Pesticides and Volatile Organic Compounds in Surface and Ground Water of the Palouse Subunit, Central Columbia Plateau, Washington and Idaho, 1993-95

By Richard J. Wagner and Lonna M. Roberts

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<URL:http://wwwrvares.er.usgs.gov/nawqa/nawqa_home.html>

FOREWORD

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

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

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

•Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.

•Describe how water quality is changing over time.

•Improve understanding of the primary natural and human factors that affect water-quality conditions.

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

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

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

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

Robert M. Hirsch
Chief Hydrologist

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FIGURES

Maps showing:

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CONVERSION FACTORS

Multiply	By	To obtain
microgram (μg)	3.53×10^{-8}	ounce
micrometer (μm)	3.937×10^{-5}	inch
liter (L)	0.296	gallon
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
acre	4.046×10^{-3}	square kilometer
square mile (mi^2)	2.590	square kilometer
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
pound per day (lb/day)	0.4536	kilogram per day
pound per year (lb/yr)	0.4536	kilogram per year

Temperature: To convert temperature given in this report in degrees Celsius (°C), to degrees Fahrenheit (°F), use the following equation: °F = 1.8 x °C + 32.

Abbreviations:

μm	micrometer
L	liter
μg/L	microgram per liter
mg/L	milligram per liter
$NO_2 + NO_3$	nitrite plus nitrate

Acronyms:

USGS	U.S. Geological Survey
GC/MS	gas chromatography/mass spectrometry
HPLC	high-performance liquid chromatography
NAWQA	National Water-Quality Assessment Program
NWQL	National Water Quality Laboratory
SPE	solid-phase extraction
USEPA	U.S. Environmental Protection Agency
MCL	Maximum Contaminant Level
MDL	method detection limit
VOC	volatile organic compound
CRBG	Columbia River Basalt Group
NWIS	National Water Information System
PVC	polyvinyl chloride
RSD	risk-specific dose
DAR	desethylatrazine-to-atrazine ratio

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ABSTRACT

As part of the National Water-Quality Assessment (NAWQA) Program, the U.S. Geological Survey began collecting water samples in 1993 for analysis of pesticides from surface and ground water in the Central Columbia Plateau study unit. Samples were collected from 1993-95 to document the occurrence, distribution, and transport of pesticides in surface and ground water of the Palouse subunit and to provide a basis for future studies to determine trends in pesticide concentrations and distributions. This report describes the distribution and transport of selected pesticides in surface and ground water of the Palouse subunit of the Central Columbia Plateau study unit; the relation between the presence of pesticides in surface and ground water and pesticide use, environmental factors, and the chemical properties of pesticides; how observed pesticide concentrations compare with water-quality criteria and drinking water standards; the mass transport of pesticides in surface water; and the pathways by which pesticides enter surface and ground water.

One surface-water site was sampled for pesticides monthly or more frequently for 1 year, and 10 additional sites were sampled during storms, periods of pesticide applications, or periods of low flow to describe the occurrence and transport of pesticides in surface water. Thirty different pesticides were found in surface water of the Palouse subunit, primarily during storm runoff. In addition, 34 shallow monitoring wells and 19 deeper wells were sampled to examine the effects of land use, pesticide use, and other environmental factors on the occurrence and distribution of pesticides in ground water. Six pesticides, one pesticide metabolite, and seven volatile organic compounds (VOCs) were detected in 28 percent of the ground-water samples. Only ground water was sampled for VOCs. No pesticides were detected in ground water (the primary source of drinking water) at concentrations that exceed drinking water standards whereas three pesticides were detected in surface water at concentrations that exceed the freshwater-chronic criteria for the protection of aquatic life; concentrations of two pesticides exceed the U.S. Environmental Protection Agency risk-specific dose health advisory for drinking water associated with a 1 in a million cancer risk. Although many of the pesticides detected in surface and ground water are applied for agricultural purposes, roadside applications and domestic use also may be significant sources of pesticides in some cases.

INTRODUCTION

The Central Columbia Plateau study unit is one of more than 50 study units being investigated by the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (Hirsch and others, 1988; Leahy and others, 1990). The goals of NAWQA are to describe the current water-quality conditions and how water quality is changing over time in the Nation's ground- and surface-water resources and to gain a better understanding of the natural and human factors that affect the quality of water resources. The study units, which are distributed throughout the Nation, contribute to the overall goals of NAWQA (Gilliom and others, 1995) by providing water-quality information that is relevant to the study unit and that can be used in combination with the information from other study units to assess water quality at regional and National scales.

This report describes the occurrence, distribution, and transport of selected pesticides in surface and ground water of the Palouse subunit of the Central Columbia Plateau NAWQA study unit. Data were collected from 1993-95. This information will provide a basis for future studies to determine trends in pesticide concentrations and distributions.

Purpose and Scope

The purposes of this report are to describe (1) the occurrence, distribution, and transport of pesticides in surface and ground water of the Palouse subunit of the NAWQA Central Columbia Plateau study unit; (2) the relation between the presence of pesticides in surface and ground water and current and historic pesticide use, land use, other environmental factors, and chemical properties of the pesticides; (3) how observed pesticide concentrations compare with drinking water standards and other water-quality criteria; (4) the transport of selected pesticides in surface water; and (5) the pathways by which pesticides enter surface and ground water. One surface-water site was sampled for pesticides monthly or more frequently for 1 year, and 10 additional surface-water sites were sampled during storms, periods of pesticide application, or periods of low flow to aid in describing the occurrence and transport of pesticides in surface water. Thirty-four shallow domestic wells or newly installed monitoring wells and 19 deeper public-supply wells were sampled to examine the effects of land use, pesticide use, and other environmental factors on the occurrence and distribution of pesticides in ground water.

Acknowledgments

Appreciation and thanks are extended to the reviewers and editor of this report, to those individuals who gave permission to the U.S. Geological Survey to install wells or sample on their properties, and to those municipalities that allowed the U.S. Geological Survey to sample their public-supply wells.

Special thanks are given to Brett Smith, Galen Schuster, and Jan O'Neil for their efforts in collecting the water-quality samples that make this report possible.

ENVIRONMENTAL SETTING

The Central Columbia Plateau study unit is located in east-central Washington and part of Idaho and covers approximately 13,000 mi^2 (square miles) (fig. 1). For a more complete description of the entire study unit and the three subunits, refer to Jones and Wagner (1995) or Greene and others (1997). It is bordered on the north by the Columbia River and the drainage basin boundaries of Crab Creek and the lower Spokane River drainage system, the Columbia River on the west, the Snake River on the south, and the drainage basin boundary of the Palouse River on the east. To help identify the causes for observed water-quality conditions, the study unit was divided into three subunits--the Palouse, the Quincy-Pasco, and the North-Central on the basis of geology, hydrology, and land use. This report covers only water-quality issues in the Palouse subunit, which includes most of the 2,500 mi^2 Palouse River drainage basin, excluding the Rock Creek (954 mi^2) and Cow Creek (679 mi^2) drainage basins.

Geohydrology and Hydrography

The Columbia Plateau is underlain by extensive basalt flows of the Columbia River Basalt Group (CRBG) that cover parts of Washington and Idaho (fig. 2). The basalts are primarily Miocene in age and are interbedded with sediments. The individual basalt flows range in thickness from a few inches to several hundred feet with composite thicknesses reaching up to 16,000 feet near Pasco (Drost and Whiteman, 1986).

During and after the extrusion of the basalt, the region was warped into a broad basin with several sub-basins caused by steep folding and faulting. Two types of unconsolidated sedimentary deposits have accumulated over the basalt: glaciofluvial deposits, consisting primarily of sands and gravels, in the western and central areas of the North-Central subunit; and loess, a fine, wind-blown deposit, in the Palouse subunit. Loess deposits, also known as the Palouse Formation, can be anywhere from a few inches to hundreds of feet thick (Foxworthy and Washburn, 1963). During the late Pleistocene, cataclysmic floods swept through the region, removing vast quantities of the overlying sediment and some basalt and leaving behind deep canyons and coulees known as the Channelled Scablands. The dominant geologic process affecting the area since the most recent floods is considered to be erosion.

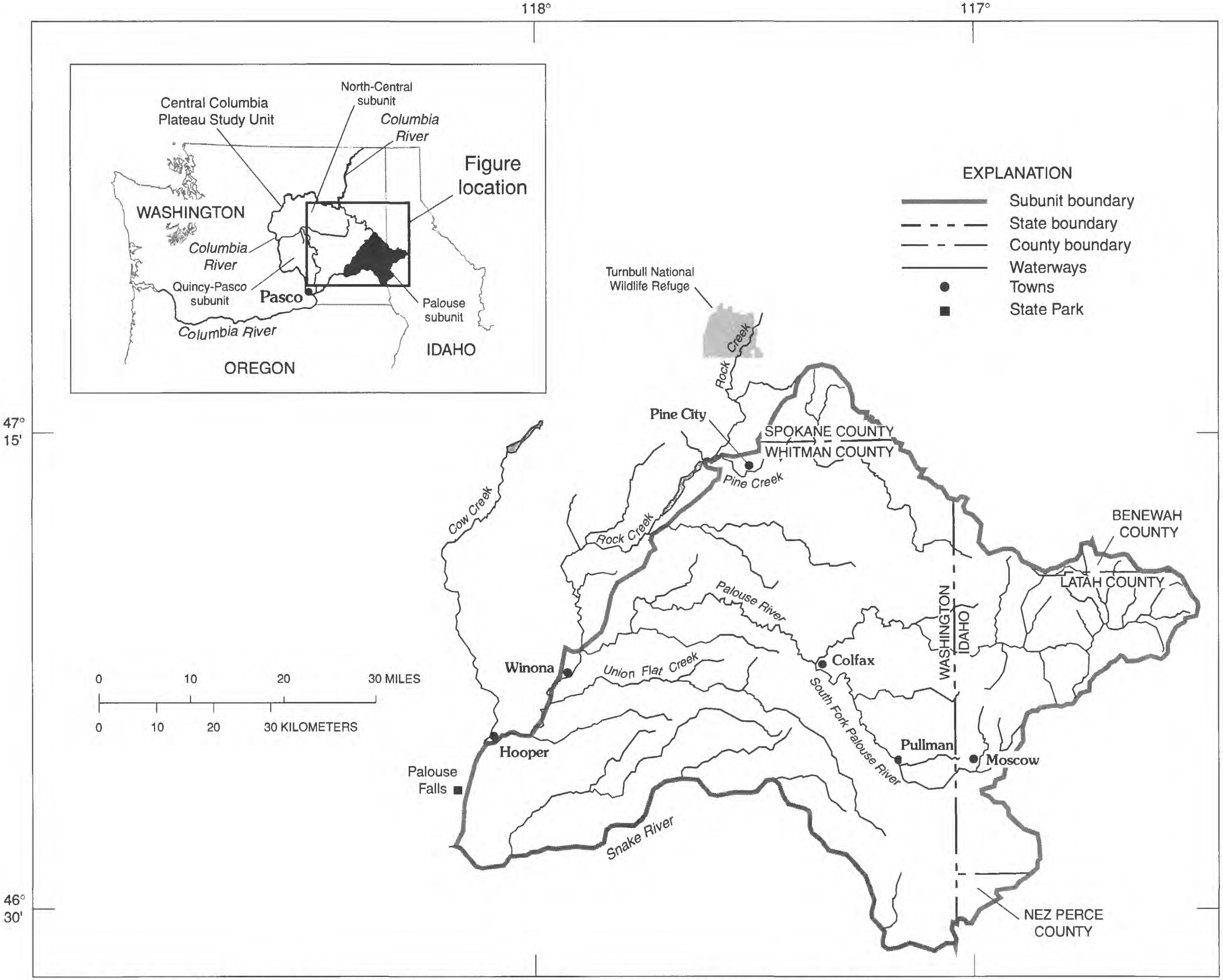

Figure 1. Location of the Palouse subunit of the Central Columbia Plateau study unit, Washington and Idaho.

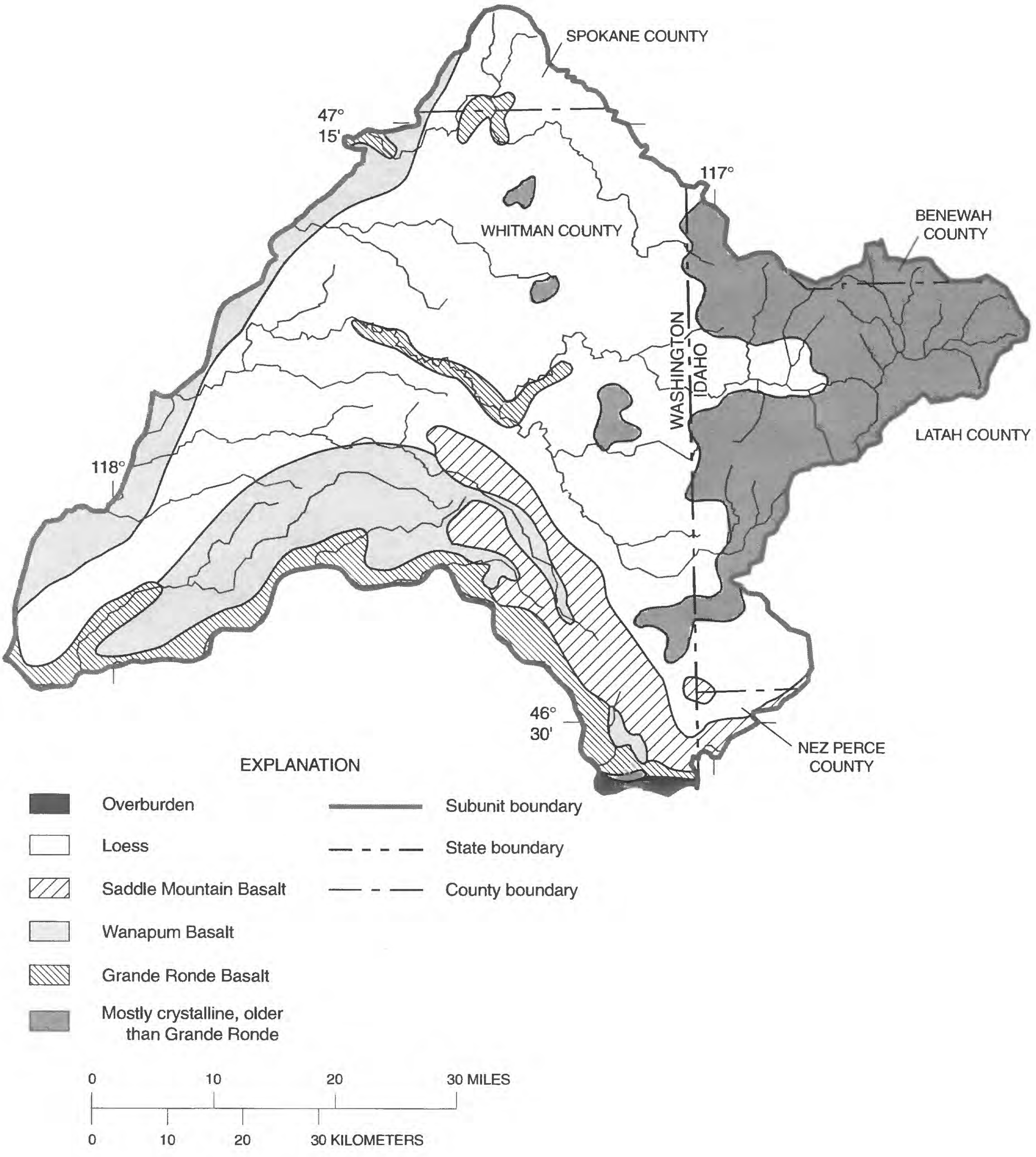

Figure 2. Surficial geology of the Palouse subunit (modified from Drost and Whiteman, 1986).

