organic compounds in native-water mixtures were quite good. The balance of this section describes a few of the quality-control results that are relevant to the interpretation of the data.

The lower limit of the NWQL's analytical capabilities are reported by one of two methods. The minimum reporting level (MRL) is the smallest measured concentration of a constituent that may be reliably reported using a given analytical method. For methods that use MRLs, concentrations that are less than the MRL are censored, and the data are reported as less than the value of the MRL. The method detection limit (MDL) is the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence as being greater than zero (Timme, 1994). For methods that use MDLs, concentrations may be reported that are less than the MDL for a given analyte; however, the chance of a false-positive detection for these results is greater than one percent. By far, most of the data included in this report were determined by methods that use MRLs. The exceptions are pesticides in filtered water analyzed under the NWQL's "schedule 2010" and under the custom analytical schedule "LC8015" (see below).

Replicate analyses for the trace-element samples generally indicated a high level of precision. Phase II stream samples submitted to the NWQL for duplicate analysis had identical concentrations for 5 of 7 trace elements in unfiltered water and 10 of 17 trace elements in filtered water. Of the remaining elements, the relative differences between the replicate samples in unfiltered water were 3.4 and 5.3 percent for chromium and lead, respectively, and in filtered water ranged from 1.8 to 67 percent. Four of the differences in filtered-water results were greater than 10 percent; however, each of these differences was at relatively low concentrations (less than 10 µg/L [micrograms per liter]), a concentration range in which the variability is typically higher. Accuracy was assessed through the USGS' internal quality assurance procedures, which indicate that during the Phase II sampling period, 3, 15, 7, and 5 percent of the dissolved cadmium, copper, nickel, and zinc quality-assurance samples, respectively, were outside of control limits (greater than 2 standard deviations from the mean sample concentration). All other dissolved trace elements were within control limits at all times.

A field-blank sample from the Phase II spring dataset indicated a possible unfiltered-water contamination of 0.2, 3, 2, and 10 µg/L for cadmium, copper, nickel, and zinc, respectively. In contrast, median detected springtime concentrations for these compounds were 4, 1, 2, and 245 µg/L, respectively. Up to 10 samples were potentially affected, although for cadmium and zinc only two of the springtime samples had detections in unfiltered water, at concentrations that were much higher than the level of contamination. In this report, unfiltered-water detections of copper (8 samples) and nickel (4 samples) from spring of 1994 that were equal to or less than the observed levels of contamination were eliminated from the data set. The contamination problem was subsequently eliminated through equipment modification; a field-blank sample from the Phase II fall sampling indicated no contamination of trace elements in unfiltered or filtered water.

Rather than customize its methods for every analyte of possible interest, the NWQL commonly develops procedures that are suitable for entire groups of analytes with similar chemical properties. The use of these "schedules" means that, if more than one schedule is requested, the concentration of a particular analyte might be determined more than once for each sample. Indeed, several organic compounds are included in more than one schedule used during the

Willamette Study. This is particularly true of the triazine herbicides, many of which were included in both schedule "2010" and in a custom schedule ("LC8015") that was used only for the low-level analysis of triazine herbicides. In both schedules, a water sample is extracted onto a cartridge packed with a carbon-based adsorbent, eluted at the NWQL with a solvent, and analyzed by gas chromatography/mass spectrometry (GC/MS) (Sandstrom and others, 1994; Zaugg and others, 1995). A comparison of results for common constituents in this study, however, indicated that the LC8015 method produced consistently poorer recoveries than the schedule 2010 method (Harrison and others, 1995). Because both schedules were used for each sample collected, and because the precision and accuracy of the schedule 2010 data were consistently better, results from schedule 2010 were used whenever possible. Results for a few constituents were only available as part of the LC8015 schedule; data for those constituents, therefore, were the only results from schedule LC8015 that were used in this report (Appendix 5).

Analogous to the overlap of constituents between schedules 2010 and LC8015, three particular compounds (carbofuran, carbaryl, and linuron) were included in both schedules 2010 and 2051. The latter schedule analyzes 41 compounds from a filtered water sample using solid-phase extraction and high-performance liquid chromatography (HPLC). Spike recoveries for the 2051 method were highly variable and, where comparisons could be made, lower than those from schedule 2010. For carbofuran, carbaryl, and linuron, the schedule 2010 results were used, and the schedule 2051 results were used generally for reference purposes only.

For the purposes of this report, data from schedule 2051 are considered to be primarily qualitative. Quality-assurance data collected from a variety of programs within the USGS have indicated that quantitative values for analytes in this schedule have a high degree of uncertainty. Percent spike-recovery data show relatively low and variable precision for many compounds. On the basis of limited samples, precision may be particularly variable at low ambient concentrations. However, no incidences of false-positive results have been observed. Therefore when these constituents are detected in a sample, they are considered to be present. For example, one such pesticide that was consistently detected was diuron. Recoveries for diuron samples spiked at approximately 1 μg/L ranged from 27 to 83 percent (median 51.6 percent). Nonetheless, one quarter of the native-water concentrations recorded for diuron were less than 0.11 μg/L; while these results indicated that diuron was actually present in these samples, probably at low concentrations, the exact magnitude of their concentrations is unknown.

Quality-assurance results for the organochlorine compounds (OCs) in unfiltered-water samples were mixed. Three different native-water samples were split for duplicate analyses; however, OCs were not detected in any of these samples or their respective duplicates. Duplicate spike analyses were performed on an additional sample, for which the spike recoveries were relatively low (ranging from 28 to 67 percent for the 10 compounds spiked) but repeatable. There was no evidence of contamination in blank or split samples. Comparison of results of unfiltered-water analysis for OCs with the sum of OCs in filtered water and in suspended sediment indicated that the unfiltered-water analysis usually underestimated the concentration of ΣDDX in the filtered and suspended phases. The largest discrepancy occurred in one sample from Johnson Creek, which had a unfiltered-water concentration of ΣDDX of 0.021 μg/L, whereas the ΣDDX concentration in the filtered and suspended phases was 0.064 μg/L. These differences are most likely due to the high partitioning of chlorinated organic compounds to suspended sediment, such that a greater mass of the analyte is usually available for analysis in the suspended phase compared to a unfiltered-water sample. In the limited number of suspended and filtered phase samples, no other OCs were detected so additional comparison is not possible.

RESULTS

Hydrologic Conditions

Because precipitation and runoff influenced the water quality characteristics of samples collected in this study, the hydrologic conditions must be considered along with chemical data. Daily rainfall amounts in Portland and Eugene for the Phase II study periods are shown in figure 4. Although rainfall in Portland and Eugene does not completely represent rainfall in other parts of the Willamette River Basin, the data indicate the general timing of storms and their relative strength.

Although one intent of Phase II was to sample during "high flow" in the spring following the application of pesticides, late-spring rains were unusually light and infrequent in 1994 (fig. 4). Average springtime (April to June) precipitation in Portland and Eugene from 1961–90 was 5.9 and 6.7 inches, respectively, whereas springtime rainfall in 1994 was 3.2 and 4.7 inches, respectively (Oregon Climate Service, 1996). On the basis of discussions with personnel from ODEQ and the WRTASC, it was decided that the sampling program would proceed at most sites after May 15, regardless of flow conditions, in the hopes that streamflows would not have receded so far that they would qualify as "low flow." Several storms contributed small amounts of rainfall, most notably on May 14 and June 5, 1994, but they did not produce basinwide high flow conditions.

In contrast to spring conditions, rainfall during the fall of 1994 was much more substantial and more evenly distributed throughout the basin. Average fall (October to December) precipitation in Portland and Eugene from 1961–90 was 14.1 and 20.3 inches, respectively; however, fall rainfall in 1994 was 19.2 and 23.2 inches at these two locations, respectively (Oregon Climate Service, 1996). Sampling commenced on October 27th (table 8) after the large storm on October 25–27 increased flows in rapidly responding small urban streams as well as in larger and slower responding streams draining agricultural and mixed-use basins. Sampling was conducted throughout October and November as rainfall continued to be near or above average. The final series of storms that were sampled occurred at the end of November and lasted through December 5, 1994 (fig. 4, table 8).

Because of these rainfall patterns, Phase II sampling at most sites occurred during relatively low-flow conditions in spring and high-flow conditions during fall. Figure 5 illustrates the hydrologic conditions encountered during the Phase II sampling periods at four gaged sites, including an urban, an agricultural, and two mixed-use sites. Because streamflow was not gaged at the sampling site on Johnson Creek at Palmblad Road, streamflow records from the nearest gaged site downstream (Johnson Creek at Sycamore) were used to indicate the relative timing of sampling. The fall samplings for several sites occurred during streamflows that are exceeded by only 10 percent of the recorded daily mean flows; springtime samplings occurred at streamflows that are exceeded by about 60 percent of the daily mean flows. As a result, the detected concentrations and the frequency of detections of trace elements and organic constituents during the spring sampling may not accurately reflect normal runoff conditions or land-use activity for typical spring conditions. Furthermore, data from the Phase II fall sampling may be similar to those which might have been found during spring runoff in years with more normal rainfall patterns because of the dry antecedent conditions, from April to October, after many potential pesticide-applications periods.

Trace Elements

Summary statistics for detections of trace elements from all Phase I and Phase II samplings are shown in Appendix 1. Trace elements were primarily sampled at urban sites, particularly during Phase II. Because one objective of these studies was to sample at sites where detections of trace elements or organic compounds were expected, sites were not selected at random. Finally, some sites were sampled more often than other sites. For these reasons, the analytical results represent episodic conditions for specific sites but may not accurately reflect basinwide concentrations of the constituents.

Exceedances of Water-Quality Criteria

Water-quality criteria were specified by ODEQ: constituent concentrations in water were compared to Oregon's freshwater aquatic-life criteria for acute (ATC) and chronic (CTC) toxicity and criteria for the protection of human health for water and fish ingestion (HHP), at a cancer risk level of 1 in 1 million (Oregon Administrative Rules, Chapter 340, Division 41, 1994). These criteria are summarized in Appendix 2. Some caution must be used in applying the criteria to data from Phases I and II, which represent instantaneous values; some toxicity criteria for acute and chronic toxicity are time dependent. Acute toxicity criteria 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. Much of the data are from filtered water samples, whereas the standards generally are based on unfiltered-water concen-

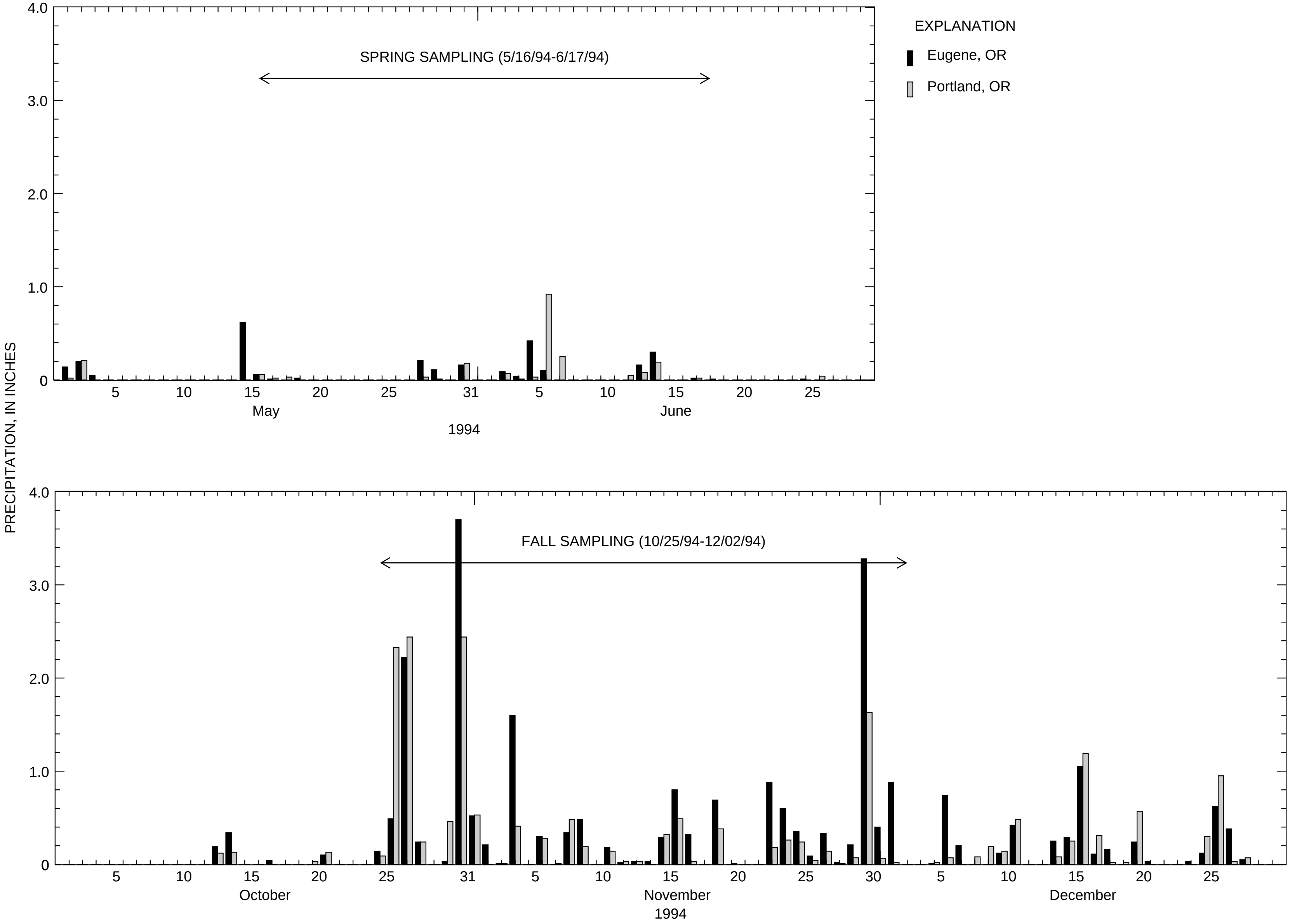


Figure 4. Daily precipitation at Portland and Eugene during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994. (Oregon Climate Service, 1986)

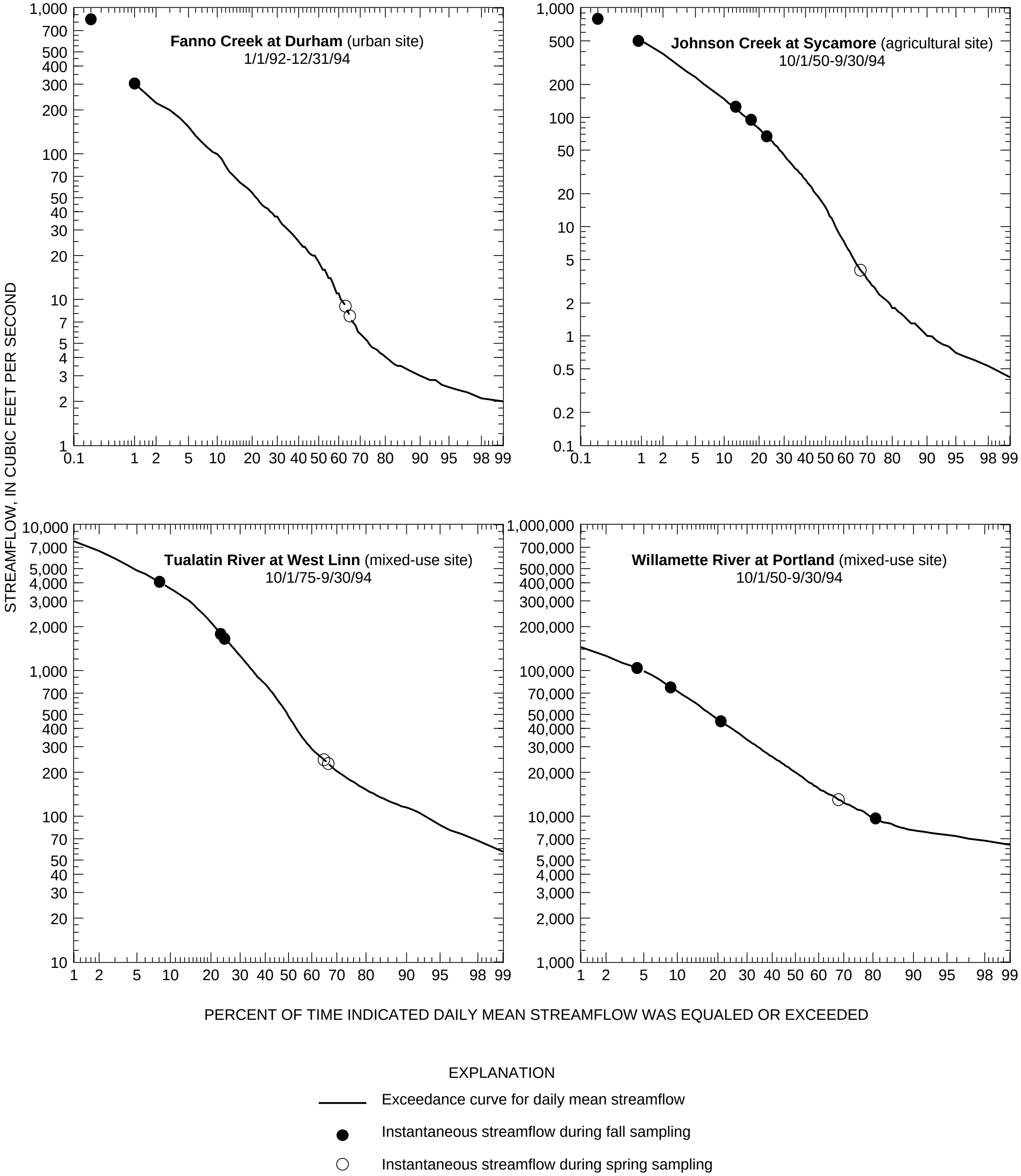


Figure 5. Percent of time daily mean streamflows were exceeded and instantaneous streamflows during sampling at four sites during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994.

trations. Many of the criterion values are lower than either conventional analytical detection limits or the relatively low detection limits achieved in this study. Consequently, some analytical results, in cases where the analytes were not detected at concentrations higher than their respective criteria, are considered inconclusive relative to criterion exceedances. These instances are noted in the appropriate tables. These aspects were not designed into the sampling plans because the large amount of additional sampling and laboratory analyses required to rigorously determine compliance with criteria was beyond the scope of the project.

Exceedances of criteria for trace-element concentrations in water are shown in table 9. Exceedances are noted if a concentration exceeded an indicated criterion on any one sampling occasion. Because the number of samples at each station varied, no attempt was made to document the number of times a given criterion was exceeded at a particular site. Codes in the table indicate the specific criterion (ACT, CTC, or HHP) for which the observed concentrations were either inconclusive or in exceedance. Exceedances for trace elements in bed-sediment samples (Phase I) are documented elsewhere (Tetra Tech, Inc., 1995).

Analyses for criteria exceedances for arsenic and mercury were inconclusive at many sites because the criteria for those trace elements are below the MRLs used (1 and 0.1 μg/L, respectively). No ATC or CTC has been defined by the State of Oregon for arsenic; however, the HHP is very low (0.0022 μg/L). For this reason, if arsenic was detected in any sample, the HHP was exceeded; otherwise, the results were inconclusive. For mercury, the ATC, CTC, and HHP values are 2.4, 0.012, and 0.144 μg/L, respectively. Mercury was detected in only one sample (A-3 Channel in Eugene, 0.1 mg/L), exceeding the CTC value; results from all other samples were inconclusive with respect to that criterion.

Water-quality criteria for cadmium, copper, lead, nickel, silver, and zinc are dependent on the hardness of the water. When hardness is low (median hardness for urban samples from Phases I and II was 46 mg/L [milligrams per liter]), the criterion may drop below the MRL, yielding inconclusive results. Consider the following example: A sample of filtered water from the urban outfall in Eugene had a cadmium concentration of less than 1 μg/L and a hardness of 73 mg/L as $CaCO_3$ (calcium carbonate). Using the equation from Appendix 2, the CTC for cadmium is 0.88 μg/L, which is less than the MRL of 1 μg/L. Because the actual concentration may have been greater or less than 0.88 μg/L, the result is inconclusive for CTC. In contrast, because the ATC for the same sample was calculated to be 2.75 μg/L, which is greater than the concentration measured, the ATC was not exceeded. Similar arguments apply for the other hardness-dependent results listed in table 9.

The criteria for trace elements in water were exceeded in a higher percentage of samples from urban sites than from agricultural or mixed-use sites. Copper, lead, and zinc exceeded either the ATC or CTC at five to six of the nine urban sites sampled. Among all sites, the most exceedances were for lead.

Samples from A-3 Channel at Wallis and Fifth Street in Eugene exceeded criteria for six of nine trace elements, and were inconclusive for cadmium and silver due to low hardness. Samples from Fanno Creek at Durham Road exceeded criteria for four of the nine constituents, and were inconclusive for cadmium, mercury, and silver. Of the sites draining predominantly agricultural areas, Dairy Creek near Route 8 in Hillsboro, Pudding River at Aurora, and Zollner Creek near Mount Angel were the only sites at which exceedances were recorded. At these two sites, arsenic and lead concentrations were higher than the HHP and the CTC, respectively. Mixed-use sites having concentrations of trace elements higher than their respective criteria included the Tualatin River at West Linn (lead) and the Willamette River at Portland (copper).

Relation to Land Use

Figure 6 shows all detected unfiltered-water concentrations of arsenic, copper, chromium, lead, nickel, and zinc at urban, agricultural, mixed-use, and forested sites during Phases I and II. Despite the inherent biases in the data set due to the variable numbers of samples collected at the different site types, urban sites typically had higher concentrations of these trace elements than did the other site types. In particular, concentrations of copper, lead, and zinc, which are often associated with urban runoff, were considerably higher at the urban sites. The most frequently detected trace element at agricultural and mixed-use sites was copper.

Three of the urban sites were storm drains or manholes (an urban outfall to the Willamette River in Eugene, a manhole accessing storm drainage from parts of downtown Portland at Southwest Harbor Way, and a manhole accessing drainage from Interstate-84 at Southeast 3rd Avenue in Portland [I-84 runoff]).

Table 9. Exceedances of State of Oregon criteria for trace elements in unfiltered and filtered water for streams sampled during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Sites are listed in downstream order by site type; water quality criteria are from Oregon Administrative Rules, Chapter 340, Division 41, 1994; trace elements for which no criteria exist, and sites for which no trace-element samples were collected, were excluded from this table; chromium was assumed to be entirely in the hexavalent state; freshwater criteria for acute and chronic toxicity for cadmium, copper, lead, nickel, silver, and zinc were calculated on the basis of measured hardness; 1, freshwater aquatic life criterion for acute toxicity; 2, freshwater aquatic life criterion for chronic toxicity; 3, criterion for protection of human health for water and fish ingestion (carcinogenic risk level of 1 in 1million); ***,** not detected, but results inconclusive because minimum reporting level (MRL) was larger than criterion for acute toxicity; **†**, not detected, but results inconclusive because MRL was larger than criterion for chronic toxicity; **‡**, not detected, but results inconclusive because MRL was larger than the human health criterion; shaded areas, not sampled; blank areas, sampled with no exceedance detected]

Site	Criteria Exceeded								
	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Silver	Zinc
Urban sites									
Urban outfall at Greenway Bicycle Bridge at Eugene	3	†		†		▨		†	
A-3 Channel at Wallis & 5th St., Eugene	3	*,†	1,2	1,2	1,2	2		*,†	1,2
Pringle Creek at Bush Park at Salem	‡	*,†		1,2	1,2	▨		*,†	1,2
Beaverton Creek at 216th Ave. near Orenco	‡					†		†	
Bronson Creek at 185th Ave. near Aloha	‡	†				▨		†	
Fanno Creek at Durham	3	*,†		2	2	†		†	1,2
Johnson Creek at Milwaukie	‡	†			2	†		†	
Urban runoff at Harbor Way at Portland	3	1,2		1,2	1,2	▨		*,†	1,2
Interstate-84 runoff at Portland	3	1,2	2	1,2	1,2,3	▨		*,†	1,2
Agricultural sites									
Muddy Creek near Peoria	‡	†				†		†	
Mill Creek at Delaney Rd. near Turner	▨					▨		▨	
South Yamhill River at McMinnville	▨	†			†	▨		▨	
Palmer Creek at Dayton	‡	†				†		*,†	
Zollner Creek near Mount Angel	3					†		†	
Pudding River at Aurora	‡	*,†			2	†		*,†	
Dairy Creek at Rte. 8 near Hillsboro	3	†			2	▨		▨	
Johnson Creek at Palmblad Rd. near Gresham	▨					▨		▨	
Mixed-use sites									
Coast Fork Willamette River at Seavey Loop Rd.	▨	*,†				†		▨	
Marys River at Corvallis	▨	†			†	▨		▨	
Willamette River below Corvallis WTP	‡	*,†			†	†		*,†	
Willamette River upstream Hwy. 219 at Newberg	‡	*,†			†	▨		*,†	
Tualatin River at West Linn	▨	†			2	▨		▨	
Willamette River at Portland	‡	*,†		1,2	†	▨		*,†	
Willamette River above St. Johns Bridge at Portland	▨	†			†	▨		▨	
Willamette River at Linnton	‡					†		*,†	
Forested site									
Coast Fork Willamette River below Big River near London		*,†			†	†		▨	

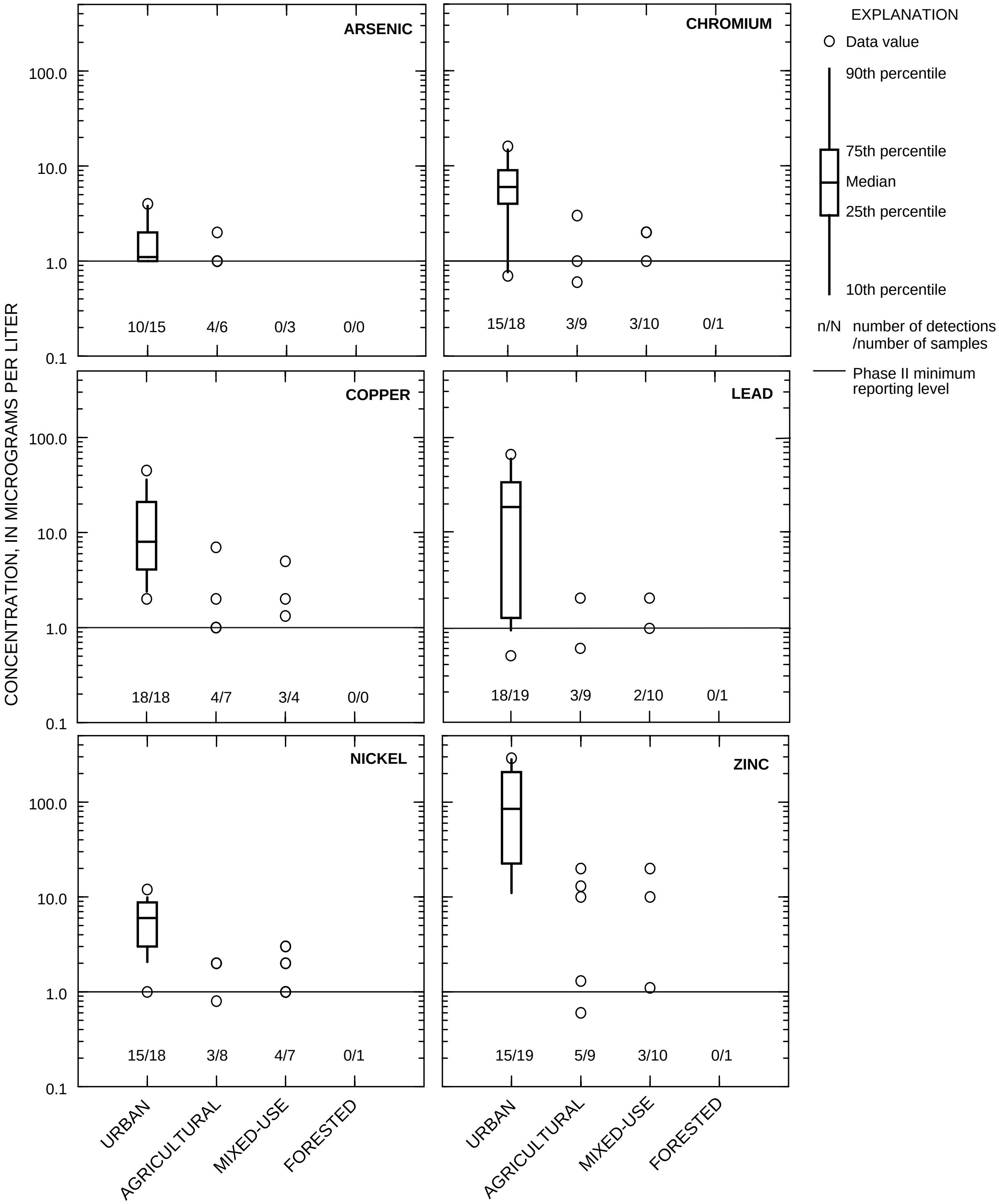


Figure 6. Concentrations of selected trace elements in unfiltered water detected at different site types during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94. (Lower minimum reporting levels [MRLs] were used in analyses of samples from Phase I than from Phase II; data values shown below the MRLs are from Phase I. When fewer than 10 data points were available, no box is shown.)

The manhole sites receive only storm runoff and are separated from any combined sewer overflow systems upstream of the sampling locations; the discharge from each enters the Willamette River directly downstream of each sampling location. The highest observed concentrations of copper and zinc (45 and 290 µg/L, respectively) occurred at the site at Harbor Way, and the highest concentrations of lead and nickel (67 and 12 µg/L, respectively) occurred at the I-84 runoff site. The highest observed concentrations of arsenic and chromium (4 and 16 µg/L, respectively) occurred at A-3 Channel in Eugene.

Relation with Suspended Sediment and Streamflow

Positive, significant ($p<0.005$) correlations were found between unfiltered-water suspended-sediment concentrations and detected unfiltered-water concentrations of chromium, copper, lead and zinc at urban sites from Phases I and II (table 10).

Table 10. Correlations of detected trace-element concentrations in unfiltered water with suspended-sediment concentrations for samples from urban sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Correlations were determined using Kendall's tau (τ), a non-parametric correlation coefficient that does not require normality (Helsel and Hirsch, 1992)]

Trace element	Number of samples with detections	Total number of samples	Kendall's tau (τ)	Significance (p level)
Arsenic	11	16	-0.2497	0.3184
Cadmium	7	19	.3705	.2664
Chromium	15	18	.7601	.0001
Copper	18	18	.4867	.0055
Lead	18	19	.6928	.0001
Nickel	15	18	.1933	.3472
Zinc	15	19	.5746	.0015

Correlations with suspended sediment for detections of arsenic, cadmium, and nickel were not significant. Cadmium may not have correlated well due to the relatively small number of detections. Because suspended-sediment concentration is highly correlated with flow and relatively independent of drainage area size, these results support the finding from Phase I that higher concentrations of trace elements occur during higher flow.

For these correlations, concentrations in unfiltered water, rather than in filtered water, were used because more unfiltered-water samples were collected and they contained detectable concentrations of trace elements more often than filtered water samples. Data were insufficient to compute correlations for agricultural or mixed use sites.

Among the urban sites sampled, two different site types are represented: (1) streams receiving mixed runoff from residential, light commercial, and light industrial land uses, hereafter referred to as residential streams, and (2) manholes, sewers, and ditches receiving runoff specifically from industrial and commercial areas, or roads, hereafter referred to as industrial streams. Of the sites listed as "urban" in tables 6, 7, and 8, the industrial sites include A-3 Channel in Eugene, Beaverton Creek near Orenco, the urban outfall at Greenway Bicycle Bridge in Eugene, commercial runoff at Harbor Way in Portland, and the I-84 runoff site. All other urban sites are considered residential streams.

The influence of residential and industrial site types on trace-element concentrations is shown in figure 7 for chromium, copper, lead, and zinc. Trace-element concentrations were the highest at industrial sites, and the apparent relations between trace-element concentrations and suspended sediment have a steeper slopes for industrial sites than for residential sites. At low suspended-sediment concentration, the relations for residential sites and industrial sites are similar; however, as the suspended-sediment concentration increases, the relations diverge with the residential trace-element concentrations becoming substantially lower than those from the industrial sites. At high suspended-sediment concentrations, the data from the two different types of urban sites appear to represent different populations.

For residential sites, more data are needed to better define the relation at moderate to high suspended-sediment concentration. Only three residential samples shown had high suspended-sediment concentrations: two from Pringle Creek at Bush Park in Salem, and one from Fanno Creek near Durham. No samples with suspended-sediment concentrations between 25 and 150 mg/L from residential sites were available to better define the intermediate part of the relation.

One possible explanation for the separation of the residential samples from the industrial samples at high sediment concentrations could be the source of the sediments. The residential streams may have experienced a large degree of bank erosion as flows increased, thus increasing the suspended-sediment

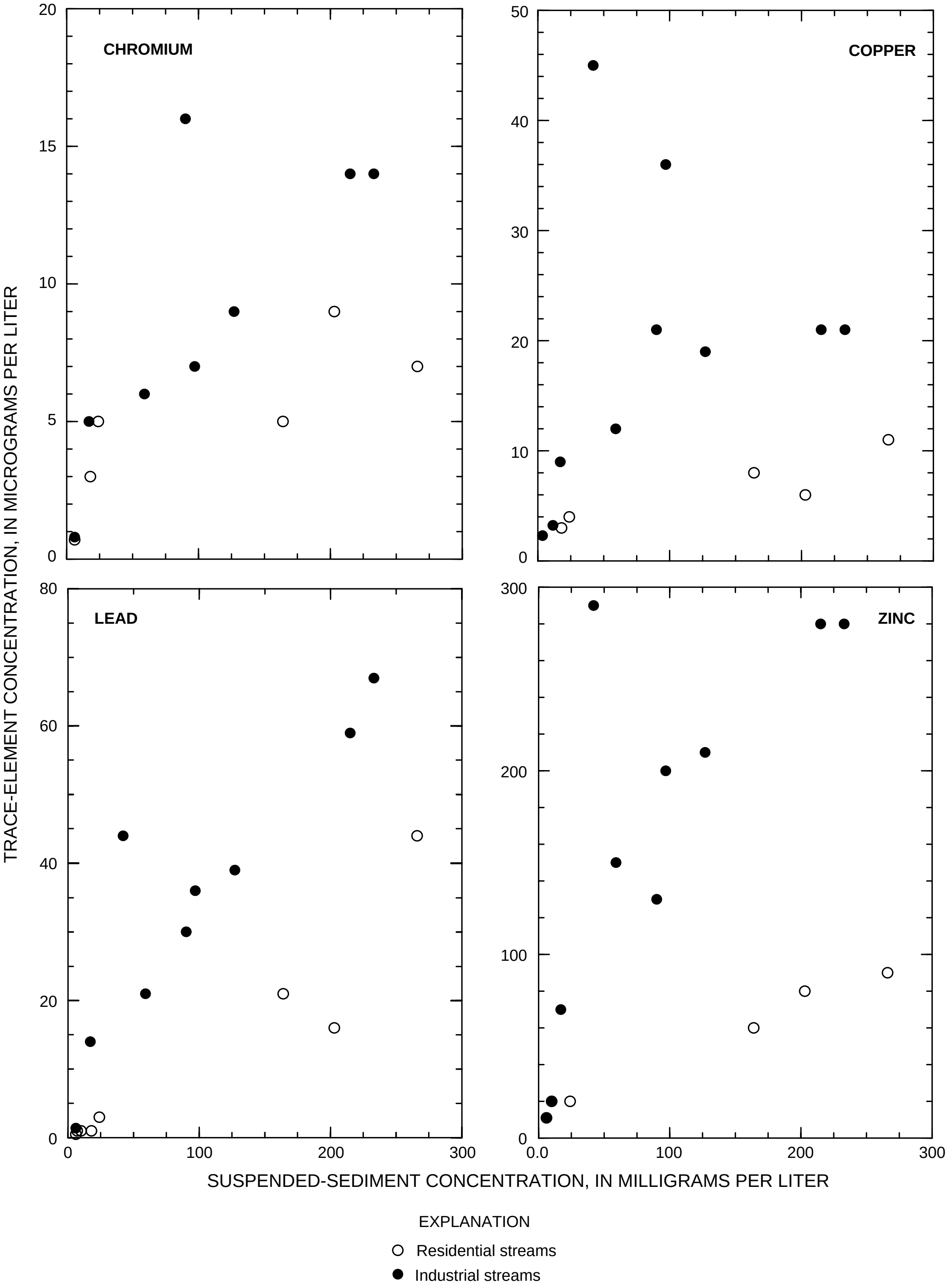


Figure 7. Relations of trace-element concentrations in unfiltered water with suspended-sediment concentrations at urban sites in the Willamette River Basin, Oregon, 1992–94. (Note that vertical scales are different for each plot. Samples for which a given trace element was not detected were excluded.)

concentration without increasing trace-element concentrations.

An extreme example of this phenomenon probably occurred at Fanno Creek at Durham on October 27, 1994. Data from that sampling were not included in figure 7 because they represented severe outliers. On this date, two prior days of storms had produced more than 3 inches of rain (fig. 4), resulting in runoff that was exceeded by less than 0.5 percent of the daily mean streamflows recorded at that site since the beginning of the flow record in 1992 (fig. 5). Water overflowed the streambanks upstream of the sampling site, and was observed to be flowing through fields and wooded areas as well as the stream channel. The sample was collected at peak flow at an instantaneous discharge of 946 ft^3/s (cubic feet per second), and had the highest suspended-sediment concentration (770 mg/L) measured during the entire Willamette Study. However, despite the high sediment concentration, unfiltered-water concentrations of copper (4 µg/L), lead (5 µg/L), nickel (3 µg/L), and zinc (30 µg/L), were no greater than their overall median concentrations for the entire study (Appendix 1). Apparently the suspended sediment was primarily derived from the erosion of streambanks and adjacent fields and did not contribute significantly to trace-element concentrations.

In contrast to residential streams, industrial streams are largely confined within pipes or other non-eroding structures. Their discharge should be almost entirely composed of more highly contaminated surface runoff from roads, parking lots, other man-made structures, and bed sediment. Industrial streams, therefore, would be expected to have relatively higher concentrations of trace elements when suspended-sediment concentrations are high, as appears to be the case. Indeed, concentrations of trace elements in suspended sediment from industrial sites were likely to be higher than from residential sites during Phase I sampling. This hypothesis is supported by two samplings that appear to be outliers on figure 7. Both samples were from industrial streams and had particularly high trace-element concentrations considering the observed suspended-sediment concentrations. A sample from a manhole in downtown Portland, collected at peak flow during a thunderstorm in spring 1994, had elevated concentrations of copper, lead, and zinc. The manhole, located at Harbor Way, contains water drained primarily from commercial areas. The suspended-sediment concentration was 42 mg/L. Unfiltered-water concentrations of copper (45 µg/L), cadmium (7 µg/L—not shown in figure 7), and zinc (290 µg/L) at this site were the highest observed during either phase of the study. The sample from A-3 Channel in Eugene during fall, 1992, had a disproportionately high concentration of chromium (16 µg/L) for a suspended-sediment concentration of 90 mg/L.

Concentrations of chromium, copper, and lead in unfiltered and filtered water, and those associated with suspended sediment are shown for all sites in figure 8. Data shown in figure 8 do not include cases where the element was detected in filtered water, but was detected at lower concentrations or not at all in unfiltered water: such cases are a result of analytical variability at low concentrations and represent a physical impossibility. For chromium, copper, and lead these included 4, 3, and 5 samples, respectively. Note also that the unfiltered and filtered water concentrations shown in figure 8, in micrograms per liter, are equivalent to parts per billion, whereas the suspended concentrations shown, in micrograms per gram, are equivalent to parts per million.

Because trace elements partition between the sediment and aqueous phases, concentrations in filtered and unfiltered water will rarely be equal. In fact, concentrations in filtered water were often substantially lower than those in unfiltered water. Lead concentrations detected in filtered water were nearly an order of magnitude less than those in unfiltered water, whereas copper concentrations in the filtered water were almost one-half of the unfiltered-water concentrations. However, considering all units in parts per billion, the suspended phase concentrations of trace elements were 5 to 7 orders of magnitude greater than dissolved phase concentrations when corrected for the concentration of suspended sediment. Thus, the suspended sediment was clearly the medium with which the greatest percentage of trace elements were associated during this study.

For the most part, concentrations of chromium, copper, and lead associated with the suspended phase were poorly correlated with concentrations in filtered water ($p<0.1$, 0.3, and 0.3, respectively). However, there are many factors in addition to suspended-sediment concentration that affect trace-element partitioning, including the potential lack of equilibrium, pH, and such sediment characteristics as the amount of iron and iron oxides, organic matter, size fraction, amount of clay minerals and colloids, and the amount of manganese and manganese oxides associated with

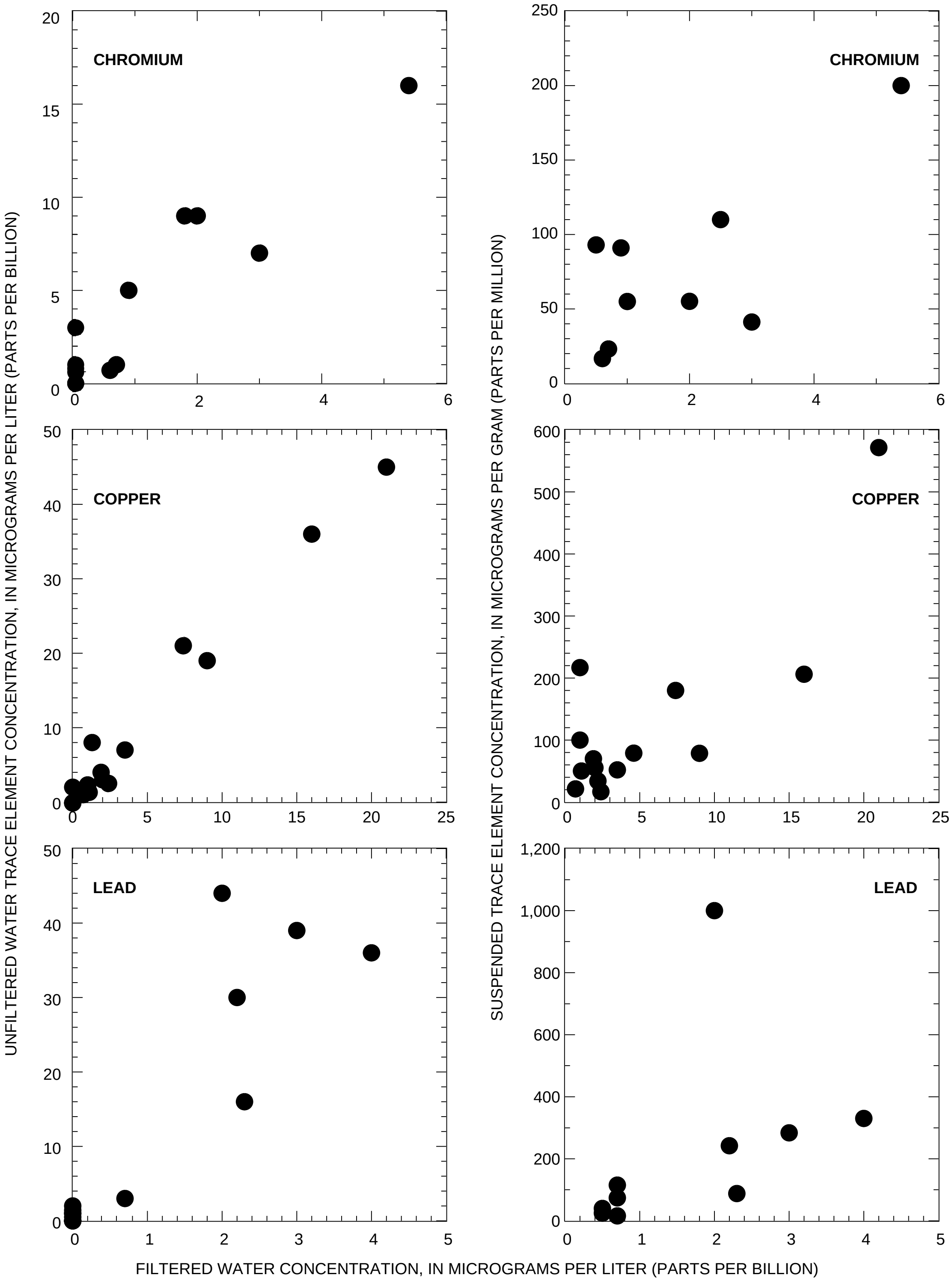


Figure 8. Unfiltered water and suspended concentrations of chromium, copper, and lead compared with filtered water concentrations in samples collected during Phases I and II in the Willamette River Basin Water Quality Study, Oregon, 1992–94. (Suspended concentrations of trace elements were determined for Phase II samples as [unfiltered water concentration - filtered water concentration / suspended-sediment concentration]. Samples from Phase I were measured in suspended sediment directly.)

the sediment (Horowitz, 1991). In fact, depending on the trace element of interest, partitioning of trace elements may be modeled by using either a linear partitioning coefficient or an isotherm (Langmuir or Freundlich) describing adsorption's dependence on the availability of potential binding sites and the relative concentrations of the trace element in solution (Drever, 1988). That the data in figure 8 do not clearly form such isotherms should not be surprising given the lack of control of environmental factors, and the probable disequilibrium during storm conditions, in the samples collected.