The Palouse subunit has two main aquifers, the Yakima Basalt aquifer and the Loess aquifer (hereafter referred to as the basalt aquifer and the loess aquifer). The deeper basalt aquifer contains the youngest subgroup of the CRBG and is composed of a sequence of generally permeable basalt flows. The basalt flows are classified into the Saddle Mountain, Wanapum, and Grand Ronde Basalts of the Yakima Basalt Subgroup of the CRBG (fig. 2). The rubble zones or sedimentary interbeds between successive basalt flows provide most of the water to the area. The shallow loess aquifer is formed from fine, silty deposits and is not a significant source of water, although some domestic wells are completed in the loess (Foxworthy and Washburn, 1963). Water in the aquifers is recharged from precipitation at rates that range from less than 0.1 to about 10 inches per year (Bauer and Vaccaro, 1990). Precipitation rates and natural recharge rates increase from west to east.

The major surface-water system in the subunit is the Palouse River system. Most of the perennial streams are in the Palouse drainage basin; a few flow directly into the Snake River. Many ephemeral streams are located in the area. For a more complete description of the geohydrology of the area, refer to Jones and Wagner (1995) or Greene and others (1997).

Climate

Most of the Central Columbia Plateau has a semiarid climate, generally receiving between 10 and 20 inches of rain per year (Bauer and Vaccaro, 1990). Rates of precipitation in the Palouse subunit increase from west to east, ranging from approximately 13 inches annually in the southwestern part of the subunit to over 25 inches per year in the mountainous headwaters of the Palouse River (fig. 3). Roughly 85 percent of the precipitation occurs between October and May, with 40 percent occurring between November and January.

Water and Land Use

Ground and surface water in the Palouse subunit is used for a variety of purposes, including irrigation, drinking water, and recreation. Surface waters also are habitat for fish and wildlife. The aquifers in the Yakima Basalt Subgroup, particularly the interflow zones, are the major source of water for agricultural, domestic, and municipal use. Most water withdrawn in the Palouse subunit is used for irrigation, primarily for land adjacent to the Palouse River and its tributaries (Nassar and Walters, 1975). Most of the ground-water irrigation in the Palouse subunit is along the Palouse River between Hooper and Winona. Sources of drinking water in the Palouse subunit are nearly all from ground water. Domestic wells are usually shallow and draw water from the shallowest basalt aquifers, whereas public-supply wells and some domestic wells generally are completed in the deeper basalt aquifers. Surface-water recreation is minimal, although several lakes and wildlife refuges are located in the Rock Creek drainage basin, a State park is located at Palouse Falls, and there is some fishing in streams in the headwaters of the Palouse River. Numerous species of birds, fish, and other wildlife can be found in and along surface waterways in the area, and the Palouse subunit is adjacent to the Turnbull National Wildlife Refuge to the northwest.

Nearly all of the land use in the Palouse subunit is dryland farming, although there is some rangeland and forest in the mountainous eastern portion (fig. 4). Wheat, barley, lentils, and peas are the major crops. The irrigated farming along the Palouse River and its tributaries contribute to less than 1 percent of land use.

Pesticide Use

Estimates of the total quantity of each pesticide applied annually were computed as the sum of annual applications of that pesticide to each crop in the Palouse subunit. The estimates were calculated as described by Wagner and others (1996). Pesticide application rates and treatment percentages were obtained from a 1995 survey by the National Center for Food and Agriculture Policy (Anderson and Gianessi, 1995); data related to pesticide use were gathered from multiple sources, and several methods were used to process the data digitally. Since crop acreages are based on data for a single year, year-to-year changes in crop distributions, which likely affect pesticide use, are not reflected in the data.

Herbicides are the predominant type of pesticide used in the Palouse subunit, and two herbicides--triallate and 2,4-D--account for nearly half of the total pesticide use (table 1). Pesticide use on wheat, dry peas, and barley accounts for three-fourths of total pesticide applications (table 2).

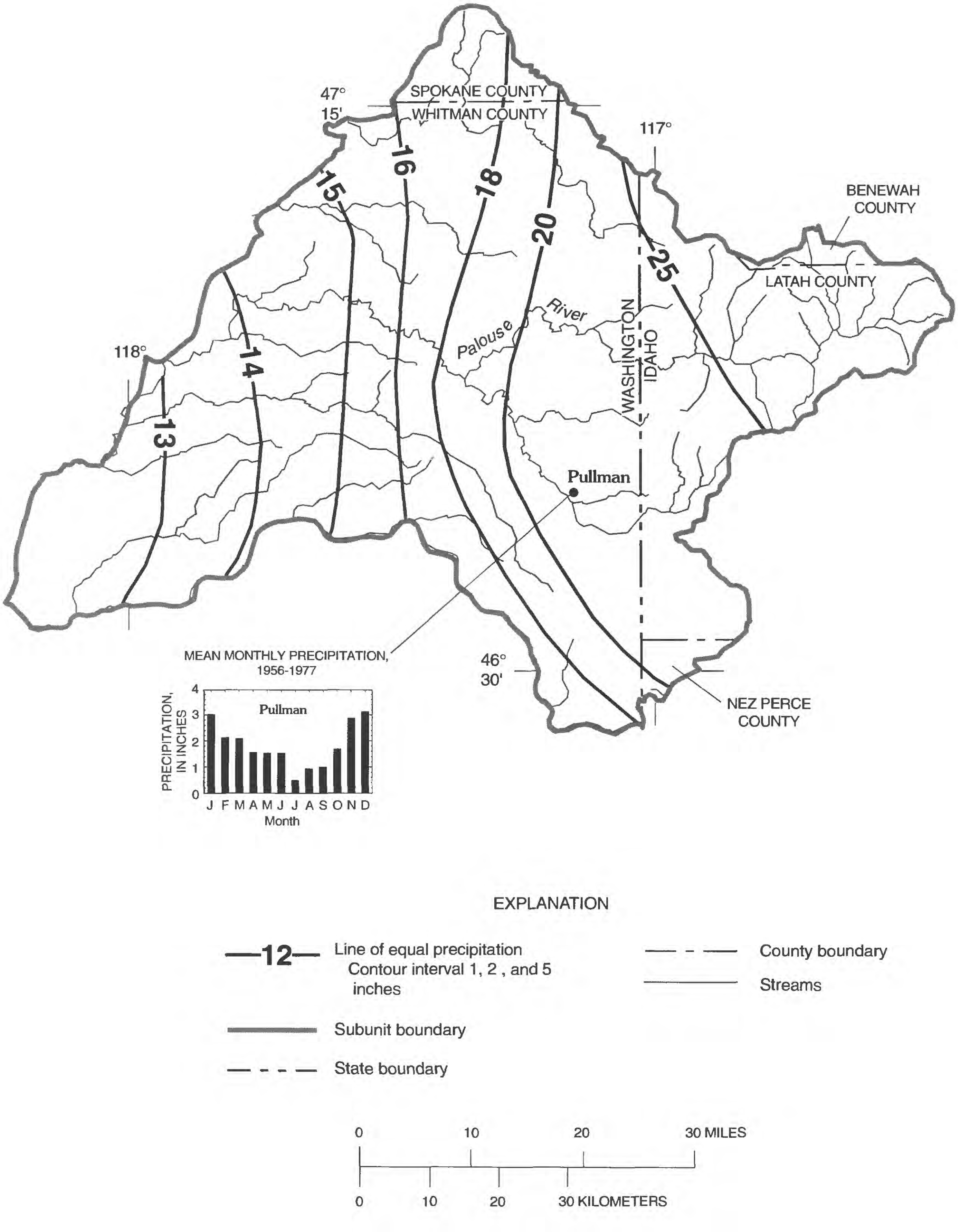

Figure 3. Mean annual precipitation in the Palouse subunit, Washington and Idaho (modified from Nelson, 1991).

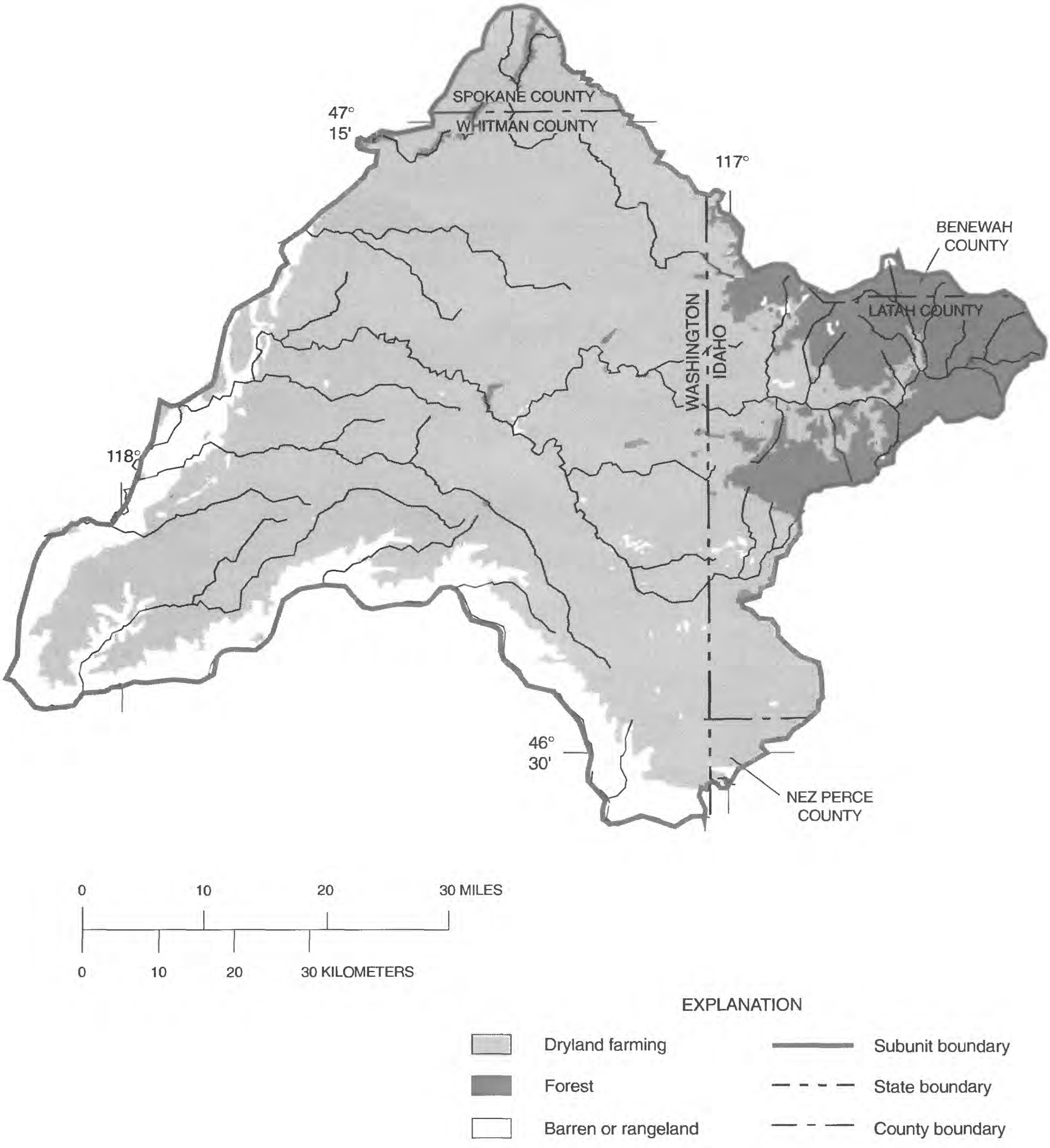

Figure 4. Land use in the Palouse subunit, Washington and Idaho.