Current water-quality criteria for trace elements are defined in terms of unfiltered-water samples. Some proposals have suggested changing the criteria to reflect filtered water analyses, presumably due to bioavailability concerns. The data from Phase I and Phase II indicate that unless analytical methods with lower reporting limits are used, analysis of filtered samples will result in fewer detections and hence may more frequently be inconclusive with respect to criterion exceedances. Analytical methods with lower detection limits exist, but the costs of both analysis and sampling would increase substantially. Because some trace elements may bioaccumulate through the food chain, concentrations of trace elements in the sediments, to which most invertebrates and many fish are exposed, may actually be as relevant as those in filtered water with respect to biological concerns. Depending on the study objectives, there may be greater value in expanding trace-element data-collection efforts to include either bed sediments or suspended sediments, or both, rather than focussing on the dissolved phase. These media, as well as the tissues of fish or other aquatic animals, are likely to provide more detailed information regarding the potential for trace-element problems than would filtered water samples.

Organic compounds

Pesticides and OCs (organochlorine compounds) were sampled at each site during Phase I and Phase II; however, because data collected by the NAWQA and Lower Columbia River Bi-State programs were included, the total number of OC samples (73) is less than that for pesticides in filtered water (92). As with the trace-element data, the analytical results presented below represent episodic conditions for specific sites but may not accurately reflect basinwide concentrations or distributions of the constituents.

Volatile Organic Compounds

Summary statistics for detections of VOCs (volatile organic compounds) in unfiltered water, OCs in unfiltered water, and pesticides in filtered water are provided in Appendixes 3 through 6. During Phase II, VOCs were sampled exclusively at urban sites because it was felt that nonurban sites would not be important. Together with the samples from Phase I, a total of 18 VOC samples were collected from 12 locations in the Willamette River Basin and analyzed for 63 VOCs (table 11). Fourteen VOCs were detected at a total of four urban sites in areas with predominantly commercial or industrial urban land uses. Frequency of VOC detections ranged from five detections for cis-1,2-dichloroethene and tetrachloroethylene to one for naphthalene, pseudocumene, and 1,3,5-trimethylbenzene (table 11). VOCs with analyte concentrations of about 1 μg/L or greater occurred for benzene (1.0 and 1.5 μg/L), tetrachloroethylene (1.1 μg/L and 1.8 μg/L), and trichloroethylene (1.3 μg/L).

Exceedances of Water-Quality Criteria— Several concentrations for benzene (I-84 Runoff site, two samples), chloroform (A-3 Channel, two samples, and the urban outfall at Eugene, one sample), 1,1-dichloroethylene (A-3 Channel, two samples, and the urban outfall at Eugene, one sample), and tetrachloroethylene (A-3 Channel, two samples) exceeded their respective HHP values (table 12). No HHP values have been established for 1,1-dichloroethane, cis-1,2-dichloroethylene, methylene chloride, naphthalene, pseudocumene, 1,3,5-trimethylbenzene, or xylene.

Organochlorine Compounds

Seventy-three water samples were collected from 39 locations in the Willamette River Basin during Phase I and Phase II and analyzed for 17 organochlorine compounds. Lindane, dieldrin, DDX compounds (DDT and/or its metabolites, DDE and DDD), PCBs, endosulfan, and heptachlor were detected at a total of 14 sites. The most frequently detected OCs were lindane, dieldrin, and DDX compounds, which were detected in roughly 30 percent of the samples in predominantly agricultural and urban areas (table 13 and fig. 9). PCBs were the next most frequently detected organochlorine compounds, found in about 8 percent of the samples at two sites located in urbanized areas.

Table 11. Summary statistics for detected unfiltered-water concentrations of volatile organic compounds in the Willamette River Basin during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

Analyte	Percent detects	Number of detects	Number of samples	Median detected concentration (μg/L)	Maximum concentration (μg/L)
cis-1,2-Dichloroethylene	28	5	18	.6	.9
Tetrachloroethylene	28	5	18	.4	1.8
Trichloroethylene	22	4	18	.8	1.3
Chloroform	17	3	18	.2	.8
1,1-Dichloroethylene	17	3	18	.3	.3
1,1,1-Trichloroethane	17	3	18	.8	.9
Benzene	17	3	18	1.0	1.5
Methylene chloride	17	3	18	.3	.8
1,1-Dichloroethane	11	2	18	—	.4
Toluene	11	2	18	—	.7
Xylene	11	2	18	—	.6
1,3,5-Trimethylbenzene	6	1	18	—	.3
Naphthalene	6	1	18	—	.5
Pseudocumene	6	1	18	—	.2

Exceedances of Water-Quality Criteria

All 19 samples with detected concentrations of DDX compounds equaled or exceeded the Oregon CTC and HHP criteria for ΣDDX (0.001 and 0.000024 μg/L, respectively) (table 12). Eleven of the detected dieldrin concentrations, which were from samples from both agricultural and urban areas, exceeded the CTC (0.0019 μg/L), whereas all 23 of the detected dieldrin concentrations exceeded the HHP (0.000071 μg/L). Only three of the detected lindane concentrations (Zollner Creek near Mt. Angel and Champoeg Creek below Mission Creek—both agricultural) and one heptachlor concentration (the I-84 runoff site—urban) exceeded the HHPs for these compounds (0.019 μg/L and 0.00028 μg/L, respectively). All six detected PCB concentrations from Pringle Creek and the I-84 runoff site exceeded both the CTC (0.014 μg/L) and the HHP for PCBs (0.000079 μg/L).

Relation to Land Use

Although the sale and transport of DDT was banned in 1973, DDX compounds were detected (relatively often) in unfiltered water, and more frequently in urban than agricultural samples (38 and 26 percent, respectively—fig. 9). However, the number of distinct sites (10) at which DDX compounds were detected was relatively small; three sites each representing agricultural and mixed land uses and four representing urban areas. DDX compounds were detected in multiple samples from several sites, including the I-84 Runoff site and Johnson Creek at Palmblad Road. DDX compounds were detected in four of six samples from the I-84 runoff site and in each of six samples from Johnson Creek at Palmblad Road. The highest unfiltered-water concentrations of ΣDDX occurred at these two sites (0.06 and 0.021 μg/L, respectively). Previous studies have documented the occurrence of DDT and other organochlorines in Johnson Creek in greater detail (Edwards, 1992, 1994).

The frequency of detections of dieldrin was similar for urban and agricultural areas (38 and 41 percent of samples, respectively), although the highest concentrations were observed at an agricultural site (Johnson Creek, 0.02 μg/L). Lindane was observed more frequently in samples representing urban areas than agricultural areas (44 and 33 percent, respectively), but the highest concentrations were from Champoeg Creek, an agricultural site. The two sites at which PCBs were detected were the I-84 runoff site and Pringle Creek in Salem, both urban sites. As a result of this study, the Oregon Department of Transportation has initiated an investigation into possible sources of organic compounds at the I-84 runoff site (Jeff Moore, Oregon Department of Transportation,

Table 12. Exceedances of State of Oregon criteria for organic chemicals in water for streams sampled during Phases I and I of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Water-quality criteria are from Oregon Administrative Rules, Chapter 340, Division 41, 1994; Constituents for which no criteria exist were not included; methoxychlor and 2,4-D were omitted because criteria were not exceeded; 2,4-dinitro-*o*-cresol had one possible detection at Mill Creek at Delaney Rd. near Turner which equalled the freshwater aquatic life criterion for chronic toxicity but is considered uncertain due to matrix interferences; method detection limits (MDLs) for mirex and toxaphene exceed all three criteria; these compounds were not detected, so that results are inconclusive at all sites; 1, freshwater aquatic life criteria for acute toxicity; 2, freshwater aquatic life criteria for chronic toxicity; 3, criteria for protection of human health for water and fish ingestion (carcinogenic risk level of 1 in 1 million); †, not detected, but results inconclusive because MDLs were larger than criteria for chronic toxicity; ‡, not detected, but results inconclusive because MDLs were larger than the human health criteria; shaded areas, not sampled; blank areas, sampled with no exceedance detected]

Site	Criteria exceeded											
	Volatile organic compounds				Organochlorine compounds					Pesticides		
	Benzene	Chloroform	1,1-Dichloroethylene	Tetrachloroethylene	DDT+DDE+DDD	Dieldrin	Heptachlor	Lindane	PCBs	Chlorpyrifos	Malathion	Parathion
Urban sites												
Urban outfall at Greenway Bicycle Bridge at Eugene		3	3		‡	‡	‡		†,‡			
A-3 Channel at Wallis & 5th St. Eugene		3	3	3	2,3	‡	‡		†,‡	1,2		
Pringle Creek at Bush Park at Salem	▨	▨	▨	▨	2,3	2,3	‡		2,3			
Beaverton Creek at 216th Ave. near Orenco					‡	‡	‡		†,‡			
Bronson Creek at 185th Ave. near Aloha					‡	‡	‡		†,‡			
Fanno Creek at Durham					‡	2,3	‡		†,‡			
Johnson Creek at Milwaukie					3	2,3	‡		†,‡			
Urban Runoff at Harbor Way at Portland					‡	‡	‡		†,‡			
Interstate-84 Runoff at Portland	3				2,3	2,3	3		2,3		2	
Agricultural sites												
Long Tom River at Bundy Bridge near Monroe	▨	▨	▨	▨	‡	‡	‡		†,‡			
Lake Creek at Pine Grove Drive	▨	▨	▨	▨	‡	‡	‡		†,‡			
Muddy Creek near Peoria					‡	†,3	‡		†,‡			
Calapooia River at Albany	▨	▨	▨	▨	‡	‡	‡		†,‡			
Thomas Creek at Kelly Rd. near Jefferson	▨	▨	▨	▨	‡	‡	‡		†,‡			
Rickreal Creek at mouth near Salem	▨	▨	▨	▨	‡	‡	‡		†,‡			
Mill Creek at Delaney Rd. near Turner	▨	▨	▨	▨	‡	†,3	‡		†,‡			
S. Yamhill River at McMinnville	▨	▨	▨	▨	‡	‡	‡		†,‡			
N. Yamhill River near McMinnville	▨	▨	▨	▨	‡	‡	‡		†,‡			
Palmer Creek at Dayton					‡	‡	‡		†,‡			
Champoeg Creek below Mission Cr. near Butteville	▨	▨	▨	▨	2,3	2,3	‡	3	†,‡			
Zollner Creek near Mount Angel					2,3	2,3	‡	3	†,‡		2	1,2
Pudding River at Aurora					2,3	†,3	‡		†,‡			
Dairy Creek at Rte. 8 near Hillsboro	▨	▨	▨	▨	‡	3	‡		†,‡			
Johnson Creek at Palmblad Rd. near Gresham	▨	▨	▨	▨	2,3	2,3	‡		†,‡	2		
Mixed-use sites												
Coast Fork Willamette River at Seavey Loop Rd	▨	▨	▨	▨	‡	‡	‡		†,‡			
Marys River at Corvallis	▨	▨	▨	▨	2,3	‡	‡		†,‡			
Willamette River below Corvallis WTP					‡	‡	‡	2,3	†,‡			
Luckiamute River near Buena Vista	▨	▨	▨	▨	‡	‡	‡		†,‡			
Santiam River at Jefferson	▨	▨	▨	▨	‡	‡	‡		†,‡			
Willamette River upstream Hwy. 219 at Newberg					‡	‡	‡		†,‡			
Molalla River near Canby	▨	▨	▨	▨	‡	‡	‡		†,‡			
Tualatin River at West Linn	▨	▨	▨	▨	2,3	3	‡		†,‡			
Willamette River at Portland	▨	▨	▨	▨	2,3	‡	‡		†,‡			
Willamette River above St. Johns Bridge at Portland	▨	▨	▨	▨	‡	‡	‡		†,‡			
Willamette River at Linnton					‡	‡	‡		†,‡			
Forested sites												
Coast Fork Willamette River below Big River near London	▨	▨	▨	▨	‡	‡	‡		†,‡			
Mack Creek near Blue River	▨	▨	▨	▨	‡	‡	‡		†,‡			
McKenzie River at mouth near Eugene	▨	▨	▨	▨	‡	‡	‡		†,‡			
Rock Creek near Philomath					‡	‡	‡		†,‡			

Table 13. Summary statistics for detected unfiltered-water concentrations of organochlorine compounds in the Willamette River Basin during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[DDT+DDE+DDD is considered a single compound for purposes of detections; nondetection of individual analytes of DDT, DDE, and DDD are assigned a value of 0 µg/L (micrograms per liter) for the purpose of summing concentrations; —, not calculated]

Analyte	Percent detects	Number of detects	Number of samples	Median detected concentration (µg/L)	Maximum concentration (µg/L)
Lindane	32	23	73	0.002	0.032
Dieldrin	32	23	73	.002	.02
DDT + DDE + DDD	26	19	73	.003	.06
DDE	21	15	73	.002	.03
DDT	19	14	73	.002	.03
DDD	11	8	73	.001	.002
PCB	8	6	73	.1	.2
Endosulfan	4	3	73	.002	.006
Heptachlor	1	1	73	—	.001

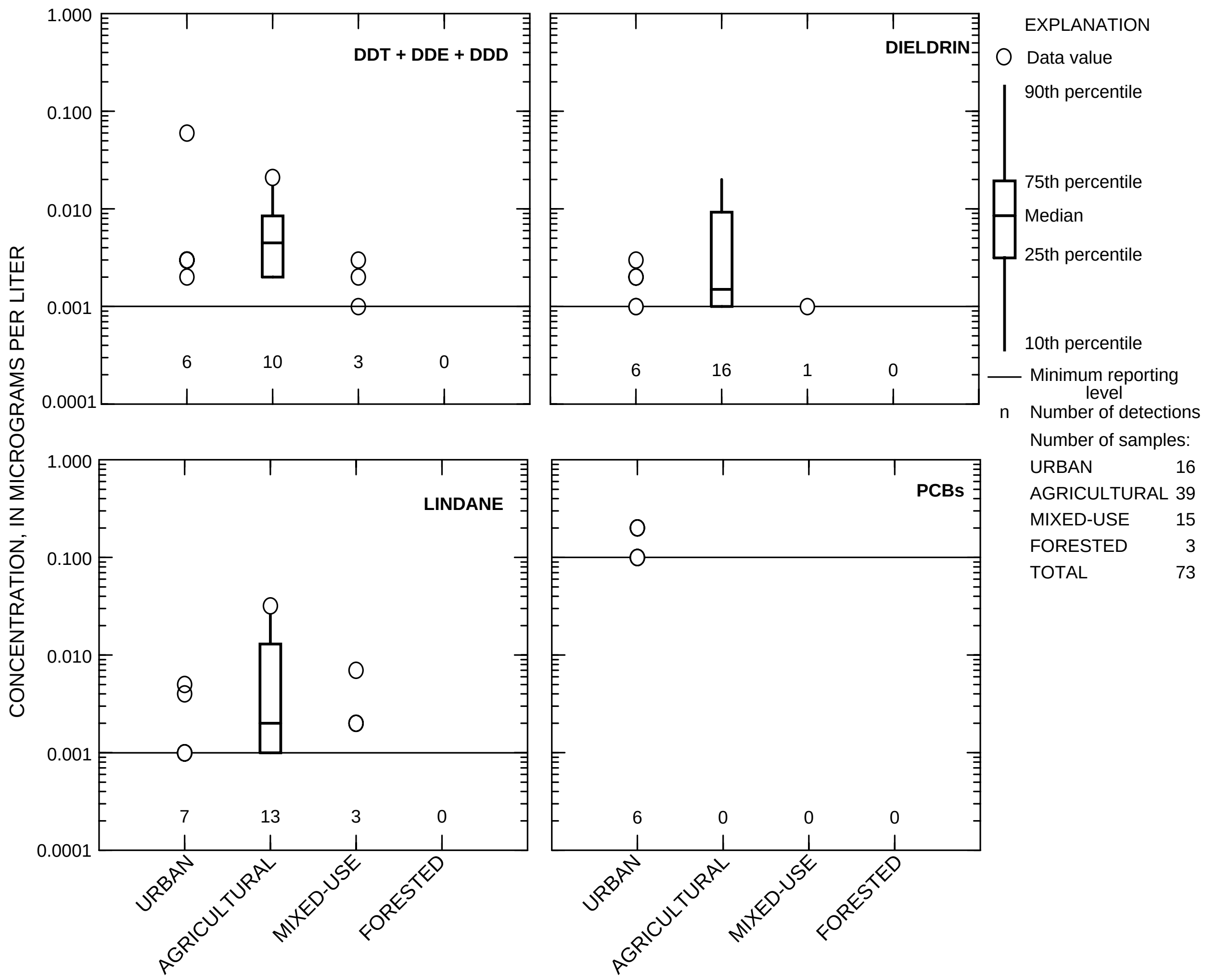


Figure 9. Concentrations of selected organochlorine compounds detected in unfiltered water in relation to various land uses during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94.

oral commun., 1995), and the City of Salem has begun a similar investigation in the Pringle Creek watershed (Genevieve Brooks Bishop, City of Salem Department of Public Works, oral commun., 1996).

Sediment-Water Partitioning

Among the samples collected during the fall 1994 high-flow period, eight water samples were collected from six sites and analyzed for OCs in the dissolved and suspended phases. Of the 17 compounds included, only DDX compounds were consistently detected in both the dissolved and suspended phases; these were found in two samples from Johnson Creek and one sample each at the I-84 runoff and Pudding River sites. Analytical results from these four samples were used to determine the partitioning between the dissolved and suspended phases and were compared to theoretical equilibrium distributions for the same samples. For the sample from the Pudding River, none of the DDX compounds were detected in the dissolved phase; for that sample, a range of possible partitioning relations were calculated using values of 0 micrograms per liter and the MRL value (0.001 μg/L).

Seventy to 89 percent of the combined mass of DDX compounds was observed to be associated with the suspended phase (fig. 10) for the four samples examined. It was expected that these compounds would preferentially associate with the suspended phase because they are known to be hydrophobic, with organic carbon-water partitioning coefficient (K_{oc}) values of 770,000 for DDD, 4,400,000 for DDE and 243,000 for DDT (U.S. Environmental Protection Agency, 1990). Theoretical computations (Appendix 7) predicted that 55 to 81 percent of the mass of the DDX compounds should have been associated with the suspended phase if the systems were at equilibrium, depending on the relative concentrations of suspended organic carbon in the samples. In all cases, the observed amounts transported in the suspended phase were only slightly greater than predicted, suggesting that the systems were near equilibrium. The actual difference between observed and predicted values for three of the samples was relatively small (8.8 to 21.4 percent), especially considering that most of the dissolved concentrations were at or near the analytical reporting limits. Also, there is considerable uncertainty associated with the published K_{oc} values, which were determined in laboratories under conditions that may not always mirror environmental conditions. The one sample where the difference was potentially large (between 17 and 44 percent) was the Pudding River sample, and resulted from the use of a range of values for the dissolved phase concentrations of DDX compounds. Concentrations of DDX compounds in the suspended phase were also relatively low, amplifying the impact of using a range of possible concentrations in the equilibrium calculations.

For the four samples discussed above, nearly 50 percent of the ΣDDX was present as DDT. This was despite the fact that the sale and transport of DDT in the United States was banned by the USEPA in 1973. About 35 percent of the total was present as DDE, and the remaining roughly 15 percent present as DDD. Results for unfiltered-water analysis in all samples from Phase II were somewhat similar, with medians of 50, 50, and 0 percent of the total mass present as DDT, DDE, and DDD, respectively. These percentages are also similar to values determined in a 1987–90 study in the Yakima River Basin, Washington (J.F. Rinella and others, 1992) and a 1990–91 study in the Owyhee and Malheur River Basins in eastern Oregon (F.A. Rinella, and others, 1994). The percentages of DDT, DDE, and DDD in unfiltered-water samples from these other studies were 30-40, 50, and 10-20 percent of mass, respectively.

The fraction of organic compounds found in the suspended phase is controlled by the K_{oc} values, the concentration of suspended organic carbon (SOC), and the degree to which equilibrium is achieved. Because the fraction associated with the suspended phase at equilibrium is directly related to the concentration of SOC, the greatest mass of these compounds will be in the suspended phase when SOC is high (fig. 10; Appendix 7). At the lowest SOC concentration of the four samples (1.6 mg/L at Pudding River), equilibrium calculations predict that over 50 percent of the mass of DDX compounds, which have relatively high K_{oc} values, should be in the suspended phase, and at the highest SOC concentration (7.4 mg/L at the I-84 Runoff site) the equilibrium fraction in suspended sediments increased to 80 percent. In contrast, dieldrin and lindane, with much lower K_{oc} values, were found almost completely in the dissolved phase, with SOC concentrations ranging from 0.5 to 5.7 mg/L.

The partitioning of dieldrin and lindane in unfiltered- and filtered-water samples from Phases I and II was also examined using the method described in Appendix 7, modified to determine the equilibrium mass in the dissolved phase. Both dieldrin and lindane have substantially lower K_{oc} values than the DDX compounds (1,700 and 1,080 mL/g, respectively [U.S.

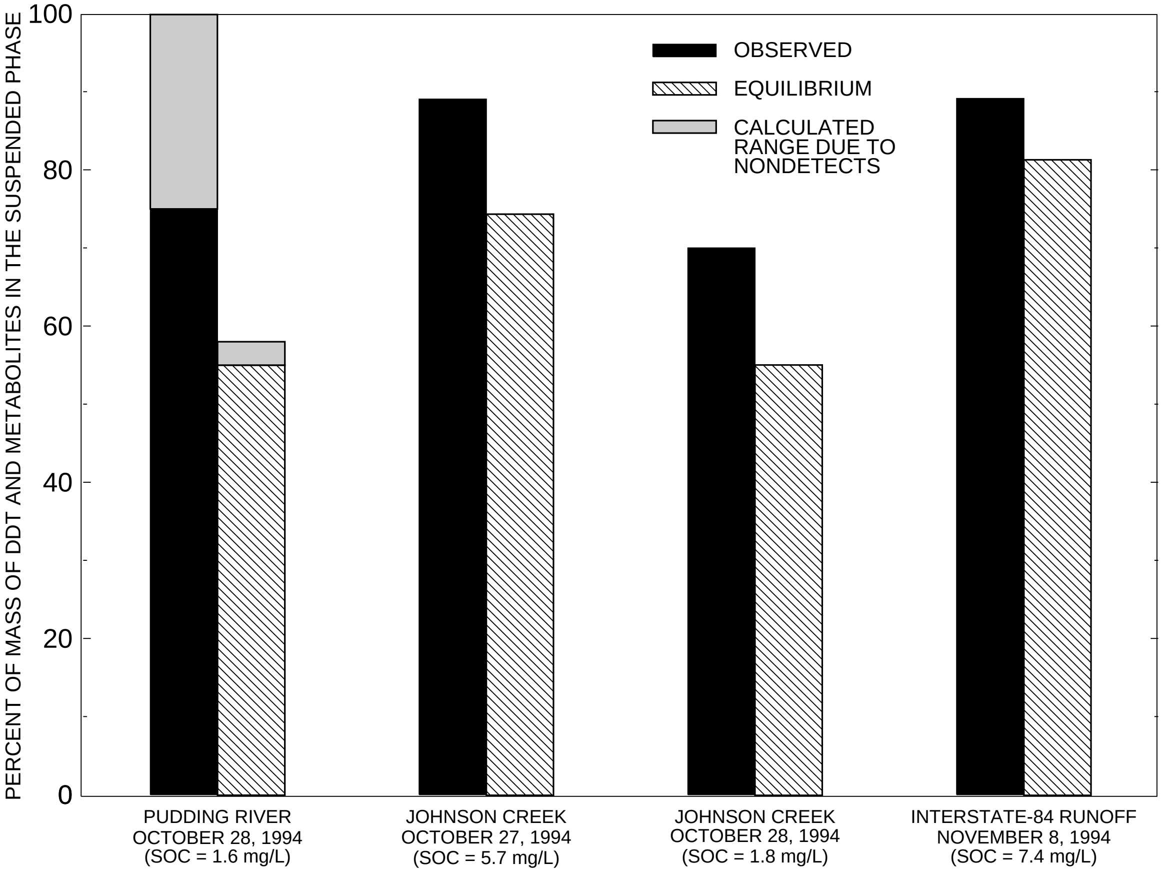


Figure 10. Observed and equilibrium fraction of DDT and metabolites present in suspended phase for four samples during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994. (Data from the Pudding River are considered to be estimates because neither DDT nor its metabolites were detected in the dissolved phase. For the purposes of this analysis, concentrations of DDT and its metabolites in the Pudding River sample were calculated assuming a range of concentrations in the dissolved phase from zero micrograms per liter [µg/L] to the value of the method detection limit [0.001 µg/L]. SOC, suspended organic carbon; mg/L, milligrams per liter. Refer to Appendix 7 for explanation of calculation.)

Environmental Protection Agency, 1990]). As a result, the proportions of each compound expected to be in the dissolved phase at equilibrium are much higher, averaging approximately 96 percent for dieldrin and greater than 99 percent for lindane at the SOC concentrations observed. Indeed, for the five samples in which dieldrin was detected in both unfiltered and filtered water, the observed proportion in filtered water ranged from 60 to 160 percent (median 105 percent). Likewise, the 4 samples in which lindane was detected in both unfiltered and filtered water had a range of 83 to 119 percent (median 101 percent) of the compound in the dissolved phase. All other detections of dieldrin or lindane in unfiltered water were at concentrations below the respective MDLs for those compounds in filtered water. Obviously, it is impossible for greater than 100 percent of a compound to be in any phase; these results illustrate the potential problems encountered when comparing data from different analytical procedures at relatively low concentrations. Nonetheless, it is apparent from the analytical that the masses of dieldrin and lindane were mostly present in the dissolved phases for these samples, a result that is in good agreement with the equilibrium calculations.

Dissolved Pesticides

Ninety-two water samples were collected from 39 locations in the Willamette River Basin and analyzed for 94 pesticides and metabolite products (Appendixes 5 and 6). Included among these were 58 water samples from 32 locations that were analyzed for a set of 21 triazine and related herbicides.

Exceedances of Water-Quality Criteria

Of the pesticides analyzed, CTC, ATC, or HHP values for the State of Oregon have been established for only six compounds (table 12). Chronic toxicity criteria were exceeded at one site each for chlorpyrifos and parathion, and at two sites for malathion. One sample at Mill Creek may have had a detection of 2,4-dinitro-*o*-cresol, although laboratory results for this sample were uncertain due to matrix interferences. Of the six compounds with established criteria, only chlorpyrifos was detected in more than 10 samples. No exceedances were found for methoxychlor or 2,4-D. It is important to note that other compounds were detected at levels that may be harmful to aquatic life, but for which State of Oregon criteria have not been established. For example, more than 50 percent of the 43 detections of diazinon exceeded the recommended threshold value of 0.009 µg/L established by the National Academy of Sciences and National Academy of Engineering (1973). The highest of these concentrations was 1.2 µg/L at Zollner Creek. Other threshold values established by the National Academy of Sciences and National Academy of Engineering that were exceeded were for azinphos methyl (0.001 µg/L), carbaryl (0.02 µg/L), and diuron (1.6 µg/L).

Relation to Pesticide Applications and Land Use

Pesticide applications—The 25 pesticide and metabolite products detected most frequently in the basin are listed in table 14, in descending order of occurrence. Between 80 and 90 percent of the water samples collected had detectable concentrations of atrazine, simazine, and metolachlor, ranging in concentration from 0.002 to 3.5 µg/L. These percentages were consistent with the 85 to 95 percent detections observed for samples collected in the Willamette River at Portland during 1994 as part of the Columbia River Bi-State Study (Fuhrer and others, 1996). Desethylatrazine, diuron, hexazinone, diazinon, cycloate, desisopropylatrazine, and terbacil were detected in 61 to 37 percent of the samples, in concentrations ranging from 0.001 to 9.0 µg/L. In addition, roughly one out of every three samples contained detectable concentrations of DCPA (dacthal), EPTC, napropamide, and prometon.

Of the 94 pesticides in filtered water that were analyzed (Appendixes 5 and6, 33 were not listed as used in the Willamette River Basin in the 1987 estimates of Reinhold and Witt (1989); these compounds were analyzed because they are included in the analytical schedules for pesticides available from the NWQL. Nonetheless, 5 of these unlisted compounds were detected during 1992–94; most notably, ethoprop and tebuthiuron were detected in 24 and 21 samples, respectively (table 14, Appendix 5). Of the remaining 61 pesticides analyzed that are used in the basin, 43 were detected at least once. Other compounds known to have been used in the basin but which were not analyzed (owing to a lack of available methods) included benomyl, captan, diclofop, ethofumesate, glyphosate, maneb, and metaldehyde (table 5).

If 1987 pesticide-use estimates accurately reflect current (1992–94) use and if these compounds behave similarly in the environment, then 1987 usage should be a useful predictor of detections in the water samples. However, data in table 14 generally indicate little relation between pesticide-use estimates and detection frequency. Although some widely used pesticides such as atrazine, diuron, and simazine were frequently detected, others, such as 2,4-D, were not. Conversely, several frequently detected compounds, including prometon, ethoprop, and tebuthiuron were not listed as used in the basin. Possible reasons for the limited success of this comparison include (1) pesticide use has probably changed considerably since 1987, (2) pesticides may be removed from the aqueous phase by sorption to sediments, partitioning into other organic material, volatilization, or biological or chemical transformation, (3) spatial and temporal variability in crop planting and rotation practices may have resulted in uncertainty in pesticide-use estimates; (4) the timing of pesticide application may not have coincided with water sample collection; (5) below average rainfall and runoff during spring 1994 may have limited pesticide transport to streams (fig. 4), and (6) analytical performance may have limited the frequency of detection of some compounds.

Land use—Detections of some pesticides did appear to be associated with particular land uses. To investigate this relation, 16 of the 25 pesticides were grouped as follows: (1) compounds primarily detected in urban areas (fig. 11), (2) compounds primarily detected in agricultural areas (fig. 12), and (3) compounds detected in both urban and agricultural areas (fig. 13). Note that the numbers of samples collected at urban, agricultural, mixed-use, and forested site types (24, 47, 19, and 3, respectively) were not equal.

Between 50 and 71 percent of the 24 samples (17, 14, and 12) collected at urban sites contained detectable concentrations of diazinon, prometon, or tebuthiuron (fig. 11), whereas, only 6 to 40 percent of the 47 samples (19, 11, and 3) collected at agricultural sites

Table 14. Summary statistics of the 25 most frequently detected pesticides in the Willamette River Basin during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Pesticide usage for 1987 from Reinhold and Witt (1989); µg/L, micrograms per liter; —, not applied; NL, not listed by Rinehold and Witt (1989)]

Analyte	Percent detections	Number of detections	Number of samples	Median detected concentration (µg/L)	Maximum concentration (µg/L)	Willamette Basin Pesticide usage, 1987	
						Pounds applied	Rank
Atrazine	90	84	93	.052	2.7	409,400	2
Simazine	82	76	93	.094	3.5	166,600	9
Metolachlor	81	75	93	.026	3.3	42,450	29
Desethylatrazine	61	56	93	.010	.27	—	—
Diuron	54	44	81	.32	9.0	552,500	1
Hexazinone	48	28	58	.003	.040	19,000	47
Diazinon	47	44	93	.015	1.2	122,400	12
Cycloate	43	25	58	.002	.020	11,872	53
Desisopropylatrazine	40	23	58	.004	.023	—	—
Terbacil	37	34	90	.027	1.0	19,170	46
DCPA (Dacthal)	35	32	93	.003	.029	365	122
EPTC	32	29	93	.008	1.0	78,600	20
Napropamide	29	27	93	.033	1.6	74,790	21
Prometon	29	27	93	.013	.068	NL	NL
Chlorpyrifos	26	24	93	.010	.043	120,710	13
Ethoprop	26	24	93	.011	3.1	NL	NL
Fonofos	26	24	93	.012	.10	114,100	15
Carbaryl	23	21	93	.010	2.0	119,500	14
Carbofuran	23	21	93	.110	9.0	10,740	54
Tebuthiuron	23	21	93	.032	.12	NL	NL
Metribuzin	21	19	93	.038	.41	3,570	80
Pronamide	20	18	93	.012	.098	21,770	42
Trifluralin	17	16	93	.006	.018	23,410	39
Trichlopyr	13	11	82	.18	.72	20,980	43
2,4-D	12	10	82	.18	.79	330,700	4

contained detectable concentrations of these pesticides. Median concentrations of diazinon, prometon, and tebuthiuron in samples from urban sites were roughly three times those observed in samples from the agricultural sites. However, the highest concentrations of diazinon were found at agricultural sites.

In contrast, carbofuran, EPTC, ethoprop, fonofos, napropamide, and terbacil were found more frequently at agricultural sites. Between 34 and 64 percent of the 47 samples (16 to 30) collected at agricultural sites contained detectable concentrations of these six pesticides, (fig. 12) compared to only 0 to 17 percent of the 24 samples (0 to 4) collected at urban sites. Median concentrations for carbofuran, EPTC, ethoprop, napropamide, and terbacil were from two to more than six times greater in samples from agricultural sites than in samples from urban sites; the median concentration for fonofos was slightly greater in samples from the urban sites, but it was based on only four detections.

Atrazine, carbaryl, chlorpyrifos, DCPA, diuron, metolachlor, and simazine were detected relatively frequently in samples from both urban and agricultural sites (fig. 13). Frequencies of detection ranged from 88, 100, and 84 percent (21, 47, and 16 samples) for atrazine in the urban, agricultural, and mixed-use sites, respectively, to 17, 29, and 16 percent (4, 14, and 3 samples), respectively, for carbaryl. Although chlorpyrifos and DCPA were detected in 13 and 14 samples (27 and 21 percent) at agricultural sites, they were detected somewhat more frequently at urban sites (9 to 13 samples, 37 to 54 percent, respectively). For all of the compounds in figure 13, the highest concentrations were observed at agricultural sites. With the exception of chlorpyrifos, the median concentrations were also highest at agricultural areas.

Spatial and temporal variations—Agricultural activities in the northern portion of the Willamette River Basin are more diverse than those in the southern portion. The northern portion includes more row crops, orchards, vineyards, and nurseries than the southern portion, where grains, hay and silage, and grass and legume seeds predominate (table 4). To illustrate the effect of differing agricultural patterns on water quality in the basin, the frequencies of pesticide detections in the northern and the southern portions of the basin were compared for the compounds represented in figures 11–13 (fig. 14). Agricultural sites located in Clackamas, Marion, Multnomah, Polk, Washington and Yamhill Counties were designated as northern, whereas those in Benton, Lane, and Linn Counties were designated as southern (fig. 1). The data analysis was limited to samples collected during 1994 because these samples represent the appropriate spatial (basinwide) and temporal (spring and fall sampling) coverages for the analysis. Detections of the same 16 compounds at urban sites were also included in figure14 for comparison purposes. The division of sites resulted in unequal group sizes, which may have introduced some bias. Additional bias may have been introduced from differences in the number of samplings at individual sites in the northern and southern portions of the basin, and in variations in hydrologic conditions among all sites at the time of sampling.

Pesticides detected in both the northern and southern agricultural areas with similar frequencies included atrazine, carbaryl, diuron, metolachlor, simazine, and terbacil. Pesticides detected in only the northern agricultural areas included carbofuran, chlorpyrifos, DCPA, diazinon, ethoprop, napropamide, and tebuthiuron. EPTC, fonofos, and prometon were detected in both parts of the basin, but generally the detection frequency was greater in the northern agricultural area. Maximum pesticide concentrations were greatest in samples collected at the northern agricultural sites with the exception of carbaryl (2.0 µg/L; Long Tom River at Monroe, 5–19–94) (Harrison and others, 1995).

To determine temporal variability, the data were further divided into spring 1994 and fall 1994 samples (fig. 15). Dividing the data in this manner can lead to difficulties because the effects of any inherent biases are amplified in the resulting smaller data sets. Detection frequencies for atrazine, carbaryl, diuron, EPTC, metolachlor, and simazine during the spring sampling in the northern agricultural areas were generally similar to those observed during the spring sampling in the southern agricultural areas. Likewise, the frequencies of detection for these six pesticides during the fall sampling were similar in the northern and southern agricultural areas with the exception of carbaryl and EPTC. In both regions, the detection frequencies for these pesticides increased slightly from spring to fall, with the exception of carbaryl and EPTC. Detection frequencies for carbofuran, chlorpyrifos, ethoprop, napropamide, tebuthiuron, EPTC, fonofos, and

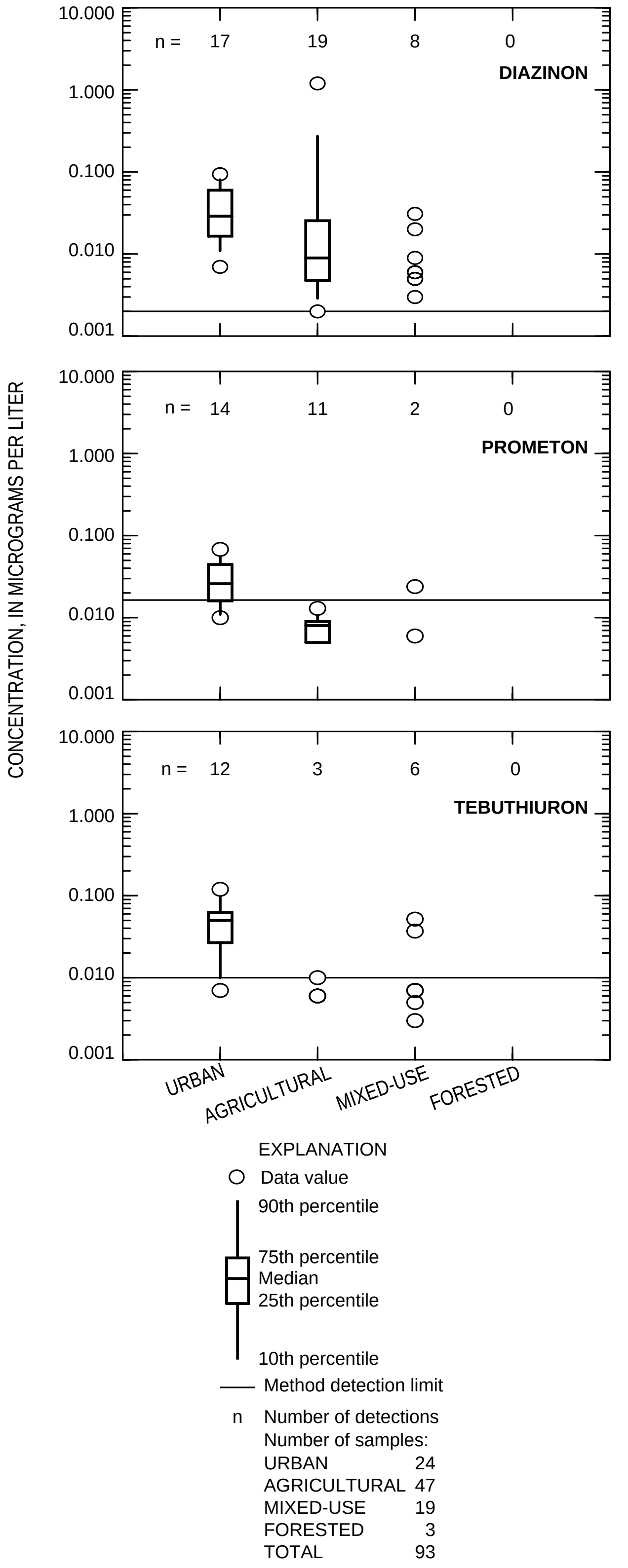


Figure 11. Concentrations of selected pesticides primarily associated with urban land use during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94. (Distributions based on detections only; the numbers of samples associated with the land-use types are given in the explanation. Data represent filtered water samples.)

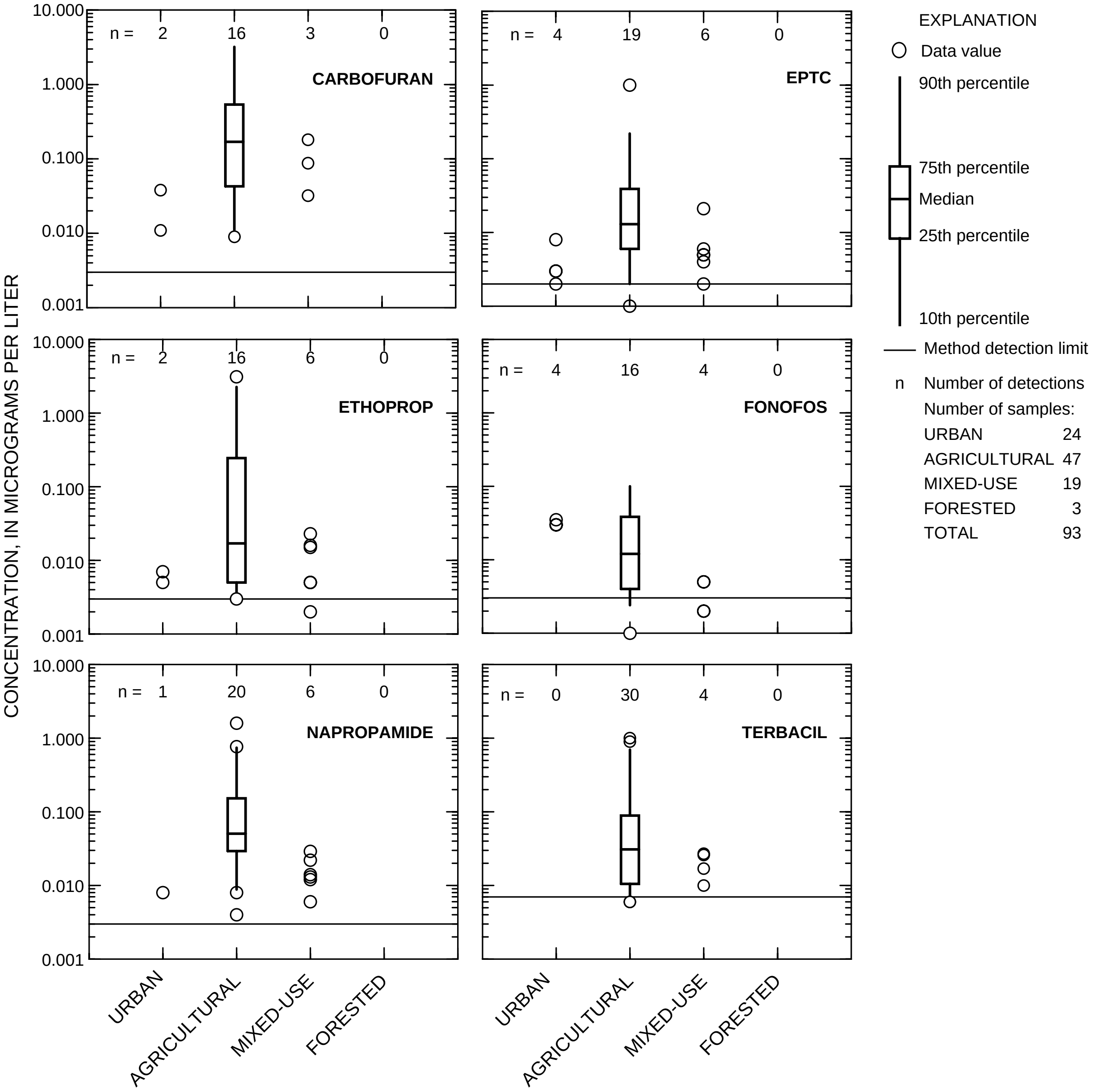


Figure 12. Concentrations of selected pesticides primarily associated with agricultural land use during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94. (Distributions based on detections only; the numbers of samples associated with the respective land-use types are given in the explanation. Data represent filtered water samples.)

prometon in the northern areas were also slightly greater during the fall than the spring. The apparent increases in detection frequencies during fall sampling may have been related to the different hydrologic conditions associated with these time periods; fall samples were obtained during high flows, while spring samples were obtained at relatively lower flows. Alternatively, the differences between the two sample times may have been an artifact of the repeated sampling at specific sites during fall 1994, which might have inflated the importance of specific pesticides at the fall sites.