Table 1.--*Amounts of pesticides applied to cropland and percent detections of pesticides in surface and ground water of the Palouse subunit, Washington and Idaho*

[Pesticides are included in table if they make up 1 percent or more of the total applied within each type classification; lbs/year, pounds per year; pesticide application rates from Anderson and Gianessi (1995); --, not analyzed for]

Pesticide	Active ingredient applied (lbs/year)	Percent of pesticides applied by type	Surface water (percent detections)	Ground water (percent detections)
		Fungicides		
Thiabendazole	23,000	46	--	--
Benomyl	21,000	42	--	--
Thiophanate methyl	5,700	11	--	--
Other	100	0	--	--
		Herbicides		
Triallate	240,000	36	4	0
2,4-D	100,000	16	17	0
Diuron	80,000	12	24	0
Imazethapyr	37,000	6	--	--
Bromoxynil	36,000	6	3	0
MCPA	33,000	5	11	0
Glyphosate	27,000	4	--	--
Diclofop	20,000	3	--	--
Paraquat	15,000	2	--	--
Metribuzin	11,000	2	43	0
Dicamba	11,000	2	4	0
Trifluralin	7,400	1	1	0
DCPA	5,700	1	39	0
Ethalfluralin	5,100	1	1	0
Difenzoquat	4,800	1	--	--
Other	17,000	3	--	--
		Insecticides		
Disulfoton	14,000	35	0	0
Dimethoate	8,600	21	--	--
Phosmet	5,700	14	--	--
Ethyl parathion	4,800	12	--	--
Methyl parathion	2,400	6	0	0
Malathion	2,000	5	1	0
Mevinphos	580	1	0	0
Chlorpyrifos	440	1	0	0
Methomyl	360	1	0	0
Propargite	360	1	0	0
Diazinon	210	1	8	0
Other	480	1	--	--
		Others		
Sulfuric acid	1,300	30	--	--
Metam sodium	1,300	30	--	--
Sethoxydim	900	21	--	--
Chloropicrin	420	10	--	--
1,3-Dichloropropene	380	9	--	0
Maleic hydrazide	4	0	--	--

Table 2.--*Pesticide use by crop type and crop acreage in the Palouse subunit, Washington*

[Pesticide application rates from Anderson and Gianessi (1995); acreage data for the Palouse subunit is for Whitman County, from the 1992 Census of Agriculture (U.S. Department of Commerce, 1994); lbs/year, pounds per year; <, less than]

Crop	Active ingredient applied (lbs/year)	Acres planted	Pounds of pesticide applied per acre
Wheat	330,000	473,000	0.7
Dry peas	140,000	91,000	1.5
Barley	81,000	168,000	0.5
Fallow land	72,000	317,000	0.2
Lentils	72,000	55,000	1.3
Pasture	14,000	268,000	<0.1
Field seed	8,700	2,340	3.7
Green peas	5,300	5,620	0.9
Alfalfa hay	3,900	6,790	0.6
Potatoes	3,800	75	51
Sod	3,200	1,740	1.8
Dry beans	900	570	1.6
Other hay	600	4,880	0.1
Canola	300	1,700	0.2
(Totals)	735,700	1,395,715	

ANALYTICAL AND SAMPLING METHODS

Pesticides analyzed for in surface- and ground-water samples were selected by the NAWQA program (Gilliom and others, 1995) from a list of about 400 of the pesticides most commonly used in the United States (Gianessi and Puffer, 1991, 1992a, 1992b). Each pesticide was selected on the basis of the following factors: a national use of more than 8,000 pounds of active ingredient annually; inclusion in the analytical schedules of other Federal monitoring or survey programs; toxicity; leachability; and its ability to be trapped and extracted from the appropriate solid-phase-concentrating matrix. The target analytes (table 3) are a broad spectrum of pesticides that were analyzed using either gas chromatography/mass spectrometry (GC/MS) or high-performance liquid chromatography (HPLC) techniques (Sandstrom and others, 1992; Zaugg and others, 1995; Lindley and others, 1996; and Werner and others, 1996). Sixty volatile organic compounds (VOCs) also were analyzed for, but only in ground-water samples. These compounds (table 4), primarily industrial solvents and chemicals, but also some agricultural fumigants and fungicides, were analyzed by purge-and-trap GC/MS. A computer library search also was used to compare mass spectra of non-target compounds with known standards as described by Rose and Schroeder (1995). Samples were collected, field-extracted or preserved, and submitted to the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) in Arvada, Colo., for further analysis.

Field Procedures

Water samples for pesticides were collected and filtered through a 0.7-micrometer glass-fiber filter, and pesticides were field-extracted from the filtrate by sequentially pumping through solid-phase extraction (SPE) cartridges. Two cartridges (one for GC/MS and one for HPLC) were processed, each cartridge containing an extraction matrix suitable for the pesticides listed in table 3. The SPE cartridges were stored in pesticide-free vials at less than 4°C for shipment to the NWQL. Detailed

Table 3.--*Pesticide target analytes, method detection limits, drinking water standards or guidelines, aquatic-life criteria, and health advisories*

[µg/L, micrograms per liter; H, herbicide; I, insecticide; M, metabolite; F, fungicide; --, no criteria established; drinking water standards are U.S. Environmental Protection Agency (USEPA) maximum contaminant levels for drinking water from USEPA (1996), unless otherwise footnoted; health advisories are the USEPA risk-specific dose health advisories for drinking water associated with a 10^{-6} (1 in a million) cancer risk from USEPA (1996); freshwater-chronic criteria for protection of aquatic life are USEPA guidelines from Nowell and Resek (1994) unless otherwise footnoted]

Pesticide target analyte	Trade or common name(s)	Type of pesticide	Chemical Abstracts Service registry number	Method detection limit (µg/L)	Drinking water standard or guideline (µg/L)	Freshwater-chronic criteria for protection of aquatic life (µg/L)	Health advisory for cancer risk (µg/L)
Gas Chromatography/Mass Spectrometry analytical method							
Acetochlor	Acenit, Sacenid	H	34256-82-1	0.002	--	--	--
Alachlor	Lasso	H	15972-60-8	0.002	2	--	0.44
Atrazine[1]	AAtrex	H	1912-24-9	[1]0.008	3	[2]2	--
Azinphos-methyl[3]	Guthion	I	86-50-0	0.001	--	0.01	--
Benfluralin	Balan, Benefin	H	1861-40-1	0.002	--	--	--
Butylate	Sutan +, Genate Plus	H	2008-41-5	0.002	[4]350	--	--
Carbaryl[3,5]	Sevin, Savit	I	63-25-2	0.003	[4]700	[6]0.02	--
Carbofuran[3,5]	Furadan	I	1563-66-2	0.003	40	[2]1.75	--
Chlorpyrifos	Lorsban	I	2921-88-2	0.004	[4]20	0.041	--
Cyanazine	Bladex	H	21725-46-2	0.004	[4]1	[7]2	--
DCPA	Dacthal	H	1861-32-1	0.002	[4]4,000	--	--
p,p'-DDE	none	M	72-55-9	0.006	[8]0.1	--	0.1
Desethylatrazine[3]	none	M	6190-65-4	0.002	--	--	--
Diazinon	several	I	333-41-5	0.002	[4]0.6	[6]0.009	--
Dieldrin	Panoram D-31	I	60-57-1	0.001	[8]0.002	0.0625	0.00219
2,6-Diethylanaline	none	M	579-66-8	0.003	--	--	--
Dimethoate[9]	Cygon	I	60-51-5	0.004	--	--	--
Disulfoton	Di-Syston	I	298-04-4	0.017	[4]0.3	[6]0.05	--
EPTC	Eptam, Eradicane	H	759-94-4	0.002	--	--	--
Ethalfluralin	Sonalan, Curbit EC	H	55283-68-6	0.004	--	--	--
Ethoprop	Mocap	I	13194-48-4	0.003	--	--	--
Fonofos	Dyfonate	I	944-22-9	0.003	[4]10	--	--
alpha-HCH	none	M	319-84-6	0.002	[8]0.006	--	0.006
gamma-HCH	Lindane	I	58-89-9	0.004	0.2	0.08	0.0265
Linuron[5]	Lorox, Linex	H	330-55-2	0.002	--	[7]7	--
Malathion	several	I	121-75-5	0.005	[4]200	0.1	--
Methyl parathion	Penncap-M	I	298-00-0	0.006	[4]2	--	--
Metolachlor	Dual, Pennant	H	51218-45-2	0.002	[4]100	[7]8	--
Metribuzin	Lexone, Sencor	H	21087-64-9	0.004	[4]100	[7]1	--
Molinate	Ordram	H	2212-67-1	0.004	--	--	--
Napropamide	Devrinol	H	15299-99-7	0.003	--	--	--
Parathion	several	I	56-38-2	0.004	--	0.013	--
Pebulate	Tillam	H	1114-71-2	0.004	--	--	--
Pendimethalin	Prowl, Stomp	H	40487-42-1	0.004	--	--	--

Table 3.--*Pesticide target analytes, method detection limits, drinking water standards or guidelines, aquatic-life criteria, and health advisories--Continued*

Pesticide target analyte	Trade or common name(s)	Type of pesticide	Chemical Abstracts Service registry number	Method detection limit (µg/L)	Drinking water standard or guideline (µg/L)	Freshwater-chronic criteria for protection of aquatic life (µg/L)	Health advisory for cancer risk (µg/L)
Gas Chromatography/Mass Spectrometry analytical method--Continued							
cis-Permethrin	Ambush, Pounce	I	57608-04-5	0.005	--	--	--
Phorate	Thimet, Rampart	I	298-02-2	0.002	--	--	--
Prometon	Pramitol	H	1610-18-0	0.018	[4]100	--	--
Pronamide	Kerb	H	23950-58-5	0.003	[4]50	--	--
Propachlor	Ramrod	H	1918-16-7	0.007	[4]90	--	--
Propanil	Stampede	H	709-98-8	0.004	--	--	--
Propargite	Comite, Omite	I	2312-35-8	0.013	--	--	--
Simazine[1]	Aquazine, Princep	H	122-34-9	[1]0.01	4	[6]10	--
Tebuthiuron	Spike	H	34014-18-1	0.01	[4]500	--	--
Terbacil[3]	Sinbar	H	5902-51-2	0.007	[4]90	--	--
Terbufos	Counter	I	13071-79-9	0.013	[4]0.9	--	--
Thiobencarb	Bolero	H	28249-77-6	0.002	--	--	--
Triallate	Far-Go	H	2303-17-5	0.001	--	[7]0.24	--
Trifluralin	Treflan, Trilin	H	1582-09-8	0.002	[4]5	[2]0.1	5
High-Performance Liquid Chromatography analytical method							
2,4-D	several	H	94-75-7	0.15	70	[6]3	--
2,4-DB	none	I	94-82-6	0.24	--	--	--
2,4,5-T	several	H	93-76-5	0.035	[4]70	--	--
2,4-5-TP[10]	Silvex	H	93-72-1	0.021	50	[6]1.4	--
3-Hydroxy-carbofuran[10]	none	M	1563-38-8	0.014	--	--	--
Acifluorfen	Blazer	H	50594-66-6	0.035	[8]1	--	1
Aldicarb[10,11]	Temik	I	116-06-3	0.55	7	--	--
Aldicarb sulfone[10,11]	Standak	M	1646-88-4	0.1	7	--	--
Aldicarb sulfoxide[11]	none	M	1646-87-3	0.021	7	--	--
Bentazon	Basagran	H	25057-89-0	0.014	[4]20	--	--
Bromacil	Hyvar, Urox B	H	314-40-9	0.035	[4]90	--	--
Bromoxynil	Buctril, Brominal	H	1689-84-5	0.035	--	[2]5	--
Carbaryl[5,10]	Sevin, Savit	I	63-25-2	0.008	[4]700	[6]0.02	--
Carbofuran[5,10]	Furadan	I	1563-66-2	0.12	40	[2]1.75	--
Chloramben	Amiben, Vegiben	H	133-90-4	0.42	[4]100	--	--
Chlorothalonil[11]	Bravo	F	1897-45-6	0.48	[8]1.5	--	1.5
Clopyralid	Stinger, Lontrel	H	1702-17-6	0.23	--	--	--
Dacthal, (mono-acid)	none	M	887-54-7	0.017	--	--	--
Dicamba	Banvel	H	1918-00-9	0.035	[4]200	[7]10	--
Dichlobenil[11]	Barrier, Casoron	H	1194-65-6	1.2	--	[6]37	--
Dichlorprop	2,4-DP, Seritox 50	H	120-36-5	0.032	--	--	--

Table 3.--*Pesticide target analytes, method detection limits, drinking water standards or guidelines, aquatic-life criteria, and health advisories--Continued*

Pesticide target analyte	Trade or common name(s)	Type of pesticide	Chemical Abstracts Service registry number	Method detection limit (µg/L)	Drinking water standard or guideline (µg/L)	Freshwater-chronic criteria for protection of aquatic life (µg/L)	Health advisory for cancer risk (µg/L)
High-Performance Liquid Chromatography analytical method--Continued							
Dinoseb	DNBP, Dinitro	H	88-85-7	0.035	7	[2]0.05	--
Diuron	Karmex, Direx	H	330-54-1	0.02	[4]10	[6]1.6	--
DNOC[11]	Trifocide, Elgetol 30	I, F, H	534-52-1	0.42	--	--	--
Fenuron	Beet-Kleen	H	101-42-8	0.013	--	--	--
Fluometuron	Flo-Met, Cotoran	H	2164-17-2	0.035	[4]90	--	--
Linuron[5]	Lorox, Linex	H	330-55-2	0.018	--	--	--
MCPA	Metaxon, Kilsem	H	94-74-6	0.17	[4]10	--	--
MCPB	Can-Trol, Thistrol	H	94-81-5	0.14	--	--	--
Methiocarb[10]	Grandslam, Mesurol	I	2032-65-7	0.026	--	--	--
Methomyl	Lannate, Nudrin	I	16752-77-5	0.017	[4]200	--	--
Neburon	Neburex, Noruben	H	555-37-3	0.015	--	--	--
Norflurazon	Evital, Solicam	H	27314-13-2	0.024	--	--	--
Oryzalin	Surflan	H	19044-88-3	0.31	--	--	--
Oxamyl[10]	Vydate	I	23135-22-0	0.018	200	--	--
Picloram[10]	Tordon	H	1918-02-1	0.05	500	--	--
Propham	Chem-Hoe, IPC	H	122-42-9	0.035	[4]100	--	--
Propoxur	Baygon	I	114-26-1	0.035	--	--	--
Triclopyr[10]	Garlon, Grazon	H	55335-06-3	0.25	--	-	--

[1] Estimated reporting limit due to contamination of atrazine and simazine in field and equipment blanks (see Results of Quality-Control Samples section).

[2] Guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Canadian Council of Ministers of the Environment (1993).

[3] Concentrations for these pesticides are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction (Zaugg and others, 1995).

[4] U.S. Environmental Protection Agency lifetime-health advisory for a 70-kilogram adult, from Nowell and Resek (1994).

[5] Analyzed by both gas chromatography/mass spectrometry and high-performance liquid chromatography methods.

[6] Criteria for the protection of freshwater aquatic life are recommended maximum concentrations in water by National Academy of Sciences and National Academy of Engineers from Nowell and Resek (1994).

[7] Interim guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Canadian Council of Ministers of the Environment (1993).

[8] U.S. Environmental Protection Agency risk-specific dose health advisory associated with a cancer risk of 10^{-6} (1 in a million), from Nowell and Resek (1994).

[9] Pesticide demonstrated small and variable recovery and was removed from the method schedule in November 1994. All data for dimethoate were removed from the data base in July 1996.

[10] Pesticide target analyte is heat and light sensitive and therefore susceptible to degradation. This may result in poor overall recovery and precision (NAWQA/NWQL Quality Assurance Committee for the Schedule 2050/2051 Pesticide Analysis Method, written commun., 1995).

[11] The concentration values for these analytes are qualitatively identified and reported with an E code because of poor overall recovery and precision (NAWQA/NWQL Quality Assurance Committee for the Schedule 2050/2051 Pesticide Analysis Method, written commun., 1995).

Table 4.--*Volatile organic compounds, minimum reporting levels, drinking water standards or guidelines, and risk-specific dose health advisories*

[µg/L, micrograms per liter; --, not available or no data; drinking water standards are U.S. Environmental Protection Agency (USEPA) maximum contaminant levels for drinking water from USEPA (1996), unless otherwise footnoted; health advisory for cancer risk, USEPA risk-specific dose health advisory for drinking water associated with a 10^{-6} (1 in a million) cancer risk from USEPA (1996)]

Volatile organic compounds	Common or alternate name(s)	Chemical Abstracts Service registry number	Minimum reporting level (µg/L)	Drinking water standard or guideline (µg/L)	Health advisory for cancer risk (µg/L)
1,1-Dichloroethane	Ethylidene chloride	75-34-3	0.2	--	--
1,1-Dichloroethene	Vinylidine chloride	75-35-4	0.2	7	--
1,1-Dichloropropene	--	563-58-6	0.2	--	--
1,2-Dibromo-3-chloropropane	DBCP	96-12-8	1.0	0.2	0.03
1,2-Dibromoethane	Ethylene dibromide, EDB	106-93-4	0.2	0.05	0.0004
1,2-Dichlorobenzene	*o*-Dichlorobenzene	95-50-1	0.2	600	--
1,2-Dichloroethane	Ethylene dichloride	107-06-2	0.2	5	0.4
cis-1,2-Dichloroethene	*cis*-Acetylene dichloride	156-59-4	0.2	70	--
trans-1,2-Dichloroethene	*trans*-Acetylene dichloride	156-60-5	0.2	100	--
1,2-Dichloropropane	Propylene dichloride	78-87-5	0.2	5	0.6
1,3-Dichlorobenzene	*m*-Dichlorobenzene	541-73-1	0.2	[1]600	--
1,3-Dichloropropane	--	142-28-9	0.2	--	--
cis-1,3-Dichloropropene	*cis*-1,3-Dichloropropylene	100-61-015	0.2	--	0.2
trans-1,3-Dichloropropene	*trans*-1,3-Dichloropropylene	100-61-026	0.2	--	0.2
1,4-Dichlorobenzene	*p*-Dichlorobenzene	106-46-7	0.2	75	--
2,2-Dichloropropane	--	594-20-7	0.2	--	--
2-Chloro-1-methylbenzene	*o*-Chlorotoluene	95-49-8	0.2	[1]100	--
4-Chloro-1-methylbenzene	*p*-Chlorotoluene	106-43-4	0.2	[1]100	--
1,1,1-Trichloroethane	Methyl chloroform	71-55-6	0.2	200	--
1,1,2-Trichloroethane	Vinyl trichloride	79-00-5	0.2	5	--
1,2,3-Trichlorobenzene	--	87-61-6	0.2	--	--
1,2,3-Trichloropropane	--	96-18-4	0.2	[1]40	5
1,2,4-Trichlorobenzene	--	120-82-1	0.2	70	--
1,2,4-Trimethylbenzene	Pseudocumene	95-63-6	0.2	--	--
1,3,5-Trimethylbenzene	Mesitylene	108-67-8	0.2	--	--
1,1,1,2-Tetrachloroethane	--	630-20-6	0.2	[1]70	1
1,1,2,2-Tetrachloroethane	Acetylene tetrachloride	79-34-5	0.2	--	--
1,1,2-Trichloro-1,2,2-trifluoroethane	Fluorocarbon-113	76-13-1	0.2	--	--
Benzene	--	71-43-2	0.2	5	--
Bromobenzene	Phenyl bromide	108-86-1	0.2	--	--
Bromochloromethane	Methylene chlorobromide	74-97-5	0.2	[1]10	--

Table 4.--*Volatile organic compounds, minimum reporting levels, drinking water standards or guidelines, and risk-specific dose health advisories--Continued*

Volatile organic compounds	Common or alternate name(s)	Chemical Abstracts Service registry number	Minimum reporting level (µg/L)	Drinking water standard or guideline (µg/L)	Health advisory for cancer risk (µg/L)
Bromodichloromethane	Dichlorobromomethane	75-27-4	0.2	100	0.6
Bromomethane	Methyl bromide	74-83-9	0.2	[1]10	--
n-Butylbenzene	1-Phenylbutane	104-51-8	0.2	--	--
sec-Butylbenzene	2-Phenylbutane	135-98-8	0.2	--	--
tert-Butylbenzene	2-Methyl-2-phenylpropane	98-06-6	0.2	--	--
Chlorobenzene	Monochlorobenzene	108-90-7	0.2	100	--
Chloroethane	Ethyl chloride	75-00-3	0.2	--	--
Chlorodifluoromethane[3]	Fluorocarbon-22	75-45-6	0.2	--	--
Chloroethene	Vinyl chloride	75-01-4	0.2	2	0.015
Chloromethane	Methyl chloride	74-87-3	0.2	--	--
Dibromochloromethane	Chlorodibromomethane	124-48-1	0.2	100	--
Dibromomethane	Methylene bromide	74-95-3	0.2	--	--
Dichlorodifluoromethane	Fluorocarbon-12	75-71-8	0.2	[1]1,000	--
Dichloromethane	Methylene chloride	75-09-2	0.2	5	5
Ethylbenzene	--	100-41-4	0.2	700	--
Hexachlorobutadiene	HCBD	87-68-3	0.2	[1]1	--
Isopropyl benzene	Cumene	98-82-8	0.2	--	--
p-Isopropyltoluene	*p*-Cymene	99-87-6	0.2	--	--
Methyl *tert*-butyl ether	MTBE	163-40-44	0.2	[1,2]20-200	--
Napthalene	--	91-20-3	0.2	[1]20	--
n-Propylbenzene	1-Phenylpropane	105-65-1	0.2	--	--
Styrene	Vinyl benzene	100-42-5	0.2	100	--
Tetrachloroethene	Perchloroethylene	127-18-4	0.2	5	0.7
Tetrachloromethane	Carbon tetrachloride	56-23-5	0.2	5	0.3
Toluene	Methylbenzene	108-88-3	0.2	1,000	--
Tribromomethane	Bromoform	75-25-2	0.2	100	4
Trichloroethene	Trichloroethylene	79-01-6	0.2	5	3
Trichlorofluoromethane	Fluorocarbon-11	75-69-4	0.2	--	--
Trichloromethane	Chloroform	67-66-3	0.2	100	6
Xylenes (total)	Dimethlybenzene	133-02-07	0.2	10,000	--

[1] U.S. Environmental Protection Agency (USEPA) lifetime-health advisory for a 70-kilogram adult, from USEPA (1996).

[2] If the proposed cancer classification C is accepted for MTBE, the lifetime-health advisory is 20 µg/L; otherwise it is 200 µg/L (U.S. Environmental Protection Agency, 1996).

[3] Non-target compound detected and identified by a computer library search.

descriptions of equipment required and the procedures used to collect, process, and extract the sample using the SPE method are given in Shelton (1994) and Koterba and others (1995). The SPE processing and extraction procedure is also discussed in Sandstrom and others (1992). All ground-water wells sampled with a portable pump or with a pump that could provide a non-aerated sample were sampled for VOCs. Samples were collected in amber vials, preserved with hydrochloric acid, and stored at less than 4°C for shipment to the NWQL. Detailed descriptions of equipment required and the procedures used to collect and preserve samples for VOCs are given in Koterba and others (1995). All equipment used to collect and process samples was cleaned with a 0.2-percent non-phosphate detergent, rinsed with deionized water, rinsed with pesticide-grade methanol, wrapped in aluminum foil, and stored in a dust-free environment prior to sample collection (Shelton, 1994).

Surface Water

Samples representative of the flow in the stream cross section were obtained by collecting depth-integrated subsamples at equally-spaced verticals across the stream using either the US DH-81 or US D-77 sampler as described by Edwards and Glysson (1988) and Shelton (1994). Both samplers hold a 3-liter Teflon sample bottle, and all parts of the sampler coming into contact with sample water are constructed of Teflon. Samples for pesticides were composited in a glass carboy in order to integrate the stream cross section at sites where more than one 3-liter bottle was needed to sample all verticals. Beginning in June 1994, all samples were composited and split using a Teflon cone splitter, as described by Shelton (1994). Samples for pesticides were collected, field-extracted, and submitted to the NWQL for further analysis of a broad spectrum of 83 pesticides and metabolites (degradation products), and analyzed using gas chromatography/mass spectrometry (GC/MS) or high-performance liquid chromatography (HPLC) techniques as described by Zaugg and others (1995), Lindley and others (1996), or Werner and others (1996).

Ground Water

All ground-water samples were collected following NAWQA protocols as described by Koterba and others (1995) in order to assure representative samples of ground water. Wells were purged to remove at least three casing volumes of water and were sampled when values of monitored field parameters (pH, specific conductance, temperature, dissolved oxygen, and turbidity) were within the allowable differences, as specified by Koterba and others (1995). In cases where domestic or public-supply wells were sampled and a volume of water equivalent to the purge volume had already been pumped during the previous 24 hours, the sampling equipment was flushed with ground water and samples were collected after assuring the stability of field parameters. All pump lines and processing equipment that came in contact with the sample water after the collection point were composed of Teflon and stainless steel. The submersible pump used to sample monitoring wells also was constructed of Teflon and stainless steel. Domestic or public-supply wells selected for sampling had pumps suitable for producing samples of acceptable quality, as described by Koterba and others (1995). Samples for pesticides were collected, field- extracted, and submitted to the NWQL. Samples also were collected, preserved, and submitted to the NWQL for the analysis of 60 VOCs using GC/MS techniques as described by Rose and Schroeder (1995). Techniques for the collection and preservation of VOC samples are described by Koterba and others (1995).

Laboratory Methods

The SPE cartridges were eluted at the NWQL and the samples were analyzed using either GC/MS or HPLC techniques (table 3), depending on the physical characteristics of the target analytes. Those compounds that were sufficiently volatile and thermally stable for gas chromatography were analyzed with the GC/MS method; the others were analyzed using the HPLC method. These techniques are described in detail by Zaugg and others (1995), Lindley and others (1996), and by Werner and others (1996). Details for purge-and-trap capillary GC/MS analysis of VOCs are described by Rose and Schroeder (1995).

Quality Assurance

About 15 percent of all samples submitted to the laboratory were quality-control samples, which included field blanks, equipment blanks, and trip blanks to measure possible contamination and bias; replicate samples to measure variability; and field-matrix spike samples to measure recovery of analytes. All samples were spiked with surrogate analytes prior to extraction to monitor the accuracy and precision of the analytical procedures. For definitions of these quality-control samples, see Shelton (1994). Additionally, quality-control samples were routinely analyzed as part of the laboratory quality-assurance plan described by Pritt and Raese (1995).

Results of Quality-Control Samples

Field- and equipment-blank samples for surface water were free of the compounds of interest, except for atrazine, which was detected at concentrations ranging from 0.003 to 0.007 micrograms per liter (µg/L) in 3 of 6 blanks, and simazine, which also was detected in 3 of 6 blanks at concentrations ranging from 0.004 to 0.009 µg/L (see Appendix A1). Field-processing blanks, composed of pesticide-free water passed through the filtration, field-extraction, and laboratory equipment, but not through the sampling equipment, also contained similarly low concentrations of atrazine and simazine, indicating that the atrazine and simazine detections in blanks were probably caused by residual contamination in the field-processing equipment. Atrazine and simazine were detected only in field and equipment blanks for surface-water samples; because different sets of equipment were used for the collection and processing of ground-water samples, the contamination had no impact on the interpretation of ground-water samples. All surface-water environmental samples of atrazine and simazine are affected by this contamination: all detections of atrazine could have a positive bias of 0 to 0.007 µg/L and for simazine of 0 to 0.009 µg/L. Therefore, all atrazine values in surface water are reported at no lower than 0.008 µg/L and all simazine values are reported no lower than 0.01 µg/L, with one significant figure. These values are footnoted to indicate this bias. From a total of 72 surface-water samples, 8 detections of atrazine and 18 detections of simazine were censored.

Field- and equipment-blank samples for ground water were free of compounds of interest except for one detection each of chloroform, toluene, and methylene chloride. The chloroform and methylene chloride detections are most likely the result of the acid preservation process (Paul Squillace, U.S. Geological Survey, written commun., 1997). No alteration of the data set was made based on these results. Additional information about the results of quality-control samples is described by Wagner and others (1996) or is available in files of the USGS in the Washington District office in Tacoma, Washington. All samples were spiked with surrogate analytes to monitor the accuracy and precision of the analytical procedure. Analytical recoveries of surrogate compounds were good for GC/MS and VOC analytical data and marginal for HPLC analytical data (see fig. A1).

Precision data were obtained for three sets of replicate samples (see Appendix A2). Concentration differences ranged from 0.0 to 40.0 percent as measured by relative percent difference. No modifications were made to the data set based on these results. Precision and percent recoveries of HPLC target analytes were generally lower than the precision and recoveries of GC/MS target analytes, and the analyte recoveries and precision of field-matrix spike samples were generally lower than laboratory-reagent spike samples (see Appendix A3). VOC field-matrix spikes exhibited lower precision and higher percent recoveries than laboratory-reagent spikes, but results were usually within the range of 80 to 160 percent, which is generally acceptable for data interpretation. Precision and recoveries for most of the 39 HPLC analytes generally are high enough and consistent enough that the data are acceptable for publication and are useful for data analysis (NAWQA/NWQL Quality Assurance Committee for the Schedule 2051/2051 Pesticide Analysis Method, written commun., 1995). However, because of the lower recoveries, the probability of false negatives is greater for the HPLC target analytes, and the effective detection level is proportionally larger. Precision and recoveries for these analytes need to be considered when interpreting the data.