Despite the potential biases, distinct differences are apparent in the patterns of pesticide runoff between the northern and southern portions of the Willamette River Basin. These patterns reflect the agricultural diversity in the north, where row crops, orchard fruits and nuts, and nursery plants are important products in addition to grass seed, wheat, and other grains, and where many different pesticides are frequently found in the runoff. On the other hand, fewer crops consume the largest percentage of the agricultural lands in the southern portions of the basin

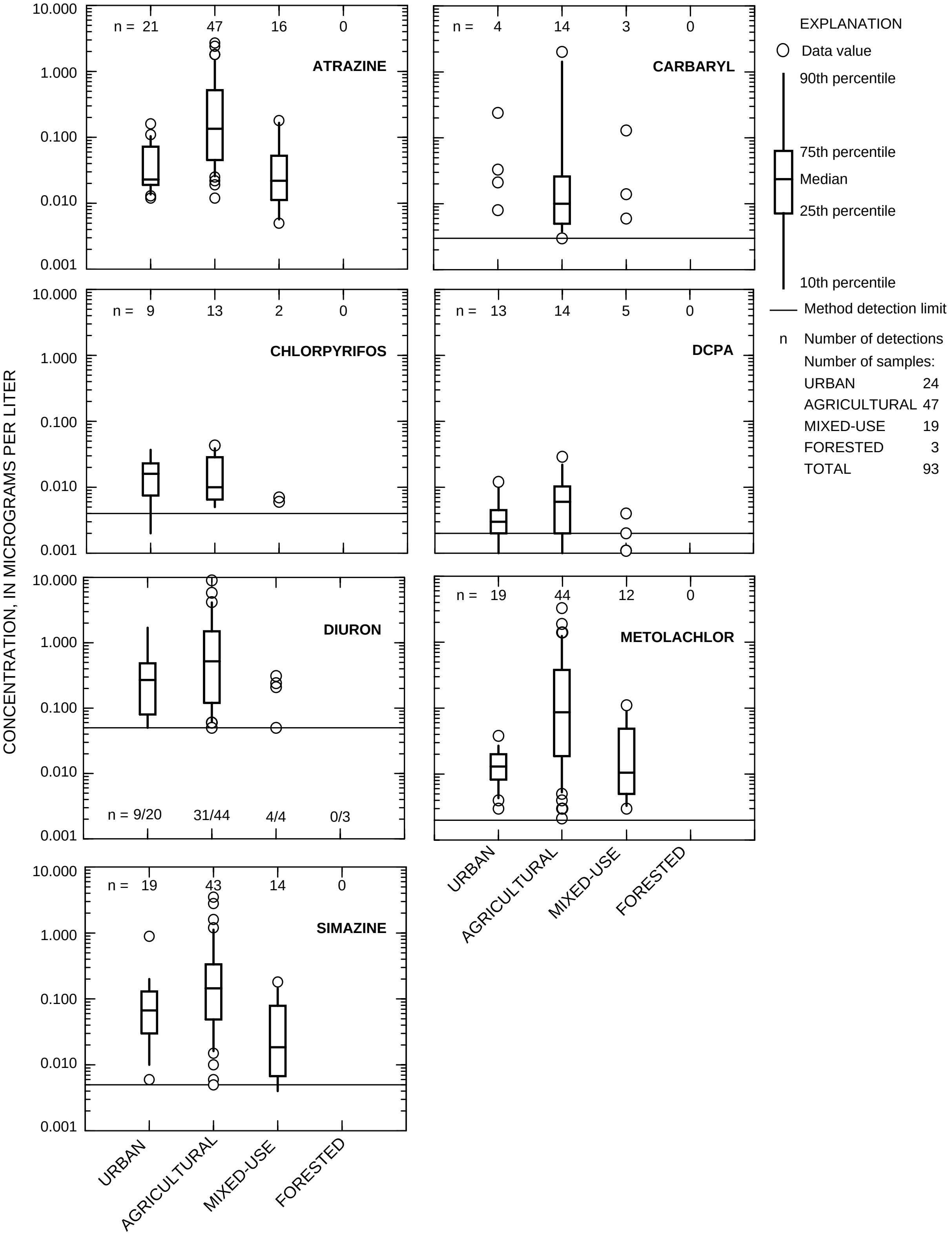


Figure 13. Concentrations of selected pesticides associated with both agricultural and urban land uses during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94. (The method detection limit for atrazine is 0.001micrograms per liter. Distributions are based on detections only; the numbers of samples associated with the respective land-use types are given in the explanation. The numbers of samples at the various sites types were different for diuron and are given in the plot for diuron. Data represent filtered water samples.)

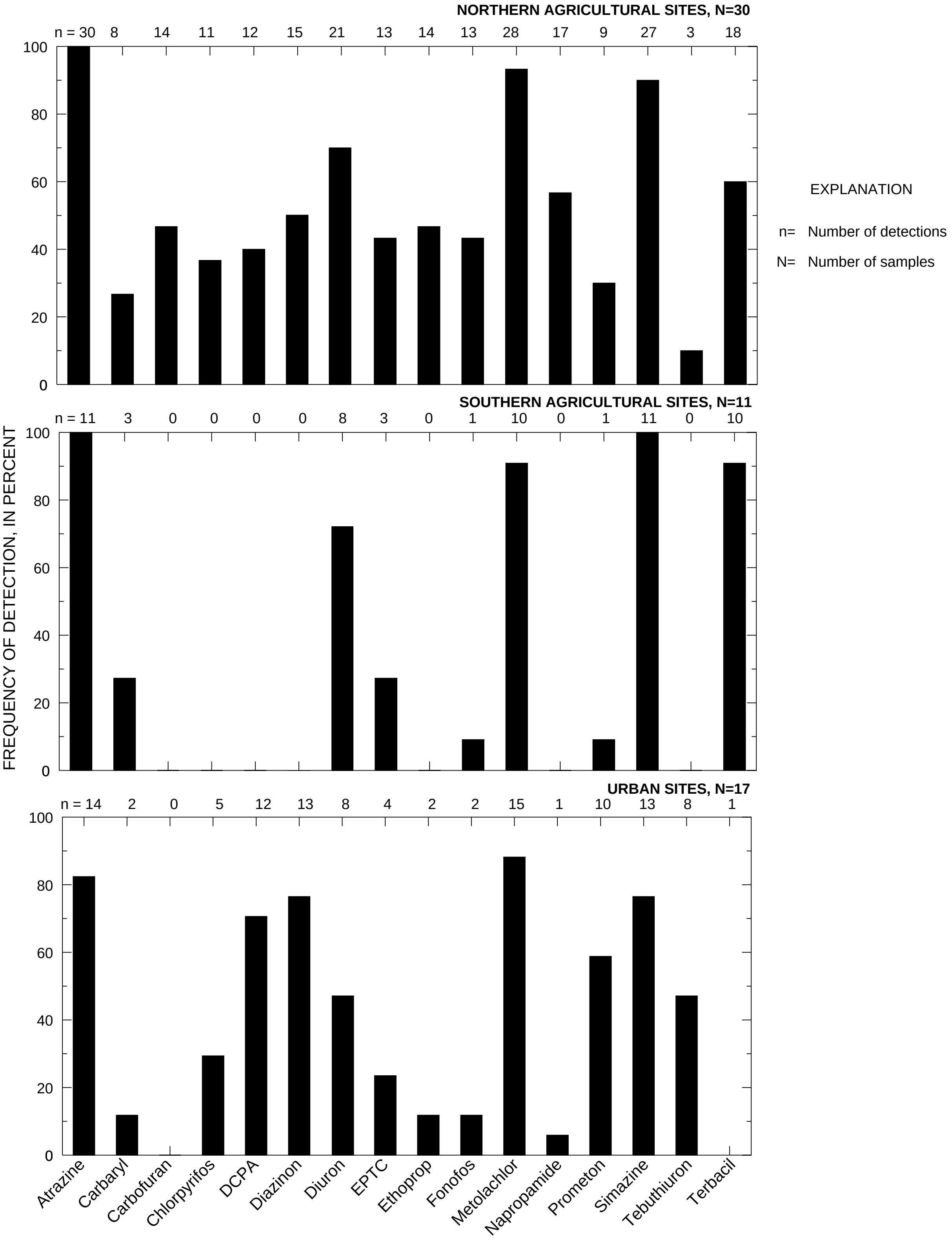


Figure 14. Detection frequencies for selected pesticides at northern agricultural, southern agricultural, and urban sites during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994.

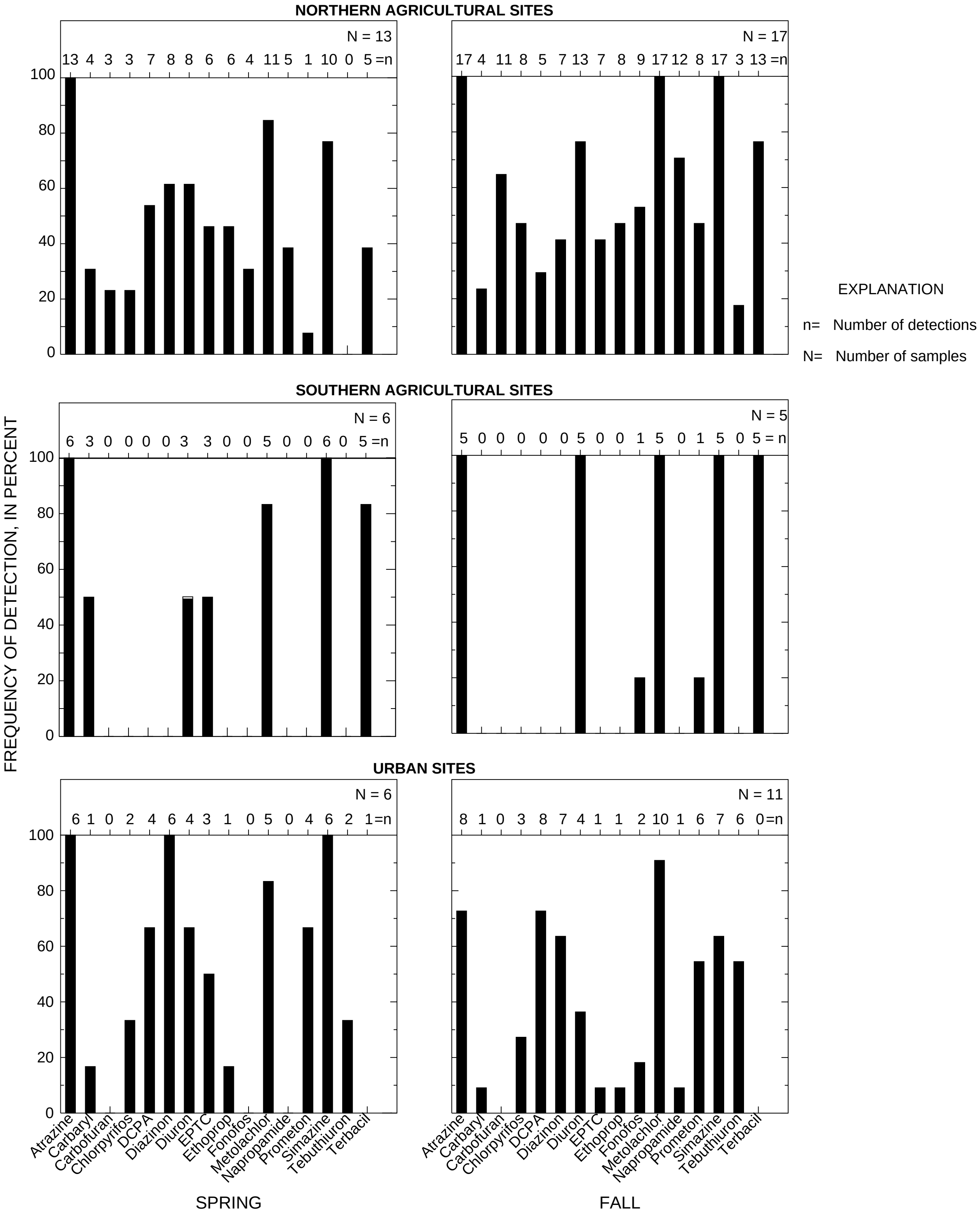


Figure 15. Comparison of spring and fall pesticide detection frequencies at northern agricultural, southern agricultural, and urban sites during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994.

(table 4), where the numbers of pesticides detected were fewer but were at relatively high frequencies. Figures 14 and 15reflect and corroborate the findings from figures 11–13. Diazinon, which was detected somewhat more frequently at urban sites than agricultural sites (figs. 11 and14), was not detected at all at southern agricultural sites. Diazinon was also detected more frequently during spring at urban sites but was detected more frequently during the fall at the northern agricultural sites (fig. 15). Terbacil was not detected at any urban sites (figs. 12 and 14), and was detected somewhat more frequently in the fall than in the spring at the agricultural sites.

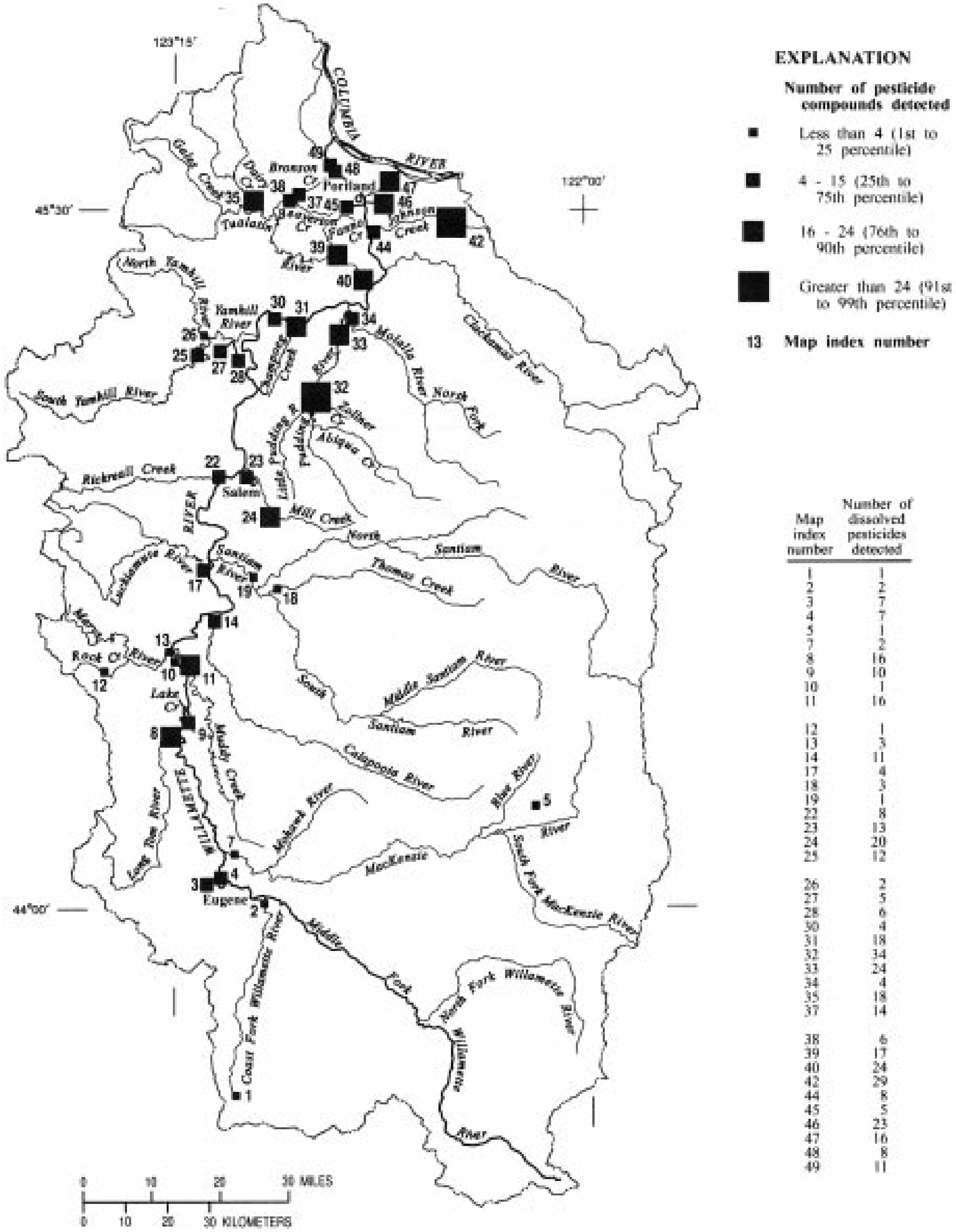
The number of different dissolved pesticides detected at individual sites is shown in figure 16. Among all sites, the 25th, 50th, 75th, and 90th percentiles of the number of detected pesticides were 3, 8, 15, and 24 compounds, respectively. The greatest numbers of pesticides were detected at Johnson Creek near Palmblad Road and Zollner Creek near Mt. Angel, with 29 and 34 different compounds found, respectively.

Some caution is required in the interpretation of figure 16. Note that the figure does not indicate the concentrations of the detected pesticides, or the frequency at which given pesticides were detected, nor does it include other organic compounds such as VOCs or OCs in unfiltered water. The numbers of pesticides detected are undoubtedly affected by the frequency of sampling at the respective sites; some sites such as Johnson Creek, Zollner Creek, and the Willamette River at Portland were sampled as many as five or six times during Phases I and II, and at a variety of flow conditions, whereas other sites such as mainstem sites on the Willamette River at Corvallis or Newberg, and small tributary sites such as Palmer Creek near Dayton or Rickreal Creek near Salem, were sampled just once each at low flows. However, sites were chosen for multiple samplings based on their likelihood of reflecting the most important or indicative pesticide loading processes in the Willamette River Basin, and the relative differences in the number of compounds detected may not have changed significantly had all sites been sampled at equal frequencies.

At several sites just one pesticide was detected in the water. Cycloate was found at forested sites on Lookout Creek, the Coast Fork Willamette River, and Rock Creek. Concentrations of cycloate in each sample at these sites were below the MDL of 0.01 µg/L (Harrison and others, 1995) and the probability of false positive detections is, by definition, greater than 1 percent, even though cycloate was never detected in blank samples. Cycloate was also the only pesticide detected in filtered water at the Santiam River near Jefferson and was one of two pesticides detected at the North Yamhill River near McMinnville, also at concentrations below the MDL.

Of considerable interest in figure 16 are the sites with the most compounds detected (16 or greater, representing the highest quartile). This group includes 8 agricultural sites (Muddy Creek at Peoria, Long Tom River at Bundy Bridge, Mill Creek at Turner, Champoeg Creek at Champoeg Park, Zollner Creek near Mount Angel, Pudding River at Aurora, Dairy Creek at Route 8 near Hillsboro, and Johnson Creek near Palmblad Road), 2 sites reflecting mixed uses upstream (the Tualatin River at West Linn, and the Willamette River at Portland), and 2 urban sites (Fanno Creek near Durham and the I-84 runoff site). To a large extent this list includes the sites with the highest observed concentrations of many of the individual pesticides, especially agricultural sites during storm runoff. For example, Zollner Creek accounted for the highest observed concentrations of atrazine, carbofuran, diazinon, diuron, EPTC, and simazine (3.1, 9, 1.2, 9, 1, and 3.3 µg/L, respectively), Champoeg Creek accounted for the highest observed concentrations of metolachlor and napropamide (3.3 and 1.6 µg/L, respectively), Mill Creek was the location of the highest concentrations of ethoprop and terbacil (3.1 and 1 µg/L, respectively), and the highest concentration of carbaryl (2 µg/L) was observed at the Long Tom River (Appendixes 5 and 6; Harrison and others, 1995). Of these high concentrations, all values except those for diazinon and diuron at Zollner Creek were from samples collected during storm flow.

The mixed use sites that are included in the highest quartile provide good examples of sites that reflect a variety of upstream land and pesticide uses, even though the observed concentrations were only rarely high. For instance, 24 different pesticides were detected in the Tualatin River at West Linn, which receives runoff from the large variety of land uses within Washington County (including rapidly expanding urban and industrial uses and a diverse set of agricultural crops; see table 4). Among these pesticides were those reflecting primarily urban usage (diazinon, prometon, and tebuthiuron; fig. 11, agricultural usage (carbofuran, EPTC, ethoprop, and napropamide; fig. 12), and both



Map index number	Number of dissolved pesticides detected
1	1
2	2
3	7
4	7
5	1
7	2
8	16
9	10
10	1
11	16
12	1
13	3
14	11
17	4
18	3
19	1
22	8
23	13
24	20
25	12
26	2
27	5
28	6
30	4
31	18
32	34
33	24
34	4
35	18
37	14
38	6
39	17
40	24
42	29
44	8
45	5
46	23
47	16
48	8
49	11

Figure 16. Number of pesticides in filtered water detected at sites in the Willamette River Basin during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94. (Some sites were sampled more frequently than others; however, the numbers of pesticides detected were not corrected for the frequency of samplings at individual sites. Map index numbers are from Harrison and others [1995]. Phase I sites that were only sampled for bed sediment are not included. Refer to tables 6–8 for identification of sites by map index numbers.)

urban and agricultural usage (atrazine, carbaryl, chlorpyrifos, diuron, DCPA, metolachlor, and simazine; fig. 13. Upstream sites that were sampled in the Tualatin River Basin included urban sites such as Fanno Creek at Durham (17 pesticides including the highest observed concentration of prometon, at 0.068 µg/L), Bronson Creek (14 pesticides), and Beaverton Creek (6 pesticides, Phase I only), as well as the agricultural site on Dairy Creek (18 pesticides).