SITE LOCATIONS

Selection of Surface-Water Sites for Sampling

Eleven surface-water sites in the Palouse subunit were sampled for pesticides at least once from March 1993 through November 1995 (fig. 5 and table 5). The Palouse River at Hooper site (PAL018) was chosen to include most of the drainage basin and to integrate agricultural, urban, and forested land uses. This site was sampled one to three times a month from March 1993 to May 1994 and up to six times a month during storms or periods of low flow between November 1994 and November 1995. Samples were collected and analyzed for filtered pesticides to determine seasonal and short-term temporal variability of pesticides and their transport; samples were also analyzed for major ions, nutrients, and suspended sediment.

Ten additional sites (also referred to as "synoptic sites") were chosen to represent relatively homogeneous land use within their drainage basins. Samples from these sites were collected in April and May 1994 during storms, periods of low flow, and periods of pesticide applications to assess the spatial distribution and possible sources of pesticides (fig. 5, table 5).

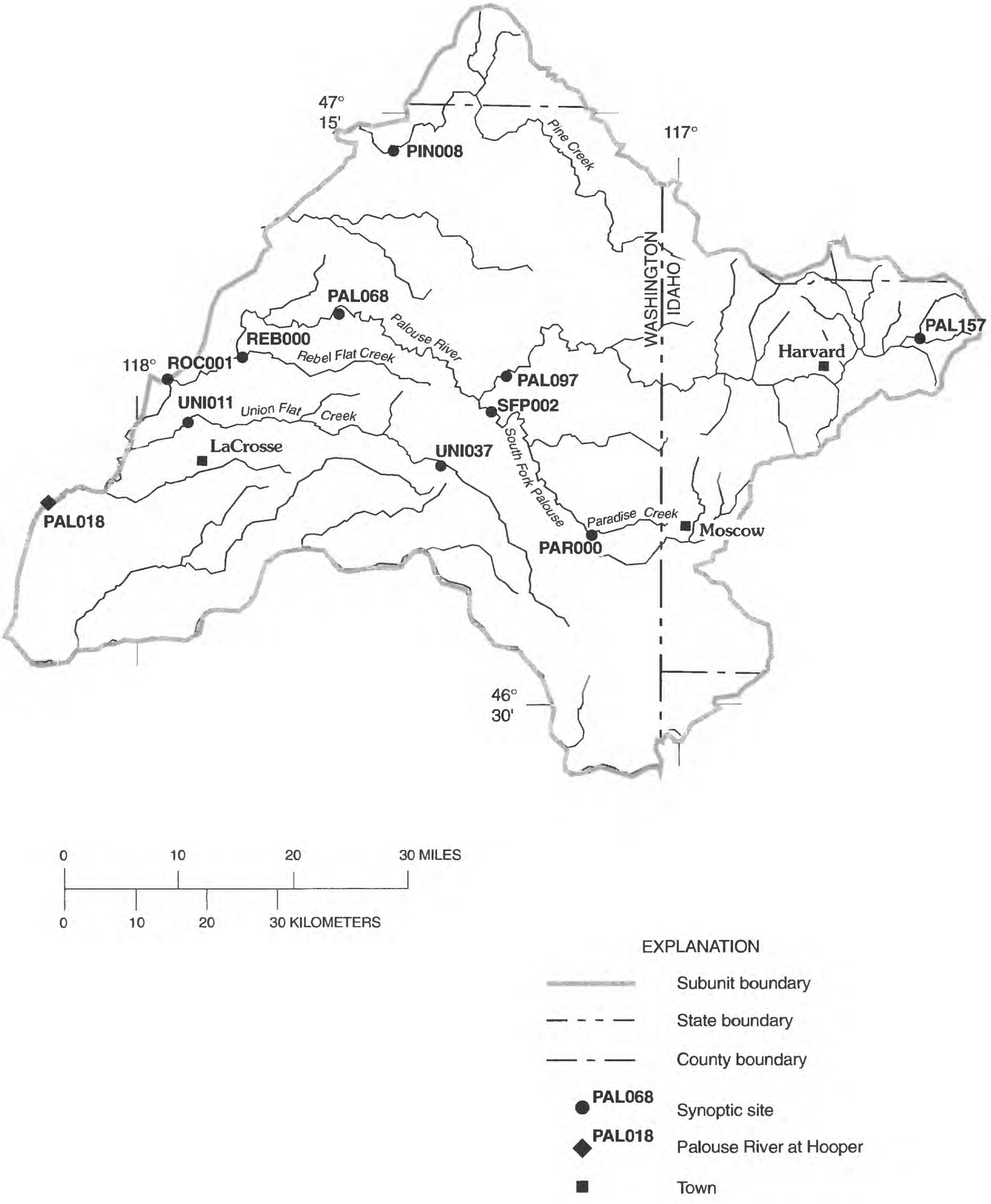

Figure 5. Location of surface-water sites sampled for pesticides in the Palouse subunit, Washington and Idaho, 1993-1995. See table 5 for site names.

Table 5.--*Surface-water sites sampled for pesticides in the Palouse subunit, Washington and Idaho, 1993-95*

[Site code, identifier used for surface-water sites (see figure 5); site name and station number are those that are assigned for the U.S. Geological Survey National Water Information System]

Site code	Site name	Station number	Drainage area, in square miles	Number of samples	Sampling period of pesticide samples
PAL097	Palouse River near Colfax, Washington	13346000	487	5	April and May 1994 July 1995
PAR000	Paradise Creek at Pullman, Washington	13346990	34	1	April 1994
SFP002	South Fork Palouse River at Colfax, Washington	13349200	274	5	April and May 1994 July 1995
REB000	Rebel Flat Creek at Winona, Washington	13349320	78.8	6	April, May, and November 1994 July 1995
PIN008	Pine Creek at Pine City, Washington	13349410	306	5	April-June 1994
ROC001	Rock Creek near Winona, Washington	13349900	954	1	April 1994
UNI037	Union Flat Creek near Colfax, Washington	13350500	189	1	April 1994
UNI011	Union Flat Creek near La Crosse, Washington	13350700	291	1	April 1994
PAL018	Palouse River at Hooper, Washington	13351000	2,500	44	March 1993-November 1995
PAL068	Palouse River at Endicott-St. John Road near Colfax, Washington	465950117371000	896	1	April 1994
PAL157	Palouse River at Laird Park near Harvard, Idaho	465637116381400	47.1	2	April and May 1994

To help assess the potential movement of pesticides from ground water to surface water, samples also were collected at base-flow conditions from three of the synoptic sites (PAL097, SFP002, REB000) in July 1995 and from PAL018 in November 1995.

Selection of Wells for Sampling

Most of the well sites used for three types of ground-water studies were selected at random (Scott, 1990). A one- or two-letter prefix and sequential number were assigned to each well, depending upon the study (table 6). The primary objective of the first study was to determine the extent to which shallow ground-water quality is influenced by the hydrogeology of the Palouse subunit and by the predominant land use--dryland farming of wheat and small grains. Two types of wells were used in this land-use study: newly drilled, shallow monitoring wells (LN wells) and shallow domestic wells (LE wells). For the second study, public-supply wells (SU wells) were sampled to determine the occurrence and broad-scale distribution of pesticides in aquifers of the Palouse subunit. The third study included monitoring wells (U, M, L, and P wells) along a flow path which were sampled to study the small-scale effects of land use.

All of the monitoring wells were installed in the shallow loess aquifer, whereas most of the domestic wells draw water from the upper levels of the basalt formations. The deeper basalt formation is the primary aquifer unit for public-supply wells in the Palouse subunit.

Seven shallow monitoring wells (LN wells) were installed near the water table and sampled for pesticides and VOCs to look for early indications of potential water-quality problems; eight additional monitoring wells were installed along a transect as part of the flow-path study (fig. 6 and table 6). Samples also were collected from 19 shallow domestic wells (LE wells, fig. 6 and table 6). Locations of monitoring and domestic wells were selected randomly (except for wells for the flow-path study), and alternate locations were included in the selection process. Final locations for monitoring wells were determined in the field by searching near the desired sampling location for sites that could be drilled; shallow domestic wells were chosen from the USGS National Water Information System (NWIS) data base and further investigated in the field. Additional criteria for the selection of domestic wells were depth below land surface less than 100 feet, no PVC pipe glue used in the plumbing, and a sampling port located prior to any treatment or holding tanks. Monitoring wells were drilled within 50 feet of the targeted land use, constructed of flush-threaded, 2-inch-diameter, Schedule 40 PVC casing, and sealed with bentonite annular seals and cement surface seals.

In 1994, the USGS cooperated with the Washington Department of Health in a statewide sampling program to assess the vulnerability of Washington public water systems to pesticides (Ryker and Williamson, 1996). Class A public-supply wells (having more than 15 hook-ups) from across the state were selected randomly so that results would be representative of the regional ground-water quality (Ryker and Williamson, 1996a). Most samples from these wells were collected and analyzed by contract laboratories; the USGS analyzed replicate samples only. Nineteen wells (SU wells, table 6 and fig. 6) were sampled in the Palouse subunit as part of this study: samples from 10 wells were collected and analyzed for pesticides and VOCs by the USGS, and samples from 9 wells were collected by private contractors and submitted to the USGS NWQL for analysis of pesticides only.

RESULTS

Thirty different pesticides or pesticide metabolites were detected in surface water at sites in the Palouse subunit, primarily during storm runoff; and 14 different organic compounds (pesticides, pesticide metabolites, or VOCs) were found in 15 of the 53 wells sampled. Pesticides were detected in 97 percent of surface-water samples, and pesticides or VOCs were detected in 28 percent of samples from ground water. Pesticides were detected in samples from all surface-water sites except for Palouse River at Laird Park (PAL157), which is located in the headwaters of the Palouse River upstream of any agricultural or urban land use sources of pesticides. Most pesticides were found at very low concentrations. Although many of the detected pesticides are applied for agricultural purposes, other significant uses are roadside applications, residential use, and applications to fallow land. Ten of the most commonly applied agricultural pesticides were detected in surface-water samples, but none of the most commonly applied pesticides were detected in samples of ground water.

Pesticides Detected in Surface Water

Most of the 30 pesticides detected in surface-water samples are herbicides; only 7 insecticides and 2 insecticide metabolites were detected. Of the 20 most commonly used pesticides in the Palouse subunit, 10 were detected in surface-water samples, 9 were not analyzed for, and only 1

Table 6.--*Location and well-construction data for wells sampled for pesticides and volatile organic compounds in the Palouse subunit, Washington and Idaho, 1994-95*

[Depth, in feet below land surface; S, screen; X, open hole; P, perforated or slotted; --, no data]

Well identifier					Range of open interval			
This report	Local well name	Latitude	Longitude	Depth of well (feet)	Top of first interval (feet)	Bottom of last interval (feet)	Type of opening	Primary aquifer unit
				Monitoring Wells				
LN01	17N/40E-34J01	465522	1174457	30	25	30	S	Palouse Loess
LN02	14N/43E-01K01	464337	1172016	31.5	21.5	31.5	S	Palouse Loess
LN03	16N/43E-21Q01	465131	1172404	17.5	7.5	17.5	S	Palouse Loess
LN04	20N/44E-28P01	471153	1171604	63	53	63	S	Palouse Loess
LN05	20N/42E-32P01	471054	1173249	29	17	27	S	Palouse Loess
LN07	17N/43E-18R01	465756	1172543	79.5	56.5	71.5	S	Palouse Loess
LN10	16N/41E-33Q01	464935	1173938	62.5	52.5	62.5	S	Palouse Loess
				Flow-Path Wells				
US	15N/45E-30E02	464529	1171157	52	47	52	S	Palouse Loess
UI	15N/45E-30E01	464529	1171157	72	67	73	S	Palouse Loess
UD	15N/45E-30E03	464529	1171157	88.5	83	88	S	Palouse Loess
MS	15N/45E-30E08	464527	1171157	41.8	36.6	41.5	S	Palouse Loess
MI	15N/45E-30E05	464527	1171157	49	41.6	46.6	S	Palouse Loess
MD	15N/45E-30E04	464527	1171157	54.8	49.5	54.5	S	Palouse Loess
LD	15N/45E-30E06	464527	1171157	9.65	4.35	9.35	S	Palouse Loess
P7A	15N/46E-07P03P1	464736	1170401	7.55	4.27	7.55	S	Palouse Loess
				Shallow Domestic Wells				
LE03	16N/41E-16K01	465227	1173925	90	18	90	X	Wanapum Basalt
LE04	17N/40E-16R01	465737	1174611	110	30	110	P	Grand Ronde Basalt
LE05	17N/41E-09E01	465908	1173918	95	49	95	X	Grand Ronde Basalt
LE06	18N/41E-04E01	470504	1173935	119	80	119	X	Wanapum Basalt
LE08	18N/42E-03G01	470511	1172957	100	41	100	X	Wanapum Basalt
LE09	18N/43E-32B01	470103	1172447	85	25	85	P	Wanapum Basalt
LE10	17N/42E-14C01	465823	1172859	135	21	135	X	Wanapum Basalt
LE12	14N/44E-16P01	464134	1171656	60	26	60	X	Saddle Mountain Basalt
LE13	16N/44E-24D01	465121	1171302	103	38	103	X	Wanapum Basalt
LE14	17N/43E-24P01	465651	1172000	65	20	60	P	Wanapum Basalt
LE15	18N/44E-02F01	470512	1171342	120	75	120	X	Wanapum Basalt
LE16	20N/44E-12M01	471442	1171248	145	45	145	X	Wanapum Basalt
LE17	19N/45E-16C01	470905	1170821	105	30	105	X	Wanapum Basalt
LE18	19N/46E-31J01	470602	1170242	183	120	183	X	Wanapum Basalt

Table 6.--Location and well-construction data for wells sampled for pesticides and volatile organic compounds in the Palouse subunit, Washington and Idaho, 1994-95--Continued