There are many potential sources for the 23 different dissolved pesticides detected at the sampling site on the Willamette River at Portland. The site is downstream of all other sampling sites in the entire basin, with the exception of the sites on the main stem at Linnton and at St. Johns, which were sampled once each. Flow in the Willamette River is tidally influenced (although no estuarine water actually enters the Willamette River) and hence at times the direction of flow is reversed, causing mixing of inputs from the industrial and residential areas downstream of downtown Portland, and from combined sewer overflows (CSOs) and other storm drains in the lower reaches of the river. Furthermore, the Tualatin and Pudding Rivers each had 24 different dissolved pesticides detected at their lowest sampling sites. These basins, which are considered to be among the basins contributing the largest loads of sediments and nutrients in nonpoint runoff in the basin (Tetra Tech, Inc., 1995), enter the Willamette River not far upstream and probably contribute significantly to the variety of pesticides detected at the sampling site near downtown Portland.

The I-84 runoff site, the water from which enters the Willamette River underneath the Burnside Bridge in downtown Portland, is interesting for the unexpectedly large variety of organic compounds detected despite the fact that the site represents a very specific and limited type of land use (downtown Portland freeway traffic). In addition to trace metals and VOCs, which might be expected because they are indicative of automobile traffic and derivatives of gasoline, several organochlorines (DDT, PCBs, dieldrin, heptachlor, and lindane) and 16 different dissolved pesticides (including atrazine, metolachlor, simazine, diuron, chlorpyrifos, and others) were detected. Possible sources for these compounds include (1) use by the Oregon Department of Transportation for landscaping and maintenance purposes along the freeway corridor, (2) spills from vehicles transporting the chemicals through the Portland area, (3) dirt from other locations such as farms that was transported to the freeway and deposited, (4) illicit dumping or drainage connections that discharge to the freeway or directly to the storm drain, and (5) wet and dry deposition from airborne particles. It is unknown to what extent these sources actually contribute to the occurrence of the large variety of compounds detected at the I-84 runoff site.

Influences of Hydrologic Conditions

The variability of constituent concentrations and loads over the course of one or several storms (particularly during the first major storms following prolonged dry periods) was assessed at a variety of sites in the fall of 1994. Samples were collected several times during individual or successive storms (table 8) at three urban sites (Pringle Creek, I-84 runoff site, Fanno Creek), two mixed-use sites (Tualatin River at West Linn, Willamette River at Portland Harbor), and five agricultural sites (Muddy Creek, Mill Creek, Zollner Creek, Pudding River, and Johnson Creek). Because some of these sites were ungaged, and hence have no continuous record of flow, strict comparison of the results of the individual samplings to the overall hydrographic response was not possible. However, partial streamflow records for some of the sites were available; the relation of selected constituent concentrations and loads to streamflow are shown in figure 17A and 17B, respectively, for an agricultural site (Johnson Creek) and figure 18A and 18B, respectively, for a mixed use site on the main stem Willamette River (Willamette River at Portland).

Pesticides shown in figures 17 and 18 were selected to represent as wide a range of chemical characteristics and runoff processes as possible given the types of compounds detected at the site. For instance, DDT, dieldrin, and metolachlor, shown in figures 17A and 17B, have relatively high (approximately 100,000), medium (10,000), and low (200) sediment partitioning coefficients, respectively. Due to the lack of detected concentrations of the more hydrophobic compounds such as DDX compounds at the Willamette River site, compounds are shown in figures 18A and 18B that have a more narrow range of partitioning coefficients (100, 22, and 200 for atrazine, carbofuran, and metolachlor, respectively).

Although the water-quality sampling site for Johnson Creek during Phase II was at Palmblad Road (river mile 18.0), daily mean streamflows for Johnson Creek in figures 17A and 17B are from the USGS gaging station at Sycamore Road (river mile 10.2) (U.S. Geological Survey, in press). Travel time between the two sites is estimated to be roughly 4 to 8 hours at flows indicated. Instantaneous discharges measured at the Palmblad Road site at the time of sampling are also shown for comparison. Constituent loads in figure 17B are instantaneous loads; calculations are based on streamflows measured at the Palmblad site and on constituent concentrations for the individual samplings. At the site on the Willamette River at Portland, only estimated daily mean flows are available (U.S. Geological Survey, in press), and constituent loads in figure 18B are therefore calculated using the instantaneous concentrations and the daily mean flows. Note that concentrations and loads in figures 17 and 18 are displayed on a logarithmic scale to allow all constituents to be shown together.

The pattern of constituent concentrations observed is highly dependent on streamflow conditions at the time of sampling. Suspended sediment concentrations typically are greater when flow is increasing than when it is decreasing, and concentrations are greatest just prior to peak discharge. For compounds that tend to sorb preferentially to suspended sediment or are influenced by sediment movement, this implies that peak concentrations will be observed at or near the time of peak sediment concentration, and that the instantaneous transport (the load, in mass per unit time) will be greatest during these times. Furthermore, the movement of waters from interstitial areas in soils, both within and outside of the streambed, will be greatest after the soils and sediments have been recently disturbed (for instance, after a long dry period such as summer) and when additional water from rainfall can wash out the soils. Therefore the timing of sampling relative to the timing of peak discharge can have a marked effect on the concentrations observed. For this reason the results in figures 17and 18must be viewed with the knowledge that concentrations and instantaneous loads are unknown for time periods other than those sampled, and therefore one can only speculate about the magnitude of loads integrated over an entire event or time period.

Precipitation during fall 1994, was sparse until October 25. Beginning in late October there were two strong storms, the first during October 25–27 and the second during October 30–November 1. The weather was generally wet through most of November and into December (fig. 4). The response time of flow in the various streams in the Willamette River Basin was dependant on such factors as rainfall intensity and duration, land use (especially the amount of impervious surface area), the size of the contributing watershed, and antecedent soil moisture conditions.

Discharge at the site on Johnson Creek at Palmblad Road, which has predominantly agricultural land use upstream, did not fully respond to the initial rainfall until October 27 (figs. 17A and 17B). The first significant peak in flow occurred on October 27, however the second storm, during October 30–November 1, produced higher peak flows, even though the total precipitation from the first storm was the greatest of the two (in the Portland area, where Johnson Creek is located). This disproportionate runoff was presumably due to dry soils prior to October 25, which became saturated as a result of the rain during October 25–27 and afterward required decreasing amounts of rainfall to respond. According to field observations, water-quality sampling during both storms occurred at or near the peak flows on October 27 and November 1, with additional samples taken on the receding limbs of the two storm hydrographs on October 28 and November 3, respectively.

Sampling results at Johnson Creek indicate that sampling of the first major runoff peaks, as envisioned during planning for this project, was accomplished. Despite the somewhat lower peak flow during the first storm, constituent concentrations were generally the greatest during the peak runoff period for that storm, and declined overall during the course of successive storms. This observation holds for almost every constituent examined, including suspended sediment and unfiltered-water concentrations of ΣDDX and dieldrin. Although the concentrations of ΣDDX and dieldrin near peak flow during the second storm were decreased from those during the receding limb at the end of the first storm, instantaneous loads of these constituents increased slightly due to the increased flow. Likewise, the instantaneous load of metolachlor during the peak of the second storm was almost equal to that from the peak of the first, despite a 40 percent decrease in concentration between the two samplings. Loads for all of the constituents were equivalent or slightly lower during the last sampling on November 23, when flow was increasing, than loads on the receding limb of the second storm. In general there was a very similar pattern of concentration changes among metolachlor, dieldrin, and ΣDDX at Johnson Creek despite the differences in the hydrophobic characteristics of the three compound types. Many of the other dissolved pesticides detected at Johnson Creek during the fall 1994 samplings, including atrazine and

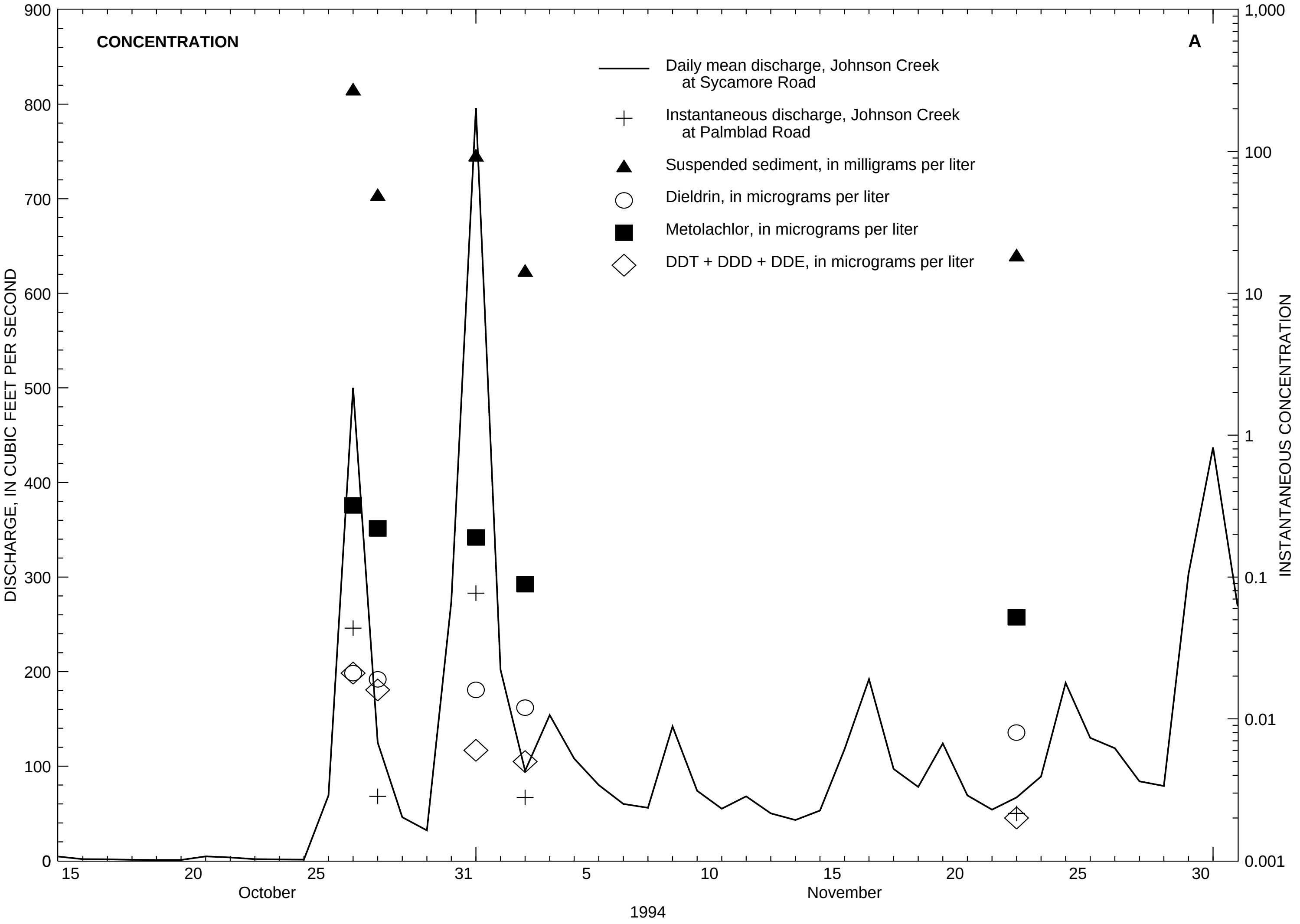


Figure 17A. Response of flow and concentration of suspended sediment and three organic pesticides to the first fall storms at Johnson Creek during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994. (Daily mean discharge from the USGS gaging station at Johnson Creek at Sycamore Road [river mile 10.2] is plotted to indicate the overall pattern of flow in Johnson Creek. Instantaneous discharge and constituent concentrations were measured on Johnson Creek at Palmblad Road [river mile 18.0].)

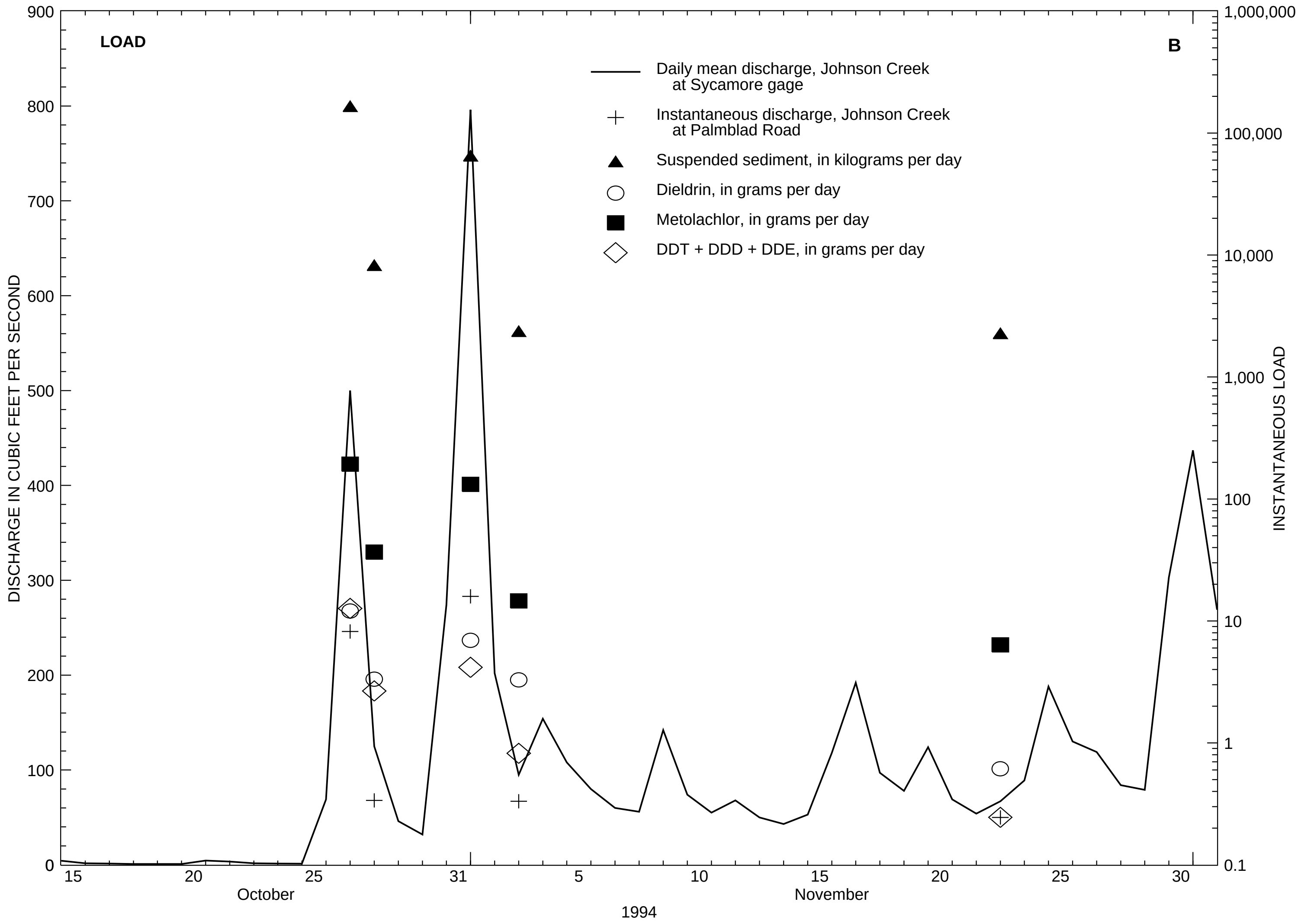


Figure 17B. Response of flow and loads of suspended sediment and three organic pesticides to the first fall storms at Johnson Creek during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994. (Daily mean discharge from the USGS gaging station at Johnson Creek at Sycamore Road [river mile 10.2] is plotted to indicate the overall pattern of flow in Johnson Creek. Instantaneous discharge and constituent concentrations were measured on Johnson Creek at Palmblad Road [river mile 18.0].)

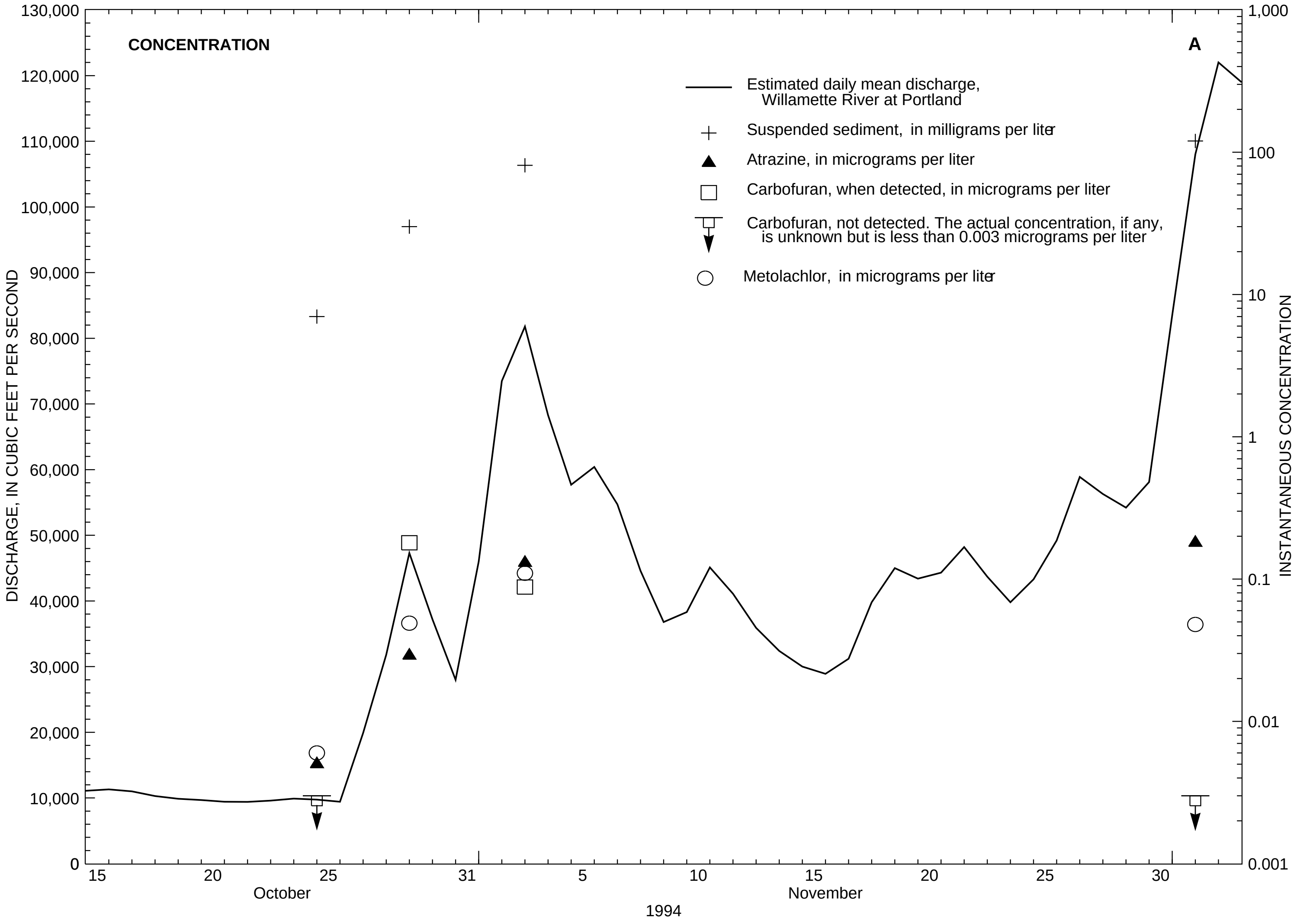


Figure 18A. Response of flow and concentrations of suspended sediment and three organic pesticides to the first fall storms at Willamette River at Portland during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994. (Carbofuran was not detected on October 25 or December 1, 1994. The method detection limit for carbofuran is 0.003 micrograms per liter.)