Well identifier					Range of open interval			
This report	Local well name	Latitude	Longitude	Depth of well (feet)	Top of first interval (feet)	Bottom of last interval (feet)	Type of opening	Primary aquifer unit
Shallow Domestic Wells--Continued								
LE19	17N/45E-06E01	470003	1171121	57	44	57	X	Wanapum Basalt
LE21	14N/45E-23R02	464038	1170608	159	29	159	X	Wanapum Basalt
LE22	12N/46E-07B02	463233	1170517	80	70	80	S	Saddle Mountain Basalt
LE25	40N/06W-24L01	464732	1170206	60	--	--	--	--
LE27	41N/05W-03DBC1	465515	1165650	41	34	41	X	Wanapum Basalt
Public-Supply Wells								
SU01	20N/43E-10R01	471431	1172208	308	170	308	X	Grand Ronde Basalt
SU02	20N/42E-13M02	471316	1172813	269	60	269	X	--
SU03	20N/43E-34R01	471101	1172202	--	--	--	--	--
SU04	18N/46E-06B01D1	470536	1170252	907	684	907	X	Grand Ronde Basalt
SU05	18N/41E-01J01	470458	1173444	278	--	--	X	--
SU06	18N/43E-35N02	470029	1172132	510	--	--	--	--
SU07	17N/43E-24C02	465730	1171952	100	59	100	X	Wanapum Basalt
SU08	17N/44E-32A02	465547	1171644	105	80	105	X	Grand Ronde Basalt
SU09	17N/41E-30R01	465559	1174105	175	55	175	X	Wanapum Basalt
SU10	16N/45E-16F01	465235	1170854	170	140	170	X	Wanapum Basalt
SU11	16N/43E-20E02	465153	1172607	100	55	100	X	--
SU12	16N/43E-20E01	465153	1172604	89.8	54	89.8	X	Wanapum Basalt
SU13	15N/39E-02Q01	464847	1175233	273	--	--	--	--
SU14	15N/43E-23K01	464611	1172120	150	130	150	P	--
SU15	15N/42E-25H01	464537	1172740	150	--	--	--	--
SU16	13N/45E-34A03	463418	1170737	80	--	--	--	--
SU17	12N/46E-07B01	463233	1170438	130	--	--	--	--
SU18	11N/46E-19D01	462525	1170554	530	415	530	X	--
SU19	18N/46E-06G01	470518	1170256	225	--	--	X	--

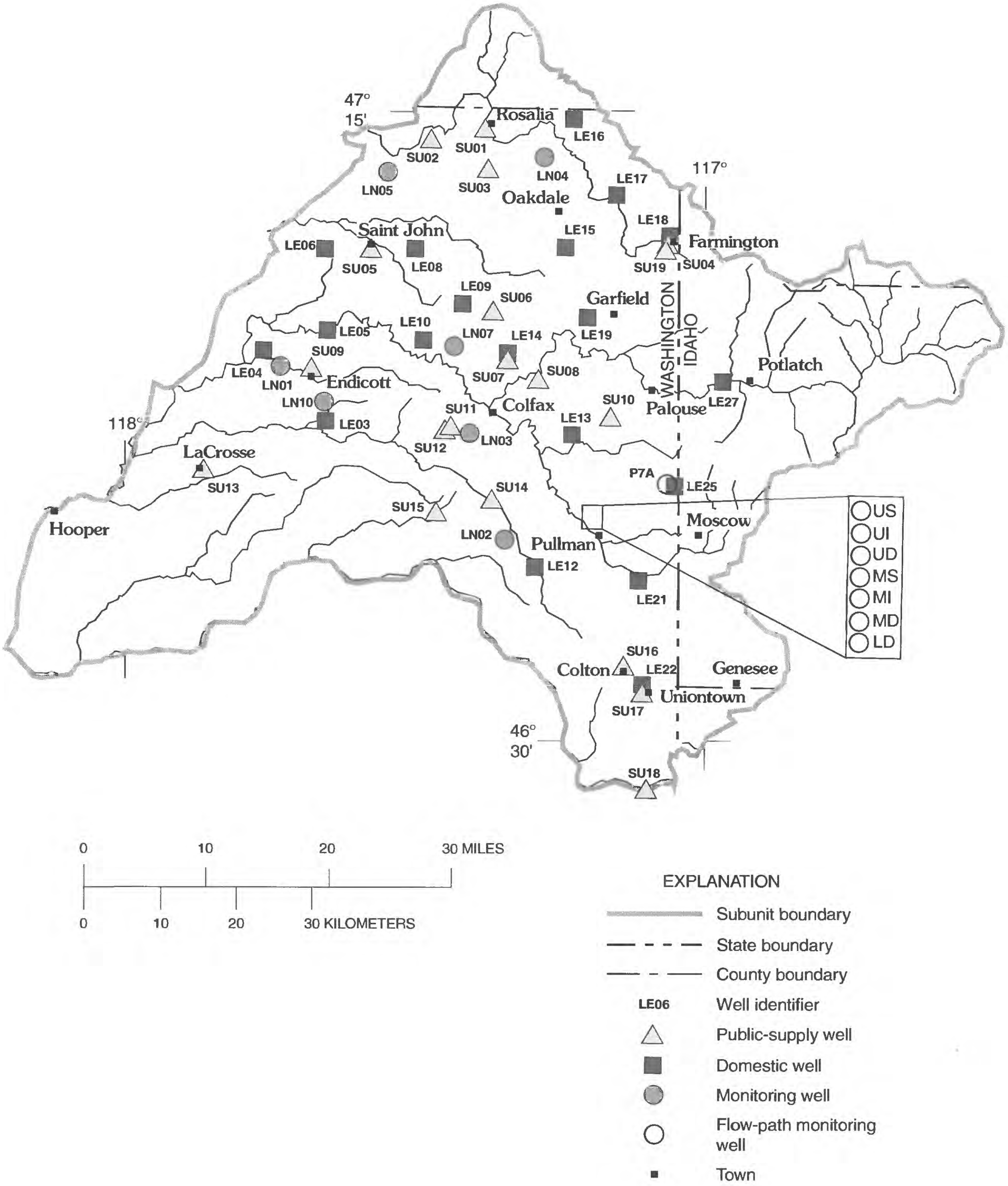

Figure 6. Location of wells sampled for pesticides and volatile organic compounds in the Palouse subunit, Washington and Idaho, 1994-1995. See table 6 for well names and characteristics.

(disulfoton) was not detected. Twenty-nine pesticides or pesticide metabolites were detected in samples collected from the Palouse River at Hooper (PAL018) from March 1993 through November 1995 (table 7). Seventeen pesticides or metabolites were detected in samples from the 10 surface-water synoptic sites (table 8), and samples from all sites except Palouse River at Laird Park had detections of at least 1 pesticide. The herbicides atrazine, triallate, and prometon were the most frequently detected pesticides in surface water of the Palouse subunit, ranging in concentration from the method detection limit (for example, 0.001 µg/L for triallate) to a maximum of 0.49 µg/L for triallate.

Spatial Distribution of Pesticides Detected in Surface Water

Triallate, DCPA, and atrazine were the most frequently detected pesticides at the synoptic surface-water sites (table 8). Concentrations of pesticides from samples at these sites ranged from at or near their method detection limits to a maximum of 1.8 µg/L for 2,4-D at South Fork Palouse River at Colfax (SFP002). Of the 10 synoptic sites, SFP002 had the highest number of detections and elevated concentrations of pesticides, probably because of the additional influence of urban land use in and around the town of Colfax. The predominant land use for all surface-water sites is agriculture, except for Palouse River at Laird Park, which is a forested land use. Three pesticides associated with urban land use, the herbicides prometon and tebuthiuron and the insecticide diazinon, were detected at SFP002 and PIN008, REB000, and PAL018. The detections of pesticides associated with urban land use at PAL018 are due to both the large number of samples and the integration of many small sources from a large drainage basin. Detections of these urban pesticides at PIN008 and REB000 are probably due to the close proximity of the small agricultural communities of Pine City and Winona.

Temporal Variations of Pesticide Concentrations at Palouse River at Hooper

Factors that have been found to affect the observed distribution of pesticide concentrations include the intensity of pesticide use, pesticide persistence and mobility, irrigation or precipitation, and soil characteristics (Barbash and Resek, 1996; Flury, 1996). The major factors that influenced temporal variations in pesticide concentrations in surface water of the Palouse subunit were antecedent weather conditions, pesticide properties, and the occurrence of rainfall soon after application. Rainfall occurring soon after the period of pesticide application increases the likelihood that certain pesticides will dissolve in water or sorb to soil particles and be transported off fields during storm runoff (fig. 7). Pesticide transport in rainfall-related surface-water runoff is dependent upon the physical properties of the pesticide (its solubility and ability to bind to organic matter on soil particles), as well as soil properties (percent organic matter), soil conditions (whether the ground was frozen or saturated), and the available rainfall or snowmelt for storm runoff. The relation of concentrations of pesticides, corresponding streamflows, and reported periods of application (if available) is shown graphically for triallate, atrazine, and *gamma*-HCH at Palouse River at Hooper (fig. 7).

Data collected at the Palouse River at Hooper site (PAL018), as well as additional data described in Wagner and others (1996), showed that the most frequent detections and the largest concentrations of some pesticides, such as triallate, occur during or shortly after pesticide application or periods of surface runoff. Based on these observations, sampling of surface-water synoptic sites was scheduled during the periods of pesticide application in April and May. The detections of some pesticides at PAL018 during periods of base-flow conditions, such as atrazine, led to additional sampling of pesticides at selected synoptic sites during July 1995.

Relation to Drinking Water Standards or Guidelines and Water-Quality Criteria

No surface water in the Palouse subunit is used for public drinking supplies. However, comparing observed concentrations of pesticides to drinking water standards is a useful measure of surface-water quality. No pesticides were detected in samples from surface water at concentrations that exceed the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for drinking water. Concentrations of at least one of three pesticides (dieldrin, *gamma*-HCH, and *alpha*-HCH) exceed the USEPA risk-specific dose (RSD) health advisory for drinking water in nine samples from Palouse River at Hooper, and concentrations of *gamma*-HCH exceed the RSD health advisory in two samples from SFP002 and in one sample from PAR000 (see Appendix A4). RSD health advisories are non-regulatory limits of concentration for contaminants in drinking water that may be used for guidance in the absence of regulatory limits; RSD health advisory values must be associated with a

Table 7.--*Summary of pesticide detections and concentrations at Palouse River at Hooper, Washington, March 1993 through November 1995*

[μg/L, micrograms per liter; aquatic-life criteria are U.S. Environmental Protection Agency (USEPA) freshwater-chronic criteria for the protection of aquatic life, unless otherwise footnoted (see table 3); health advisories, USEPA risk-specific health advisory for drinking water associated with a 10^{-6} (1 in a million) cancer risk; H, herbicide; I, insecticide; M, metabolite; <, less than. Aquatic-life criteria and health advisory cancer risks are from Nowell and Resek (1994) and USEPA (1996). **Pesticides in bold exceed the freshwater-chronic criteria for protection of aquatic life** (see table 3)]

Compound name	Type of pesticide	Method detection limit (μg/L)	Concentrations Median (μg/L)	Concentrations Maximum (μg/L)	Number of detections	Number of detections that exceed aquatic-life criteria	Number of detections that exceed health advisory for cancer risk
Triallate	H	0.001	0.028	**0.49**	44	**[1]4**	--
Atrazine[2]	H	[2]0.008	[E]0.02	[E]0.2	36	--	--
Simazine[2]	H	[2]0.01	[E]0.01	[E]0.07	31	--	--
Prometon	H	0.018	[E]0.011	0.058	30	--	--
Desethylatrazine[3]	H	0.002	[E]0.0025	[E]0.009	24	--	--
Metribuzin	H	0.004	0.007	0.052	23	--	--
***gamma*-HCH**	I	0.004	0.005	**0.081**	22	**1**	8
Tebuthiuron	H	0.01	<0.01	0.012	13	--	--
DCPA	H	0.002	<0.002	0.006	13	--	--
Diuron	H	0.02	<0.02	0.470	11	--	--
EPTC	H	0.002	<0.002	0.012	7	--	--
MCPA	H	0.17	<0.17	0.24	6	--	--
2,4-D	H	0.15	<0.15	0.15	6	--	--
Dicamba	H	0.035	<0.035	0.03	3	--	--
Bentazon	H	0.014	<0.014	0.09	3	--	--
Metolachlor	H	0.002	<0.002	0.004	3	--	--
Dieldrin	I	0.001	<0.001	0.01	3	--	3
p,p'-DDE	M	0.006	<0.006	0.003	3	--	--
Alachlor	H	0.002	<0.002	0.012	3	--	--
Bromoxynil	H	0.035	<0.035	0.6	2	--	--
Ethoprop	I	0.003	<0.003	0.005	2	--	--
Triclopyr	H	0.25	<0.25	[E]0.12	1	--	--
Propoxur	I	0.035	<0.035	0.02	1	--	--
Dinoseb	H	0.035	<0.035	0.02	1	--	--
Trifluralin	H	0.002	<0.002	0.007	1	--	--
alpha-HCH	M	0.002	<0.002	0.007	1	--	1
Ethalfluralin	H	0.004	<0.004	0.013	1	--	--
Diazinon	I	0.002	<0.002	**0.012**	1	**[1]1**	--
Carbaryl[3]	I	0.003	<0.003	[E]0.007	1	--	--

[1] Interim guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Canadian Council of Ministers of the Environment (1993).

[2] Estimated reporting level due to contamination of atrazine and simazine in field and equipment blanks for surface-water samples (see Results of Quality-Control Samples section).

[3] Concentrations for these pesticides are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction (Zaugg and others, 1995).

[E] Concentration reported is an estimated value because of problems with gas chromatography or extraction (Zaugg and others, 1995) or because value is less than the method detection limit or because of possible bias in concentrations of atrazine and simazine.

Table 8.--*Summary of pesticide detections and concentrations at surface-water synoptic sites in the Palouse subunit, Washington and Idaho, 1993-95*

[µg/L, micrograms per liter; aquatic-life criteria are U.S. Environmental Protection Agency (USEPA) freshwater-chronic criteria for the protection of aquatic life, unless otherwise footnoted (see table 3); health advisories, USEPA risk-specific health advisory for drinking water associated with a 10^{-6} (1 in a million) cancer risk; H, herbicide; I, insecticide; <, less than. Aquatic-life criteria and health advisories are from Nowell and Resek (1994) and USEPA (1996). **Pesticides in bold exceed the freshwater-chronic criteria for protection of aquatic life** (see table 3)]

Compound name	Type of pesticide	Method detection limit (µg/L)	Concentrations		Number of detections	Number of detections that exceed aquatic-life criteria	Number of detections that exceed health-advisory
			Median (µg/L)	Maximum (µg/L)			
Triallate	H	0.001	0.014	0.095	26	--	--
Atrazine[1]	H	[1]0.008	[E]0.01	[E]0.08	15	--	--
DCPA	H	0.002	0.002	0.007	15	--	--
Prometon	H	0.018	<0.018	0.2	12	--	--
Desethylatrazine[2]	H	0.002	<0.002	[E]0.01	12	--	--
Simazine[1]	H	[1]0.01	<0.01	[E]0.08	10	--	--
gamma-HCH	I	0.004	<0.004	0.047	10	--	4
Metribuzin	H	0.004	<0.004	0.23	8	--	--
EPTC	H	0.002	<0.002	0.006	8	--	--
Tebuthiuron	H	0.01	<0.01	0.042	7	--	--
Diuron	H	0.02	<0.02	0.95	6	--	--
2,4-D	H	0.15	<0.15	1.8	6	--	--
Diazinon	I	0.002	<0.002	**0.27**	5	[3]**4**	--
MCPA	H	0.17	<0.17	0.18	2	--	--
Bentazon	H	0.014	<0.014	0.04	1	--	--
Malathion	I	0.005	<0.005	0.004	1	--	--
Carbaryl[2]	I	0.003	<0.003	0.02	1	--	--

[1] Estimated reporting level is used due to contamination of atrazine and simazine in field and equipment blanks for surface-water samples (see Results of Quality-Control Samples section).

[2] Concentrations for these compounds are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction (Zaugg and others, 1995).

[3] Interim guidelines for the protection of freshwater aquatic life are Canadian Water Quality Guidelines from Canadian Council of Ministers of the Environment (1993).

[E] Concentration reported is an estimated value because of problems with gas chromatography or extraction (Zaugg and others, 1995) or because value is less than the method detection limit or because of possible bias in concentrations of atrazine and simazine.

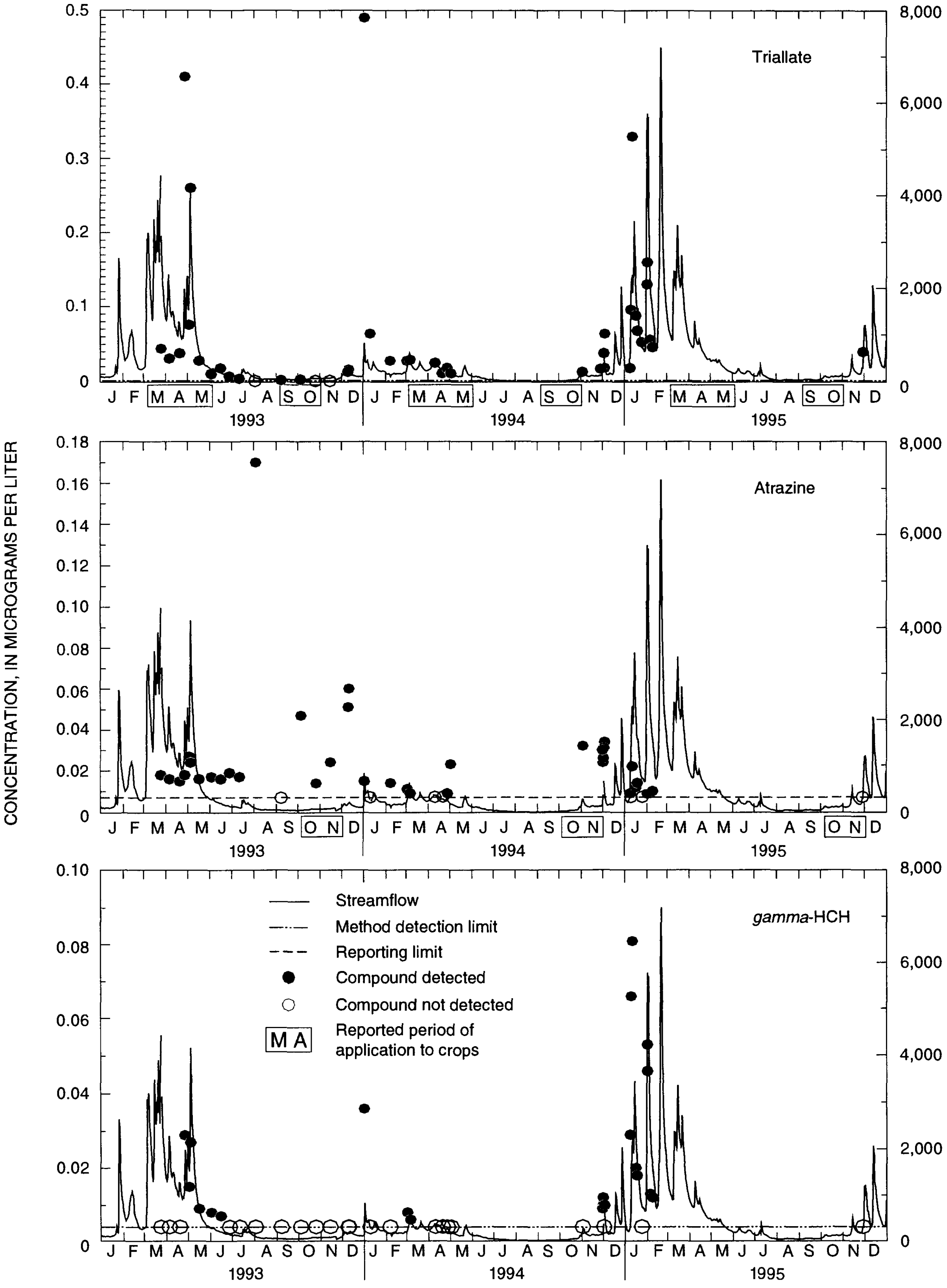

Figure 7. Concentrations of triallate, atrazine, and *gamma*-HCH, and corresponding streamflows at Palouse River at Hooper, Washington.

specific cancer risk level, usually between 10^{-4} and 10^{-7}, and in this report, a 10^{-6} (1 in a million) cancer risk level is used (Nowell and Resek, 1994).

Concentrations of at least one of three pesticides (*gamma*-HCH, triallate, and diazinon) exceed the USEPA freshwater-chronic criteria for the protection of aquatic life in nine samples from four surface-water sites: PAL018, PAL097, PAR000, SFP002 (see Appendix A5). Concentrations of diazinon exceed its criterion in five samples at four sites; concentrations of triallate exceed its criterion only in four samples from only one site, PAL018; and concentrations of *gamma*-HCH exceed its criterion only once at PAL018.

Pesticides and Volatile Organic Compounds Detected in Ground Water

Samples from 15 of 53 wells (28 percent) had detections of pesticides or VOCs, and 6 wells had detections of more than 1 pesticide or VOC. Six pesticides, one pesticide metabolite, and seven VOCs were detected in samples from ground water (table 9). Atrazine was the most commonly detected pesticide with seven detections; desethylatrazine, an atrazine metabolite, was the second most commonly detected compound with three detections; simazine was detected in samples from two wells; and the other four pesticides (tebuthiuron, carbaryl, prometon, and bromacil) were detected once each in samples from four

Table 9.--*Summary of pesticide and volatile organic compound detections in ground water of the Palouse subunit, Washington and Idaho, 1994-95*

[µg/L, micrograms per liter; H, herbicide; M, metabolite; I, insecticide; V, volatile organic compound; --, not enough detections]

				Concentrations			
Compound	Common or trade name(s)	Type of compound	Method detection limit[1] (µg/L)	Median (µg/L)	Maximum (µg/L)	Number of detections	Well identifier at site of detection
Atrazine	Aatrex	H	0.001	0.006	0.027	7	LN02, LE27 SU13, SU16 SU17, SU18 MI
Desethylatrazine[2]	none	M	0.002	^{E}0.007	^{E}0.01	3	SU16, SU17, SU18
Simazine	Aquazine, Princep	H	0.005	0.005	0.009	2	LE13, SU17
Bromacil	Hyvar, Urox B	H	0.035	--	0.51	1	LE17
Carbaryl[2]	Sevin	I	0.003	--	^{E}0.009	1	MI
Tebuthiuron	Spike	H	0.01	--	0.059	1	SU17
Prometon	Pramitol	H	0.018	--	^{E}0.005	1	SU16
Chlorodifluoromethane[3]	Fluorocarbon-22	V	0.2	--	[3]0.3	1	SU13
Chloroethane	Ethyl chloride	V	0.2	--	0.3	1	LE14
Tetrachloroethene	Perchloroethylene	V	0.2	--	1.8	1	LE16
Tetrachloromethane	Carbon tetrachloride	V	0.2	--	1.1	1	LE22
Tribromomethane	Bromoform	V	0.2	--	^{E}0.16	1	SU08
Trichloromethane	Chloroform	V	0.2	--	0.5	1	LE22
1,1,2-Trichloro-1,2,2-trifluoroethane	Fluorocarbon-113	V	0.2	0.2	0.2	2	MD, UD

---

[1] Method reporting limit is listed for volatile organic compounds.

[2] Concentrations for these pesticides are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction (Zaugg and others, 1995).

[3] Non-target compound detected and identified by a computer library search.

[E] Concentration reported is an estimated value because of problems with gas chromatography or extractions (Zaugg and others, 1995) or because value is less than the method detection limit.

wells. Herbicides were the most common type of pesticide detected in samples from ground water; only one insecticide, carbaryl, was detected. Six of the seven VOCs detected (bromoform, chloroethane, chloroform, tetrachloroethane, carbon tetrachloride, and chlorodifluoromethane) were detected once each in samples from five wells, and 1,1,2-trichloro-1,2,2-trifluoroethane was detected in samples from two wells located at the flow-path transect.

Spatial Distribution of Pesticides and VOCs Detected in Ground Water

Samples were collected from randomly selected monitoring, domestic, or public-supply wells that were evenly distributed throughout the subunit (figs. 6 and 8). Pesticides or VOCs were detected in most parts of the subunit and in all types of ground-water systems sampled (monitoring wells installed at the water table, shallow domestic wells, and deeper public-supply wells), but most detections were from wells which were screened or had open casings in fractured basalts. Detections of pesticides or VOCs also occurred in both the loess aquifer and the basalt aquifer; samples from 10 of the 34 shallow domestic or monitoring wells (29 percent) contained pesticides or VOCs, and samples from 5 of the 19 deeper public supply wells (26 percent) contained pesticides or VOCs.

Most of the pesticides detected in ground water are used in agriculture, but tebuthiuron and prometon are commonly used on non-agricultural areas such as industrial sites or right-of-ways; both of these pesticides were detected only in samples from public-supply wells. Detections of VOCs in ground water are not clearly related to land use. The detection of tetrachloromethane, however, is probably related to its historical use as a fumigant in grain silos. Tetrachloroethene is a commonly used cleaning solvent.

Relation to Drinking Water Standards or Guidelines

No pesticides or VOCs were detected in samples from ground water at concentrations that exceed USEPA MCLs for drinking water, but concentrations of the VOCs tetrachloroethene and tetrachloromethane in samples from two wells (LE16 and LE22) exceed the USEPA RSD health advisory for drinking water associated with a 10^{-6} (1 in a million) cancer risk. Not all of the compounds detected in ground water have drinking water standards or guidelines, nor are there any standards for combinations of pesticides in drinking water.

DISCUSSION

Some of the factors that affect the detection of pesticides in surface and ground water and the transport of pesticides to surface and ground water are pesticide use, environmental conditions, and the physical and chemical properties of pesticides. Many pathways exist for pesticides to enter surface and ground water, such as runoff from storms or snowmelt to surface water and preferential flow paths to ground water. A simple model of surface-water mass transport of pesticides is described below.

Relation of Pesticide Detections to Pesticide Use, Environmental Factors and Pesticide Properties

Pesticide application rates, climate, weather, soil type, and physical properties of a pesticide can influence the fate and transport of pesticides in both surface and ground water (Barbash and Resek, 1996). After application, a complex series of events can lead to the transport of pesticides from their sites of application. Soon after application, pesticides are subject to plant uptake, volatilization, photolysis, and microbial or chemical degradation; and under certain environmental conditions, they may be transported by wind, surface runoff, or ground-water leachate (Flury, 1996; Smith and others, 1987).

Pesticide Use

All of the herbicides most commonly applied to cropland in the Palouse subunit were detected in samples from surface water, whereas diazinon was the only insecticide reportedly applied and detected. However, none of the commonly used agricultural pesticides were detected in samples from ground water (tables 1 and 9). The concentrations and types of pesticides detected in ground water are not dependent on the amounts and types of pesticides applied for agricultural purposes. Four of the pesticides detected in samples from ground water (bromacil, prometon, simazine, and tebuthiuron) are not reported as commonly used in agriculture, but they are used for brush control in non-crop areas, roadside applications, and domestic use. Another compound detected in ground water, desethylatrazine, is a metabolite of atrazine, a herbicide that is also not commonly used for agricultural purposes in the Palouse subunit, but is used as a pre- or post-planting herbicide and on Christmas tree farms in the forested portions of the Palouse (Alex Ogg, U. S. Department of Agriculture, written commun., 1995).