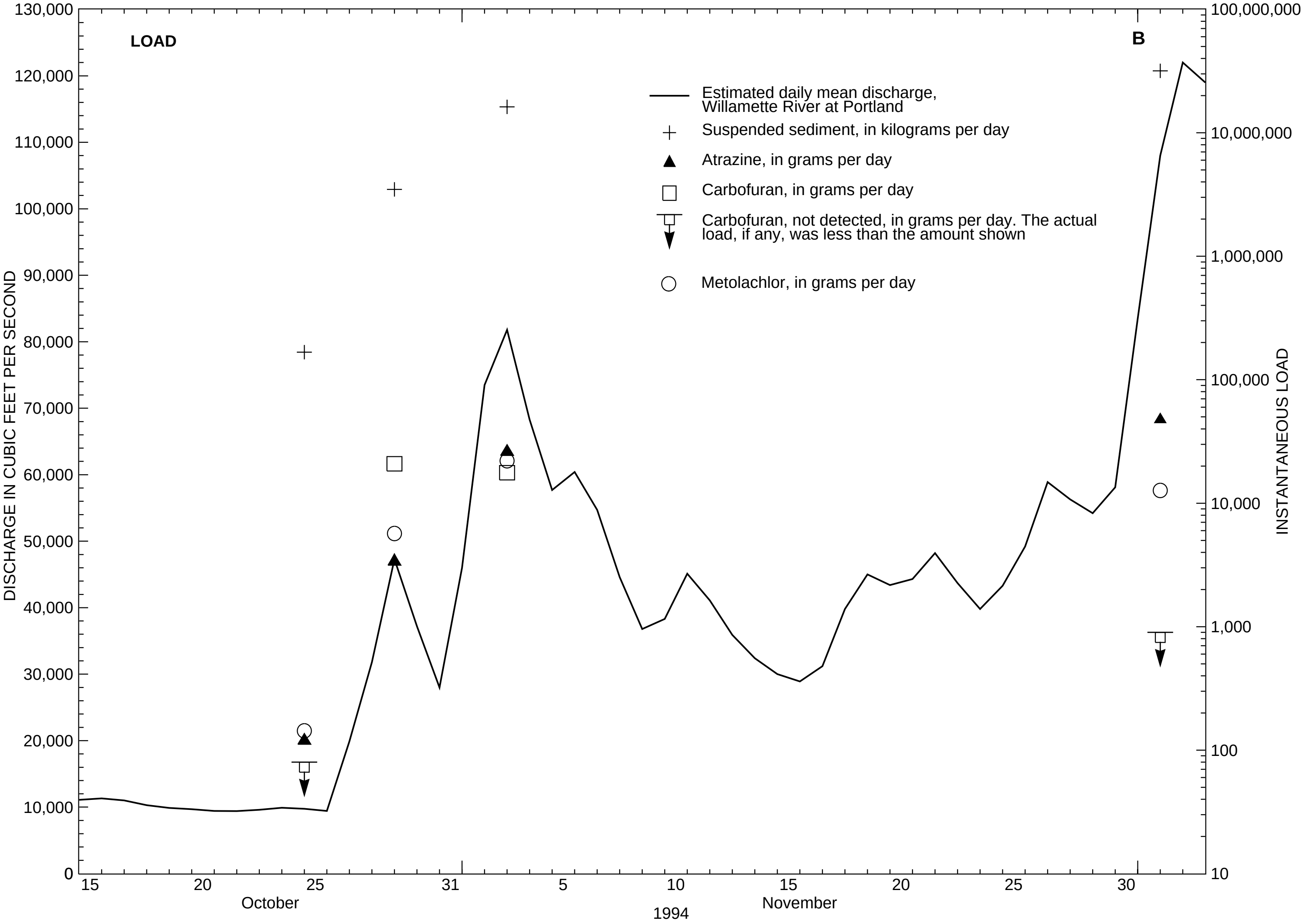


Figure 18B. Response of flow and loads of suspended sediment and three organic pesticides to the first fall storms at Willamette River at Portland during Phase II of the Willamette River Basin Water Quality Study, Oregon, 1994. (Carbofuran was not detected on October 25 or December 1, 1994. The method detection limit for carbofuran is 0.003 micrograms per liter.)

simazine, have K_{oc} values in the same range as metolachlor and tended to behave similarly at that site (Harrison and others, 1995), albeit at different concentrations.

As stated, field observations indicated that sampling at Johnson Creek occurred at peak discharge during the first and second major storms, on October 27 and November 1, 1994. However, several subsequent events of lesser magnitude were not sampled at all, and the final sample, although it was taken as flow was increasing, was collected during a relatively minor storm. Thus a significant amount of data are not available regarding the response of the constituents examined during the duration of the runoff periods, and quantitative determination of the overall transport of these compounds and the contributions from individual storms cannot be made. Nonetheless, it appears that the initial storms accounted for the highest concentrations of most constituents and that concentrations declined overall during subsequent periods. Consequently, the initial storms appear to have been very important with respect to transport of contaminant loads in addition to causing high concentrations.

Correlations (using Kendall's τ, with $n=5$) between flow, concentrations of suspended sediment, suspended organic carbon (SOC), and dissolved organic carbon (DOC) with pesticide concentrations were generally poor for the fall samplings at Johnson Creek. Although suspended sediment concentration was well correlated ($p < 0.05$) with DOC and SOC, it was poorly correlated with instantaneous discharge ($p > 0.1$), as were DOC and SOC. DOC was well correlated with concentrations of ΣDDX, atrazine, metolachlor, and simazine, whereas correlations of suspended sediment and SOC were significant ($p < 0.05$) only with concentrations of atrazine.

It is somewhat surprising that ΣDDX, in particular, did not correlate well with suspended sediment or SOC because ΣDDX is typically associated with sediments and sediment movement in streams. It is possible that the concentrations of DOC at Johnson Creek (median = 3.9 mg/L) may have been high enough to facilitate dissolution of DDX compounds into the dissolved phase or associations with colloidal forms of organic carbon. However, correlations with SOC or suspended sediment were not improved by subtracting filtered water concentrations of p,p'-DDE, the most soluble metabolite of DDT, from the unfiltered-water concentration of ΣDDX. Other possible explanations for the lack of correlation of ΣDDX with suspended sediment and SOC concentrations include the probability that the sediments sampled during the various storms were from varying sources, such as bed sediments and surface soils, and that sampling at different times on the hydrographs of the respective storms provided sediments of differing characteristics relative to the overall mass sediment movement. This could have happened if the waters and sediments from the storm on October 27 originated primarily within the streambed, while saturation of the ground during the storm provided more opportunities for soil erosion from adjacent lands to contribute in greater proportions during subsequent storms.

As was observed at Johnson Creek, the Willamette River at Portland appears to have experienced an initial flush as a result of the first major storms in the fall of 1994 (figs. 18A and 18B). However, the pattern of flow and constituent runoff in the Willamette River was somewhat different from that at Johnson Creek, and reflects the considerable differences in basin size and upstream land uses between the two sites. These differences and similarities are described below.

Much of the land contributing to streamflow in the Willamette River main stem at Portland includes high elevations in the Cascade Range which may have contributed to increased flow and suspended sediment concentrations in the Willamette River during one or two storms. Rainfall was greater in the mountains than in the Willamette Valley or Portland during the storms from October 25–29 and October 31–November 2 storms (National Oceanic and Atmospheric Administration, 1994). Rainfall was also greater in Eugene, in the southern part of the basin, than in Portland during the same two storms (fig. 4). A large storm in the end of November and early December, which produced the highest flow in the Willamette River at Portland during the fall, began as rain on snow in the Cascade Mountains (George Taylor, State Climatologist, oral commun., 1995), particularly in the northern parts of the basin, adding to the volume of water entering the Willamette from high elevations.

The source of the runoff to the Willamette River is important because water originating in the higher elevations is likely to be more dilute, and carry fewer pesticides, than water originating as agricultural or urban runoff in the lower elevations of the valley. Johnson Creek, like most of the agricultural streams sampled, originates in the lower elevations of the Willamette River Basin and therefore, is not subject to runoff from high elevations. As a result, the pattern of flow in the Willamette River at Portland (figs. 18A and 18B) was somewhat different from that at Johnson Creek (figs. 17A and 17B), especially after the storm on October 31–November 2, when the entire Willamette River Basin, which by that time probably had fully saturated soils, began to contribute runoff to the main stem.

A sample collected on the Willamette River at Portland on October 25, just prior to the initial flow increases, had relatively low concentrations and loads of dissolved pesticides (figs. 18A and 18B). As flow increased and peaked during the first storm, the concentrations of suspended sediment and dissolved pesticides such as carbofuran, metolachlor, and atrazine all increased. The concentrations and loads of suspended sediment, atrazine, and metolachlor increased again by the time of peak flow of the second storm, on November 3. This result is different from the observations at Johnson Creek, when the highest concentrations were found during the first major storm. In the Willamette River, atrazine and metolachlor were not diluted by the increased flow during the second storm, which may be a result of contributions from the far upland agricultural or urban areas of the basin; some of the water may have even originated in the first storm, taking several days to make its way to the Portland site. In contrast to atrazine and metolachlor, the concentration of carbofuran, which was not detected in the initial sampling prior to the storms, peaked during the first storm and then decreased somewhat during the second storm (fig. 18A). The load of carbofuran, however, remained essentially unchanged between the 1st and 2nd storm samplings due to the increased flow (fig. 18B).

The third major storm, at the end of November and early December, produced rain-on-snow in the northern portions of the Cascades. The combination of increased runoff from the rain on snow, together with a general washing of constituents from soils and riverbeds within the basin, appears to have resulted in decreased concentrations of most constituents at the time of sampling compared to the storm of October 30–November 2, despite the increased flow. Carbofuran was again nondetectable at the MDL of 0.003 μg/L (fig. 18A). The instantaneous loads of atrazine and suspended sediment, however, were actually greater during the final storm than previously, due to the highly increased flow rates (fig. 18B).

An additional consideration is the effect of the CSO system in Portland, which requires only a small amount of rain (approximately 0.25 inches in one storm) to become temporarily activated. When CSOs are discharging directly to the Willamette River, contact recreation is discouraged due to high bacterial levels. While it is probable that there are additional organic contaminants discharged to the river at these times, it is uncertain to what extent these storms contribute to measured concentrations of pesticides or other organic compounds in the Portland Harbor. Other complicating factors include the large basin size and heterogeneity of land uses contributing to the water quality in the Willamette River at Portland. Pesticides in runoff, from the entirety of the diverse agricultural, urban, and forested land uses in the basin, are integrated in the Willamette River by the time it reaches the Portland site. In fact, the observations for the Willamette River at Portland are interesting primarily with respect to the water quality at that site alone; they do not reveal much about the contributing factors upstream because the linkages between sources and observed water quality are poorly defined for such large river sites.

As in the case of Johnson Creek, there are no data available for the intervening periods between the major storms, nor are there sufficient data to completely describe concentrations over individual storm hydrographs in the Willamette River at Portland. All of the qualifications about the data from Johnson Creek apply equally to main-stem sites in the Willamette River. However, it is evident from figures 18A and 18B that high flows resulting from storm runoff resulted in the transport of a large amount of suspended sediments as well as dissolved pesticides.

SUMMARY AND CONCLUSIONS

This report presents results of sampling for trace elements and organic compounds conducted by the U.S. Geological Survey (USGS) as part of Phase II of the Willamette River Basin Water Quality Study. USGS data from Phase I were included where constituents and media were common to both studies. Samples were analyzed for trace elements in unfiltered water (8 elements) and filtered water (17 elements), volatile organic compounds in unfiltered water (63 compounds), organochlorine compounds in unfiltered and filtered water and suspended sediment (17 compounds), and pesticides in filtered water (94 compounds). During Phase I, 16 water samples were collected from 11 sites between 1992 and 1993; during

Phase II, 39 samples were collected from 32 sites during spring, 1994, and 39 samples were collected from 17 sites during fall, 1994. Overall, 94 water samples were collected from a total of 40 sites between Phases I and II. Data described in this report were compiled by Harrison and others (1995).

Many potentially toxic trace elements and organic compounds were detected in nonpoint source runoff in the basin, in some cases exceeding State of Oregon water-quality criteria or at otherwise high concentrations. However, no single overriding set of compounds or processes that water managers might address to effect improvements in water-quality basin-wide was apparent. Instead, there are a variety of localized concerns, probably resulting from current or historical land use practices, in both agricultural and urbanized areas, that may require water managers to consider site- or subbasin-specific measures to achieve improvements in water quality. For instance, DDX compounds (DDT, DDD, or DDE) were detected in water at only 10 of the 40 sites sampled; however, all detected concentrations exceeded the freshwater aquatic life criterion for chronic toxicity and the criterion for protection of human life for water and fish ingestion for those compounds. Several of these sites, such as Johnson Creek at Palmblad Road or the I-84 runoff site, had concentrations of ΣDDX (the sum of the concentrations of DDX compounds) that were very high, indicating locations at which some form of best management practices may be warranted. Likewise, although concentrations of most of the 43 dissolved pesticides detected (out of 61 documented as used) were usually relatively low, numerous concentrations that were potentially harmful to aquatic life were observed at isolated sites. Several compounds (atrazine, simazine, metolachlor, and diuron) were observed at almost all except forested sites. In general, concentrations of organic compounds were at their highest during stormflow, particularly during the first major storms during the fall.

Dissolved pesticide concentrations in samples collected from larger streams, usually draining a mixture of land uses, were generally lower than concentrations observed in smaller drainages draining predominantly agricultural or urban lands. It is expected that these concentrations might be even higher at sampling locations farther upstream, closer to the contributing nonpoint source activities. However, for many of the trace elements, pesticides, or other organic compounds detected such as some volatile organic compounds (VOCs), no water-quality criteria or guidelines have been established; nonetheless, there may be deleterious effects on aquatic organisms from these compounds. This may be particularly true at locations where multiple compounds are found, sometimes at high concentrations, that may act in concert to diminish the survival of aquatic organisms (Sprague, 1995; Thompkins, 1995; Yang, 1995). Furthermore, recent findings have suggested that some of the compounds detected in this study, including DDX compounds, atrazine, metribuzin, carbaryl, and 2,4-D, may act as estrogen imitators, potentially hindering reproductive success at a variety of levels within the food chain (Colborn and others, 1993). Although neither the toxicology of mixtures of compounds, nor the issue of estrogen imitators was investigated in this study, it is appropriate to consider these aspects when examining the data for toxicological impacts.

In samples from 26 sites, State of Oregon freshwater criteria for the protection of aquatic life (acute and chronic toxicity) and for the protection of human health were exceeded at 6, 11, and 7 sites, respectively, for trace elements in unfiltered water; urban sites had the most exceedances. Lead exceeded the acute toxicity criterion (ATC) or the chronic toxicity criterion (CTC) at nine sites, six of which were urban. Zinc, which did not exceed any criteria at agricultural or mixed land-use sites, exceeded both the ATC and CTC at five of nine urban sites. Comparisons to the criteria for cadmium, arsenic, lead, mercury, and silver were inconclusive at many sites because even the low laboratory reporting limits used in this study were higher than the respective criteria. Sites with the greatest numbers of trace elements exceeding water-quality criteria (6) included a site at Southeast 3rd Avenue in Portland draining only Interstate Highway 84; water from this site is discharged into the Willamette River immediately downstream of the sampling location. A-3 Channel at Wallis and Fifth Street in Eugene, with a large amount of industrial activity upstream of the site, also exceeded criteria for six trace elements including mercury. Mercury was not sampled at the Interstate-84 runoff site in Portland.

In general, the highest trace-element concentrations were found at urban sites that receive a large part of their runoff from industrial sources. Unfiltered-water trace-element concentrations of chromium, copper, lead, nickel, and zinc correlated well ($p<0.005$) with suspended sediment concentrations at these and other urban sites. Unlike sites in the more residential basins, at which concentrations of some trace elements, most notably zinc and copper, appeared to approach a maximum or even to decline as suspended-sediment concentrations increased, sites in industrial basins continued to receive increasing trace-element concentrations as suspended-sediment concentrations increased. Whether the industrial source was enriched due to higher trace-element concentrations in the aqueous phase or in suspended sediment was not directly assessed. However, an analysis of partitioning of trace elements indicated that the greatest percentage of trace elements was most likely associated with the suspended phase.

Fourteen VOCs were detected at four locations predominantly in commercial/industrial or residential urban areas. Exceedances of the criterion for the protection of human health for water and fish ingestion, cancer risk level 1 in 1 million (HHP) occurred for benzene, chloroform, 1,1-dichloroethylene, and tetrachloroethylene. In addition, several other VOCs for which water-quality criteria have not been established were observed at relatively high concentrations (greater than 1 μg/L).

Eight organochlorine (OC) compounds were detected at 14 of the 40 sites sampled. Lindane, dieldrin, and DDX compounds were detected in roughly 30 percent of the samples, predominantly in the agricultural and urban areas. Polychlorinated biphenyl (PCB) compounds were detected in samples from two urban sites. All 19 samples (at 10 sites) in which DDX compounds were detected contained concentrations that equaled or exceeded the CTC and the HHP. Eleven of the 23 detected dieldrin concentrations from a mixture of agricultural and urban areas exceeded the CTC value, whereas all 23 of the detected dieldrin concentrations exceeded the HHP concentration. Only three of the detected lindane concentrations from two agricultural sites and one heptachlor concentration from an urban site exceeded their respective HHP values. Six detected PCB concentrations from two urban sites exceeded both the CTC and the HHP values.

Nine samples were analyzed for OCs in suspended sediment and in filtered water to investigate partitioning. Only DDX compounds, which are considered to be very hydrophobic, were detected consistently enough in these samples to allow interpretation of equilibrium conditions, and then only in four samples. The largest percentage of the mass of ΣDDX was found in suspended sediment, and in general these compounds appeared to be near equilibrium between the sediment and water phases. The relative fractions of DDX compounds as DDT, DDD, and DDE were similar to those found in other studies in Oregon and Washington. In contrast, dieldrin and lindane, which are much more hydrophilic than DDX compounds, were almost completely (greater than 99 percent) present in the dissolved phase based on analyses in unfiltered and filtered water.

Of the 94 dissolved pesticides analyzed, CTCs were exceeded at only 1 site each for chlorpyrifos and parathion, and at 2 sites for malathion. Diazinon, azinphos-methyl, carbaryl, and diuron each exceeded recommended threshold concentrations established in 1973 for the protection of aquatic life by the National Academy of Sciences and the National Academy of Engineering.

Between 80 and 90 percent of the water samples collected had detectable concentrations of dissolved atrazine, metolachlor, and simazine; between 40 and 61 percent of the samples collected had detectable concentrations of desethylatrazine, cycloate, diazinon, desisopropylatrazine, diuron, and hexazinone; and roughly one out of every three samples contained detectable concentrations of DCPA (dacthal), EPTC, and terbacil. A comparison made between the 25 most frequently detected pesticides and 1987 estimates of pesticide usage in the basin showed generally little relation between the frequency of detection and documented pesticide usage, due in part to changes in both pesticide usage and agricultural practices since the 1987 estimates were compiled. Other important factors in the lack of agreement between observed pesticide detections and usage estimates include chemical or biological transformations in compounds in the environment, partitioning between the dissolved and suspended phases, variable hydrologic conditions throughout the basin at the time of sampling, or the ability of laboratory analytical procedures to detect low concentrations of some compounds.

Several pesticides, including diazinon, prometon, and tebuthiuron, were detected primarily at urban sites. Pesticides detected primarily or exclusively at agricultural sites included carbofuran, EPTC, ethoprop, fonofos, napropamide, and terbacil. Atrazine, carbaryl, chlorpyrifos, DCPA, diuron, metolachlor, and simazine were detected in similar percentages at all except forested sites, although concentrations for most of these compounds tended to be higher at the agricultural sites.

Atrazine, carbaryl, diuron, metolachlor, simazine, and terbacil were detected in similar percentages in both the northern and southern agricultural areas of the basin. However, carbofuran, chlorpyrifos, DCPA, diazinon, ethoprop, napropamide, and tebuthiuron were detected only in the northern agricultural areas, reflecting the diversity of agricultural crops grown there. EPTC, fonofos, and prometon were detected in both the northern and southern agricultural areas of the basin, but usually in a larger percentage of the samples in the northern agricultural area. In general, the frequency of detections for the most frequently detected pesticides was slightly higher in fall than in spring among the northern and southern agricultural sites in the valley; the lone exception was carbaryl. More frequent detections during the fall sampling period may be an artifact of repeated sampling at some of the fall sites. Because the fall sampling was performed under higher flow and runoff conditions than the spring sampling, however, the more frequent detections during the fall are also likely due to the higher flow conditions.

Sixty-one of the 94 pesticides analyzed in filtered water were reported to have been used in the basin in 1987; 43 of these were detected at least once during 1992–94. The median number of pesticides detected at each sampling site was eight. Two agricultural sites, Johnson Creek at Palmblad Road (near Gresham) and Zollner Creek near Mount Angel, were the sites with the greatest number of unique dissolved pesticides observed (29 and 34, respectively).

Although the number of compounds detected at each site was probably affected in part by unequal sampling frequencies among the various sites, the overall patterns of detections appear to reflect pesticide and land use in the basin. In general, the greatest numbers of pesticides are found either at sites higher up in tributary streams reflecting well defined, intensive land uses upstream (such as Zollner Creek and Johnson Creek, both of which are agricultural streams), or at sites integrating a large variety of upstream land uses (such as the Tualatin River at West Linn or the Willamette River at Portland). Furthermore, differences in the variety of agricultural patterns between the northern and southern portions of the Willamette River Basin are reflected in the numbers and types of pesticides detected at northern and southern sites. Agricultural sites in the northern portion of the basin tended to have a larger number of pesticides detected than sites in the southern portions of the basin, including several such as carbofuran, chlorpyrifos, DCPA, diazinon, ethoprop, napropamide, and tebuthiuron which were not detected at the southern sites.

Analytical results from repeated samplings on Johnson Creek at Palmblad Road and in the Willamette River at Portland during sequential storms in the fall of 1994 indicated that the first two major storms that produced runoff at both sites resulted in relatively high instantaneous concentrations and loads of several constituents when compared with subsequent storms. Suspended sediment, DDX compounds, metolachlor, and atrazine were at their highest concentrations or loads during peak flows of the first (in Johnson Creek) or second (in the Willamette River at Portland) significant storms of the fall. Continued wet weather and high flows effectively moved most of these compounds from their respective watersheds, so that transport during subsequent storm conditions appeared to diminish. However, data were not available to fully integrate concentrations over the course of the fall sampling period to completely evaluate the importance of specific storms in the transport of organic compounds.

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APPENDIXES

Appendix 1. Summary statistics for concentrations of selected trace elements detected in unfiltered and filtered water at all sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Statistics shown only for the detected concentrations; nondetects are not included; MRL, minimum reporting level; µg/L, micrograms per liter; —, not applicable]

Element	Medium	MRL (µg/L)		Number of detections	Number of samples	Detected concentrations (µg/L)				
		Phase I	Phase II			Minimum	25th Percentile	Median	75th Percentile	Maximum
Arsenic	Filtered water	1	1	10	25	1	1	1.5	2	3
Arsenic	Unfiltered water	1	1	14	24	1	1	1	2	4
Aluminum	Filtered water	—	1	12	13	20	25	100	180	340
Antimony	Filtered water	1	1	6	23	1	1	1.5	2	4
Barium	Filtered water	—	1	13	13	5	6	8	19	63
Beryllium	Filtered water	10	1	0	25	—	—	—	—	—
Cadmium	Filtered water	.1	1	5	25	.1	.1	.2	.2	.7
Cadmium	Unfiltered water	.5, 1	1	7	39	.1	1	2	2	7
Chromium	Filtered water	1	1	9	25	.6	.9	1.8	2.5	5.4
Chromium	Unfiltered water	.5,1	1	21	38	.6	2	5	7	16
Cobalt	Filtered water	.5	1	1	27	—	—	—	—	3.2
Copper	Filtered water	.5	1	19	23	.7	1.3	2.2	7.4	21
Copper	Unfiltered water	.5, 1	1	25	29	1	2.5	5	12	45
Lead	Filtered water	1	1	9	25	.5	.7	2	2.3	4
Lead	Unfiltered water	.5,1	1	23	39	.5	1	5	36	67
Mercury	Filtered water	.1	—	0	14	—	—	—	—	—
Mercury	Unfiltered water	.1	.1	1	15	—	—	—	—	.1
Molybdenum	Filtered water	—	1	4	13	2	—	8.5	—	11
Nickel	Filtered water	1	1	11	27	.6	1	2	4	7
Nickel	Unfiltered water	1	1	22	34	.8	2	3	8	12
Selenium	Filtered water	1	1	0	27	—	—	—	—	—
Silver	Filtered water	1	1	0	27	—	—	—	—	—
Uranium	Filtered water	—	1	0	11	—	—	—	—	—
Zinc	Filtered water	.5	1	15	25	.5	1.4	4	49	97
Zinc	Unfiltered water	10	10	24	39	.6	11	25	140	290

Appendix 2. Water-quality criteria used to calculate exceedances in water samples from Phase I and Phase II of the Willamette River Basin Water Quality Study, 1992–94

[Water-quality criteria are from Oregon Administrative Rules, Chapter 340, Division 41, 1994; For some trace elements, criteria concentrations are calculated on the basis of hardness (hd) in milligrams per liter as $CaCO_3$; the formulas for calculation of these criteria are given in lieu of hypothetical values; µg/L, micrograms per liter; —, no criteria; *, insufficient data to develop criteria; value presented is the lowest observed effect level]

Constituent	Oregon freshwater criteria for aquatic toxicity		Oregon criterion for protection of human health for water and fish ingestion, cancer risk 1 in 1 million (µg/L)
	Acute criterion (µg/L)	Chronic criterion (µg/L)	
Trace elements			
Arsenic	—	—	0.0022
Cadmium	$e^{(1.128[\ln(hd)]-3.828)}$	$e^{(0.7852[\ln(hd)]-3.49)}$	10
Chromium	16	11	50
Copper	$e^{(0.9422[\ln(hd)]-1.464)}$	$e^{(0.8545[\ln(hd)]-1.465)}$	—
Lead	$e^{(1.273[\ln(hd)]-1.46)}$	$e^{(1.273[\ln(hd)]-4.705)}$	50
Mercury	2.4	.012	.144
Nickel	$e^{(0.8460[\ln(hd)]+3.3612)}$	$e^{(0.8460[\ln(hd)]+1.645)}$	13.4
Silver	$e^{(1.72[\ln(hd)]-6.52)}$	.12	50
Zinc	$e^{(0.8473[\ln(hd)]+0.8604)}$	$e^{(0.8473[\ln(hd)]+0.7614)}$	—
Organochlorine compounds			
DDT+DDE+DDD	1.1	.001	.000024
Dieldrin	2.5	.0019	.000071
Heptachlor	.52	.0038	.00028
γ-HCH (Lindane)	2.0	.08	.0186
Methoxychlor	—	.03	100
PCBs	2.0	.014	.000079
Pesticides			
2,4-D	—	—	100
2,4-dinitro-*o*-cresol	—	—	13.4
Chlorpyrifos	.083	.041	—
Malathion	—	.1	—
Parathion	.065	.013	—
Volatile and semivolatile organic compounds			
Benzene	*5,300	—	.66
Chloroform	*28,900	*1,240	.19
1,1-Dichloroethylene	11,600	—	.033
Naphthalene	*2,300	*620	—
Tetrachloroethylene	*5,280	*840	.8
1,1,1-Trichloroethane	—	—	18,400
Trichloroethylene	*45,000	*21,900	2.7
Toluene	*17,500	—	14,300

Appendix 3. Summary statistics of concentrations of volatile organic compounds detected in unfiltered water at all sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Statistics shown only for the detected concentrations; nondetects are not included; MRL, minimum reporting level; µg/L, micrograms per liter; — not applicable]

Analyte	MRL (µg/L)	Number of detections	Number of samples	Detected concentrations (µg/L)				
				Minimum	25th Percentile	Median	75th Percentile	Maximum
Dichlorodifluoromethane	0.2	0	18	—	—	—	—	—
Chloromethane	.2	0	18	—	—	—	—	—
Vinyl chloride	.2	0	18	—	—	—	—	—
Bromomethane	.2	0	18	—	—	—	—	—
Chloroethane	.2	0	18	—	—	—	—	—
Trichlorofluoromethane	.2	0	18	—	—	—	—	—
1,1-Dichloroethylene	.2	3	18	0.2	—	0.3	—	0.3
Methylene chloride	.2	3	18	.3	—	.3	—	.8
trans-1,2-Dichloroethylene	.2	0	18	—	—	—	—	—
Methyl-tert-butyl ether (MTBE)	1	0	18	—	—	—	—	—
1,1-Dichloroethane	.2	2	18	.2	—	—	—	.4
2,2-Dichloropropane	.2	0	18	—	—	—	—	—
Bromochloromethane	.2	0	18	—	—	—	—	—
cis-1,2-Dichloroethylene	.2	5	18	.3	.4	.6	.8	.9
Chloroform	.2	3	18	.2	—	.2	—	.8
1,1,1-Trichloroethane	.2	3	18	.7	—	.8	—	.9
Carbon tetrachloride	.2	0	18	—	—	—	—	—
1,1-Dichloropropene	.2	0	18	—	—	—	—	—
Benzene	.2	3	18	.3	—	1	—	1.5
1,2-Dichloroethane	.2	0	18	—	—	—	—	—
Trichloroethylene	.2	4	18	.2	—	.8	—	1.3
1,2-Dichloropropane	.2	0	18	—	—	—	—	—
Bromodichloromethane	.2	0	18	—	—	—	—	—
Dibromomethane	.2	0	18	—	—	—	—	—
cis-1,3-Dichloropropene	.2	0	18	—	—	—	—	—
Toluene	.2	2	18	.2	—	—	—	.7
trans-1,3-Dichloropropene	.2	0	18	—	—	—	—	—
1,1,2-Trichloroethane	.2	0	18	—	—	—	—	—
Tetrachloroethylene	.2	5	18	.3	.4	.4	1.1	1.8
1,3-Dichloropropane	.2	0	18	—	—	—	—	—
Dibromochloromethane	.2	0	18	—	—	—	—	—
1,2-Dibromoethane (EDB)	.2	0	18	—	—	—	—	—
Chlorobenzene	.2	0	18	—	—	—	—	—
1,1,1,2-Tetrachloroethane	.2	0	18	—	—	—	—	—
Ethylbenzene	.2	0	18	—	—	—	—	—
Xylenes	.2	2	18	.4	—	—	—	.6
Styrene	.2	0	18	—	—	—	—	—

Appendix 3. Summary statistics of concentrations of volatile organic compounds detected in unfiltered water at all sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94—Continued

[Statistics shown only for the detected concentrations; nondetects are not included; MRL, minimum reporting level; µg/L, micrograms per liter; — not applicable]

Analyte	MRL (µg/L)	Number of detections	Number of samples	Detected concentrations (µg/L)				
				Minimum	25th Percentile	Median	75th Percentile	Maximum
Bromoform	0.2	0	18	—	—	—	—	—
Isopropylbenzene	.2	0	18	—	—	—	—	—
1,1,2,2-Tetrachloroethane	.2	0	18	—	—	—	—	—
Bromobenzene	.2	0	18	—	—	—	—	—
1,2,3-Trichloropropane	.2	0	18	—	—	—	—	—
n-Propylbenzene	.2	0	18	—	—	—	—	—
2-Chlorotoluene	.2	0	18	—	—	—	—	—
tert-Butylbenzene	.2	0	18	—	—	—	—	—
Pseudocumene (1,2,4-trimethylbenzene)	.2	1	18	—	—	—	—	0.2
sec-Butylbenzene	.2	0	18	—	—	—	—	—
p-Isopropyltoluene	.2	0	18	—	—	—	—	—
1,3-Dichlorobenzene	.2	0	18	—	—	—	—	—
1,4-Dichlorobenzene	.2	0	18	—	—	—	—	—
n-Butylbenzene	.2	0	18	—	—	—	—	—
1,2-Dichlorobenzene	.2	0	18	—	—	—	—	—
1,2-Dibromo-3-chloropropane (DBCP)	1	0	18	—	—	—	—	—
1,2,4-Trichlorobenzene	.2	0	18	—	—	—	—	—
Hexachlorobutadiene	.2	0	18	—	—	—	—	—
Naphthalene	.2	1	18	—	—	—	—	.5
1,2,3-Trichlorobenzene	.2	0	18	—	—	—	—	—
p-Chlorotoluene	.2	0	18	—	—	—	—	—
Trichlorotrifluoroethane	.2	0	18	—	—	—	—	—
1,3,5-Trimethylbenzene	.2	1	18	—	—	—	—	.3
Acrolein	20	0	13	—	—	—	—	—
Acrylonitrile	20	0	13	—	—	—	—	—
2-Chloroethyl vinyl ether	1	0	13	—	—	—	—	—

Appendix 4. Summary statistics of concentrations of organochlorine compounds from USGS schedules 1398 and 1399 detected in unfiltered water at all sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Statistics shown only for the detected concentrations; nondetects are not included; MRL, minimum reporting level; µg/L, micrograms per liter; —, not applicable]

Compound	MRL (µg/L)		Number of detections	Number of samples	Detected concentrations (µg/L)				
	Phase I	Phase II			Minimum	25th Percentile	Median	75th Percentile	Maximum
Aldrin	0.001	0.001	0	73	—	—	—	—	—
Chlordane	.1	.1	0	73	—	—	—	—	—
DDD	.001	.001	8	73	0.001	0.001	0.001	0.002	0.002
DDE	.001	.001	15	73	.001	.002	.002	.003	.030
DDT	.001	.001	14	73	.001	.002	.002	.002	.030
Dieldrin	.001	.001	23	73	.001	.001	.002	.005	.020
Endrin	.001	.001	0	73	—	—	—	—	—
Endosulfan	.001	.001	3	73	.001	—	.002	—	.006
Heptachlor	.001	.001	1	73	—	—	—	—	.001
Heptachlor epoxide	.001	.001	0	73	—	—	—	—	—
Lindane	.001	.001	23	73	.001	.001	.002	.006	.032
Methoxychlor	.01	.01	0	73	—	—	—	—	—
Mirex	.01	.01	0	73	—	—	—	—	—
PCBs	.1	.1	6	73	.1	.1	.1	.2	.2
PCN	.1	.1	0	73	—	—	—	—	—
Perthane	.01	.1	0	73	—	—	—	—	—
Toxaphene	1.0	1.0	0	73	—	—	—	—	—

Appendix 5. Summary statistics of concentrations of pesticides from USGS schedules 2010 and 8015 detected in filtered water at all sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Statistics shown only for the detected concentrations; nondetects are not included; MDL, method detection limit; µg/L, micrograms per liter; —, not applicable; (E), concentration is estimated]

Compound	MDL (µg/L)	Number of detections	Number of samples	Detected concentrations (µg/L)				
				Minimum	25th Percentile	Median	75th Percentile	Maximum
Amide compounds								
Alachlor	0.002	5	92	0.002	0.006	0.007	0.015	0.06
Metolachlor	.004	75	93	.003	.008	.026	.11	3.3
Napropamide	.004	27	93	.004	.014	.033	.097	1.6
Pronamide	.018	18	93	.004	.006	.012	.022	.098
Propachlor	.007	3	93	.004	—	.009	—	.024
Propanil	.004	2	93	.003	—	—	—	.004
Carbamate compounds								
Butylate	.002	0	93	—	—	—	—	—
Carbaryl	(E).003	21	93	.003	.006	.010	.026	2
Carbofuran	(E).003	21	93	.009	.035	.11	.36	9
EPTC	.002	29	93	.001	.005	.008	.021	1
Molinate	.003	0	93	—	—	—	—	—
Pebulate	.004	1	93	—	—	—	—	.007
Thiobencarb	.002	0	93	—	—	—	—	—
Triallate	.001	6	93	.002	.002	.007	.01	.011
Dinitroaniline compounds								
Benfluralin	.002	1	93	—	—	—	—	.006
Ethalfluralin	.004	0	93	—	—	—	—	—
Pendimethalin	.004	3	93	.011	—	.014	—	.051
Trifluralin	.002	16	93	.003	.005	.006	.0095	.018
Miscellaneous compounds								
2,6-Diethylaniline	.003	0	93	—	—	—	—	—
Propargite	.013	3	93	.003	—	.010	—	.009
Organochlorine compounds								
DCPA	.002	32	93	.001	.002	.004	.007	.029
Dieldrin	.001	5	93	.007	.012	.016	.019	.021
p,p'-DDE	.006	9	93	.001	.002	.003	.003	.006
alpha-HCH	.002	0	93	—	—	—	—	—
Lindane (gamma-HCH)	.004	5	93	.004	.005	.021	.03	.038
Organophosphorus compounds								
Chlorpyrifos	.004	24	93	.002	.007	.010	.023	.043
Diazinon	.002	44	93	.002	.006	.015	.03	1.2
Disulfoton	.017	0	93	—	—	—	—	—
Ethoprop	.003	24	93	.002	.005	.011	.088	3.1
Fonofos	.003	24	92	.001	.004	.012	.03	.1
Malathion	.005	8	93	.009	.013	.020	.066	.1
Methyl Azinphos	(E).001	1	90	—	—	—	—	.18
Methyl Parathion	.002	0	93	—	—	—	—	—
Parathion	.006	0	93	—	—	—	—	—
Phorate	.002	0	93	—	—	—	—	—

Appendix 5. Summary statistics of concentrations of pesticides from USGS schedules 2010 and 8015 detected in filtered water at all sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94—Continued

[Statistics shown only for the detected concentrations; nondetects are not included; MDL, method detection limit; µg/L, micrograms per liter; —, not applicable; (E), concentration is estimated]

Compound	MDL (µg/L)	Number of detections	Number of samples	Detected concentrations (µg/L)				
				Minimum	25th Percentile	Median	75th Percentile	Maximum
Terbufos	0.007	0	93	—	—	—	—	—
Permethrin compounds								
cis-Permethrin	.005	0	93	—	—	—	—	—
Phenyl Urea compounds								
Linuron	.002	1	93	—	—	—	—	0.78
Tebuthiuron	.01	21	93	0.003	0.007	0.032	0.052	.12
Triazine compounds								
Atrazine	.001	84	93	.005	.023	.052	.18	2.7
Cyanazine	.004	0	93	—	—	—	—	—
Desethylatrazine	(E).002	56	93	.002	.005	.010	.021	.27
Metribuzin	.004	19	93	.006	.011	.038	.064	.41
Prometon	.003	27	93	.005	.008	.013	.026	.068
Simazine	.005	76	93	.004	.026	.095	.2	3.5
Uracil compounds								
Terbacil	(E).007	34	90	.006	.011	.027	.073	1
Pesticides by custom low-level analyses (USGS schedule 8015)								
Ametryn	.006	0	58	—	—	—	—	—
Butachlor	.008	0	58	—	—	—	—	—
Cycloate	.01	25	58	.001	.002	.002	.003	.020
Desisopropylatrazine	.004	23	58	.002	.002	.004	.008	.023
Hexazinone	.013	28	58	.001	.002	.003	.006	.040
Prometryn	.007	0	58	—	—	—	—	—
Propazine	.006	0	58	—	—	—	—	—
Simetryn	.005	0	58	—	—	—	—	—

Appendix 6. Summary statistics of concentrations of pesticides from USGS schedule 2051 detected in filtered water at all sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94

[Statistics shown only for the detected concentrations; nondetects are not included; minimum reporting level for all compounds is 0.05 micrograms per liter (µg/L); —, not applicable; (E), concentration is estimated; on the basis of results from replicate and spike recovery samples, many compounds had lower than average accuracy and precision from 1993–94 (Werner and others, 1996, Appendix B)]

Compound	Number of detections	Number of samples	Detected concentrations (µg/L)				
			Minimum	25th Percentile	Median	75th Percentile	Maximum
Benzoic acid compounds							
Dicamba	1	82	—	—	—	—	0.05
Benzonitrile compounds							
Bromoxynil	1	82	—	—	—	—	.11
Dichlobenil (E)	1	81	—	—	—	—	.42
Carbamate compounds							
Aldicarb	0	81	—	—	—	—	—
Aldicarb Sulfone	0	81	—	—	—	—	—
Aldicarb Sulfoxide	0	81	—	—	—	—	—
Carbaryl	2	81	.07	—	—	—	.25
Carbofuran	4	81	.05	—	.29	—	.47
3-Hydroxy-carbofuran	0	81	—	—	—	—	—
Methiocarb	0	81	—	—	—	—	—
Methomyl	0	81	—	—	—	—	—
Oxamyl	1	81	—	—	—	—	.07
Propham	0	81	—	—	—	—	—
Propoxur	0	80	—	—	—	—	—
Chlorophenoxy acid compounds							
Bentazon	3	82	.08	—	.26	—	.41
2,4-D	10	84	.05	.08	.18	.23	.79
2,4-DB	0	82	—	—	—	—	—
Dacthal-mono-acid	0	82	—	—	—	—	—
Dichloroprop (2,4-DP)	0	82	—	—	—	—	—
MCPA	1	82	—	—	—	—	.09
MCPB	0	82	—	—	—	—	—
Silvex (2,4,5-TP)	0	84	—	—	—	—	—
2,4,5-T	0	84	—	—	—	—	—
Dinitroaniline compounds							
Oryzalin	1	81	—	—	—	—	.23
Dinitrophenol compounds							
Dinoseb (DNBP)	4	82	.06	—	.075	—	.23
Dinitrophenyl compounds							
2,6-Dinitro-*o*-cresol (DNOC) (E)	1	82	—	—	—	—	.05
Diphenyl ether compounds							
Acifluorfen	0	82	—	—	—	—	—
Naphthol compounds							
1-Naphthol (E)	0	81	—	—	—	—	—
Phenoxy acid compounds							

Appendix 6. Summary statistics of concentrations of pesticides from USGS schedule 2051 detected in filtered water at all sites during Phases I and II of the Willamette River Basin Water Quality Study, Oregon, 1992–94—Continued

[Statistics shown only for the detected concentrations; nondetects are not included; minimum reporting level for all compounds is 0.05 micrograms per liter (µg/L); —, not applicable; (E), concentration is estimated; on the basis of results from replicate and spike recovery samples, many compounds had lower than average accuracy and precision from 1993–94 (Werner and others, 1996, Appendix B)]

Compound	Number of detections	Number of samples	Detected concentrations (µg/L)				
			Minimum	25th Percentile	Median	75th Percentile	Maximum
Chloramben (Aimben)	0	81	—	—	—	—	—
Phenyl urea compounds							
Diuron	44	81	0.05	0.11	0.32	0.95	9
Fenuron	0	81	—	—	—	—	—
Fluometuron	0	81	—	—	—	—	—
Linuron	0	81	—	—	—	—	—
Neburon	0	81	—	—	—	—	—
Phthalimide compounds							
Chlorothalonil (E)	0	81	—	—	—	—	—
Pyrethroid compounds							
Esfenvalerate (E)	0	81	—	—	—	—	—
Pyridazinone compounds							
Norflurazon	0	81	—	—	—	—	—
Pyridine compounds							
Clopyralid	0	82	—	—	—	—	—
Picloram	0	82	—	—	—	—	—
Pyridyloxyacetic acid compounds							
Triclopyr	11	82	.05	.11	.18	.44	.72
Uracil compounds							
Bromacil	1	83	—	—	—	—	.2

Appendix 7. Explanation of calculations for theoretical equilibrium partitioning of DDT and metabolite compound

The theoretical equilibrium fraction of organic compounds present in the suspended phase was calculated from the individual organic carbon-water partitioning value (K_{oc}) for the compound, as well as the suspended organic carbon (SOC) concentration, using the equation:

$$X_s = \frac{1}{\left[\left(\frac{10^6}{[SOC]\cdot K_{oc}]}\right) + 1\right]}$$

where:

X_s = equilibrium mass fraction of organic compound in the suspended phase,

[SOC**]** = concentration of suspended organic carbon, in mg/L, and

K_{oc} = organic carbon-water partitioning coefficient for that compound, in mL/g.

For DDX compounds (DDT, DDD, or DDE), the calculated X_s for each compound was multiplied by the sum of the amounts observed in the dissolved and suspended phases in the sample, and summed to yield the *equilibrium* ΣDDX (sum of the individual DDX compound concentrations) in the suspended phase. Dividing this concentration by the combined ΣDDX *observed* in the dissolved and suspended phases in the sample gives the equilibrium fraction of DDX compounds present in the suspended phase. As an estimate of the state of equilibrium of DDX compounds in the water at the time of sampling, the equilibrium suspended fraction was compared to the observed suspended fraction; these two fractions are shown for four water samples in figure 10.

As an example, consider the sample from Johnson Creek on October 27, 1994 (table 7–1). The *observed* fraction of DDX compounds in the suspended phase (0.057/0.064) is 0.89, whereas the *equilibrium* fraction (0.048/0.064) is 0.75.

Table 7-1. Example computation of the partitioning of DDT and metabolite compounds in the suspended phase for Johnson Creek at Palmblad Road, October 27, 1994

[Suspended organic carbon (SOC) concentration = 5.7 milligrams per liter; sediment water partitioning coefficients (K_{oc}) are taken from the U.S. Environmental Protection Agency (1990); mL/g, milliliters per gram; X_s, expected fraction in suspended phase, at equilibrium; µg/L, micrograms per liter]

			Concentration of DDT compounds (µg/L)			
Compound	K_{oc} (mL/g)	X_S	Observed, dissolved phase	Observed, suspended phase	Sum of dissolved and suspended phases	Suspended phase, at equilibrium
DDD	770,000	0.81	0.001	0.006	0.007	0.006
DDE	4,400,000	.96	.003	.020	.023	.022
DDT	243,000	.58	.003	.031	.034	.020
Sum:	—	—	.007	.057	.064	.048