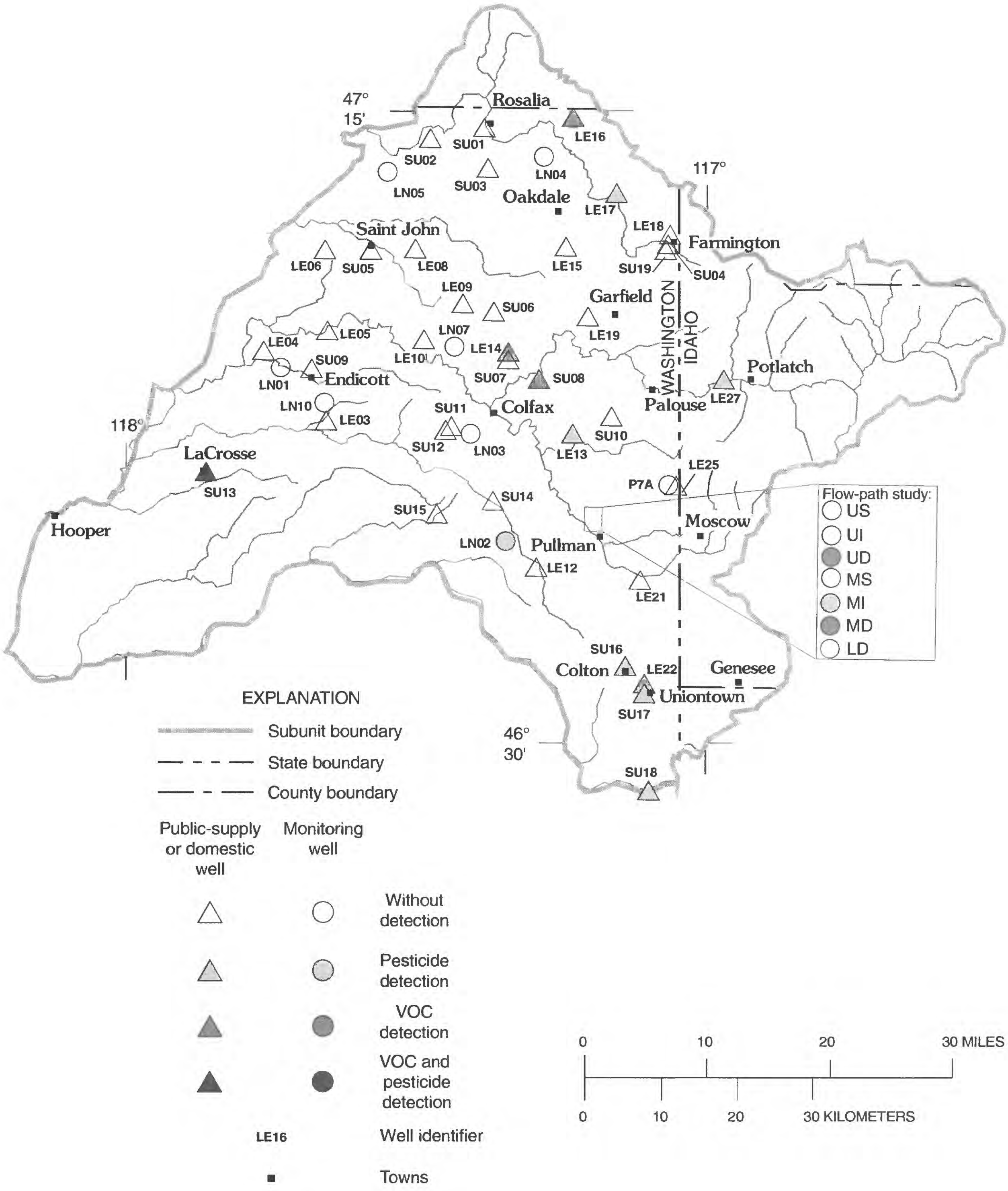

Figure 8. Location of wells and pesticides or volatile organic compounds detected in the Palouse subunit, Washington and Idaho, 1994-1995.

The occurrence of pesticides in surface water is usually related to recent pesticide application, especially when precipitation occurs immediately after application. The detection of pesticides in ground water, however, is not as closely related to recent pesticide applications. Because recharge rates vary from less than 0.1 to about 10 inches per year (Bauer and Vaccaro, 1990), it is possible that ground-water detections of some pesticides reflect applications from several years ago.

Environmental Factors

Immediately after application, pesticides begin to degrade and are subject to transport by surface runoff and by leaching into the ground water. The major environmental factor affecting pesticide detections in surface water in the Palouse subunit is rainfall occurring soon after pesticide application, which increases the likelihood that pesticides can dissolve in water and be transported off fields during surface runoff. Higher concentrations of pesticides were generally detected during times of high streamflow caused by storms or snowmelt (fig. 7). Because of the low permeability of the loess deposits in the Palouse subunit, much of the precipitation runs off, but there is some ground-water recharge during winter if the ground is not frozen (Nassar and Walters, 1975). Although the loess deposits are relatively porous and can contain a large volume of water, movement of water through the loess is generally slow because of the low permeability. Average linear pore-water velocities in the Palouse loess computed from tritium profile data by O'Brien and Keller (1993) range from less than 1 inch to about 6 inches per year. Because of the relatively slow pore-water velocities in the loess, the amount of time it takes for pesticides to leach into the ground water is partially dependent upon the thickness of the loess.

Well depth is commonly a factor in whether a contaminant will be detected in ground water. However, when the three types of wells sampled in this study are grouped by depth (median depths of 49, 100, and 172 feet for monitoring, domestic, and public-supply wells, respectively), there is no consistent relation between well depth and detections of pesticides or VOCs (table 10). Concentrations of chloride or nitrate also are commonly used to compare water from different depths. Nitrate concentration is commonly used as an indicator of ground-water contamination or leaching, and the median concentration of nitrate was lowest in the deeper public-supply wells (0.36 milligrams per liter (mg/L)), compared with domestic wells (3.6 mg/L) and shallow monitoring wells (2.0 mg/L); however, the public-supply wells had a higher percentage of wells with three or more detections of pesticides or VOCs. There is, however, a relation between well depth and the desethylatrazine-to-atrazine ratio (DAR). Because atrazine degrades to the readily detected desethylatrazine over a time scale from weeks to months, this ratio has been used as a surrogate for atrazine residence time in hydrologic systems (Adams and Thurman, 1991). The higher DAR values for the deeper public supply wells indicate that the public-supply water has had

Table 10.--*Type of well, median depth, median concentration of selected constituents, and percent detection of pesticides and volatile organic compounds in the Palouse subunit, Washington and Idaho*

[mg/L, milligrams per liter; NO_2+NO_3, nitrite plus nitrate as N, nitrogen; DAR, desethylatrazine-to-atrazine ratio; --, could not be calculated]

Well type	Number of wells	Median depth (feet below land surface)	Median concentrations		Median DAR	Percent detections of pesticides and volatile organic compounds			
			Chloride (mg/L)	NO_2+NO_3 (mg/L)		No detections	1 detection	2 detections	3 or more detections
Monitoring	15	49	6.2	2.0	[1]--	73.3	20.0	6.7	0.0
Domestic	19	100	4.8	3.6	[1]--	68.4	26.3	5.3	0.0
Public supply	19	172	[2]3.0	[2]0.36	0.75	73.7	5.3	5.3	15.8

[1] DAR is calculated only for samples that have detections of desethylatrazine. All other samples are less than the detection level.

[2] Nitrite plus nitrate and chloride data are available for only 10 public-supply wells.

a longer residence time than the water in the shallower domestic and monitoring wells. Although there is an observed relation between DAR values and possible sources or travel times of pesticides, no definitive relation was observed between environmental factors and pesticide detections in ground water in the Palouse subunit.

Pesticide Properties

Important physical properties that determine the fate and transport of a pesticide in surface and ground water are its solubility in water, ability to sorb to organic matter on soil particles, and soil half-life. Solubility and soil sorption determine whether a pesticide is more likely to partition into water or sorb to organic matter on soil, and the half-life is an indicator of its persistence in the environment (Barbash and Resek, 1996). Atrazine, for example, is relatively water soluble, has a relatively small soil sorption coefficient, and is thus more likely to partition into water rather than sorb to soil (Goss, 1992). Atrazine, therefore, is available for either surface- or ground-water transport. The solubility of atrazine, coupled with its relatively long half-life, accounts for its being one of the most commonly detected pesticides in the Palouse subunit, and its relative persistence possibly explains why the three detections of desethylatrazine were from samples from deeper public-supply wells (table 9).

Transport of Sediment and Pesticides

The movement of pesticides in the environment involves physical, chemical, and biological processes in air, water, and soil, as well as movement between the air, water, and soil phases. Once applied in the environment, pesticides may be degraded by the action of water or other chemicals, or by sunlight or microorganisms. Once dissolved in water or sorbed to soil particles, pesticides can be transported from agricultural fields to surface water if rainfall, application rates, and physical conditions of the fields are appropriate. Similarly, dissolved pesticides can leach into the ground water and be further transported by advection and hydrodynamic dispersion.

Factors Affecting Pesticide Transport

Physical, chemical, and biological processes that affect the concentration of a pesticide in the environment include hydrolysis, photolysis, volatilization, adsorption, bioaccumulation, and biodegradation (Smith and others, 1987). If a pesticide remains on the soil surface long enough for it to degrade or sorb to solids, it is less likely to reach ground or surface water. However, one or more of the pesticide metabolites may be transported, which may be more important with respect to human health or aquatic life criteria. If rainfall or irrigation water contacts the pesticide before it degrades, the pesticide can be transported laterally (to surface water) or vertically (to ground water). Important physical factors that influence pesticide transport include the type and amount of pesticide applied, the type of pesticide application, the type of soil, the type and amount of irrigation, and climatic variables (Flury, 1996).

Some pesticides bind readily to soil particles; this is dependent not only on the physical properties of the pesticide, but also on soil type, soil permeability, and the amount of organic carbon in the soil (Barbash and Resek, 1996). Pesticides that bind tightly to the soil are less likely to be transported to surface and ground water. Some pesticides degrade relatively slowly, allowing more time for them to dissolve and be transported. Use of a pesticide that readily sorbs to soil particles and quickly degrades should limit the transport of the parent compound. According to Flury (1996), the amount of pesticide applied and the timing of application also are important in determining the environmental fate of the compound: if excessive amounts of a pesticide are applied, there is more available for transport; if a pesticide is applied shortly before a storm, it is likely that some of it will be transported to surface water as runoff or will leach into the ground-water system. The method of pesticide application is also a factor in determining environmental fate (Barbash and Resek, 1996). Pesticides which are sprayed, for example, can potentially contaminate surface water by spray drift.

Agricultural practices, as well as the physical and chemical characteristics of pesticides and soils, are major determinants of whether a pesticide will dissolve in water and be transported. Some agricultural practices increase the likelihood of erosion and the possible transport of pesticides that are sorbed to soil particles. In some parts of the subunit, fields have been plowed down to the very edge of roads and through ephemeral streambeds. Runoff from fields can be limited by agricultural practices such as contour plowing, where furrows are aligned perpendicular to the slope of the hill, or strip cropping, where different crops are alternated across a field (U.S. Department of Agriculture, 1978). Strips of unplowed land next to roads and streambeds provide buffer zones that reduce soil erosion. Erosion also can be affected by the crops themselves. If stalks from the previous crop are plowed under and the field lies fallow for some time, moisture can build up in the soil before the next crop is planted. Without the plant roots to help hold the soil in place, the soil is more easily eroded. Other agricultural practices, such as no-till farming, minimal tillage, and stubble-mulch tilling maintain soil moisture and yet prevent wind and water erosion (U.S. Department of Agriculture, 1978).

Irrigation practices play an important role in the movement of pesticides because the irrigation water can dissolve pesticides and either transport the compounds directly into surface water or percolate through the soil, carrying the pesticides into the ground water. Most of the agriculture in the Palouse subunit is dryland farming, so irrigation does not play a major role. However, there is some irrigated farming along the Palouse River and its tributaries, and in those areas, the more water that is applied, the more pesticide transport is possible.

Relation of Erosion to Sediment Transport

The Palouse subunit is one of the largest grain-producing areas in the world, but it is also subject to some of the worst sediment erosion in the country (Kaiser, 1967; Boucher, 1970; U.S. Department of Agriculture, 1978). Studies by Kaiser (1967) show that erosion in the Palouse subunit often removes 50 to 75 tons of soil per acre during a single erosion season (November to April). Boucher (1970) noted that the detrimental effects of erosion in past years have been reduced locally by soil-conservation practices, but erosion is still considered to be a major problem in the Palouse subunit; during the 1975-76 erosion season, from 5 to 50 tons of soil per acre were removed from fall-seeded fields (U.S. Department of Agriculture, 1978), and the average rate of erosion in eastern Washington in 1987 was more than 12 tons per acre (U.S. Department of Agriculture Soil Conservation Service, 1988). Surface-water runoff and soil erosion introduce heavy sediment loads to streams, and pesticides may be transported by runoff sorbed to the sediment.

According to Kaiser (1967) most of the soil removed from agricultural hillsides by water and tillage erosion is deposited on lower slopes in the field from which it originated, but there is a positive correlation ($r = 0.89$, $p < 0.001$) between soil loss from fields in Whitman County, Wash., and sediment transport in the Palouse River at Hooper (fig. 9). Boucher (1970) reports the average annual sediment transport at Palouse River at Hooper during 1961-65 was 1.6 million tons per year; the average annual sediment discharge during 1961-71 was 1.1 million tons per year (James Ebbert, U.S. Geological Survey, written commun., 1996). Sediment discharge records for the Palouse River are not available prior to 1961, but Kaiser indicates that average soil losses from fields in Whitman County were 9.6 million tons per year from 1940-65 and 1.3 million tons per year from 1961-65; the extremely high soil loss in 1962-63 resulted from heavy rainfall on deeply frozen ground. Although no extensive storms or snowmelt occurred in 1994, the average sediment discharge during 1993-95 was 0.4 million tons per year. Annual sediment transport at Palouse River at Hooper varies from year to year but some evidence indicates a declining trend (James Ebbert, U.S. Geological Survey, written commun., 1996).

Pathways of Pesticides to Surface Water

Runoff from storms or snowmelt is the primary pathway of pesticide transport during winter and spring. The amount of pesticides lost from fields and transported to surface water depends on the physical and chemical properties of the pesticide, the weather, the type of soil, topography, and agricultural practices. For example, the extremely low soil loss in 1944-45 in comparison to the high soil loss in 1962-63 was attributed to the fact that there were no extensive storms at the time of frozen ground during 1944-45, whereas in 1962-63 there was heavy rainfall on deeply frozen ground (Kaiser, 1967).

Most sediment discharge is transported during storms. For example, 85 percent of the sediment discharge at Palouse River at Hooper from 1962-65 was transported during three storms, and 75 percent of the sediment discharge from 1993-95 was transported during four storms. Similarly, intensive sampling of pesticides during storms provides the opportunity to estimate daily pesticide loads and to compare times of maximum pesticide transport with sediment transport. Transport of pesticides that are in the dissolved phase is governed essentially by the water flow, and in the associated phases transport is governed by the movement of the particle or colloid (Larson and others, 1997). Thus, most pesticides are also transported during storms.

Annual pesticide loads were estimated using daily mean streamflow data and regression-based estimates of pesticide concentrations. A regression model sensitive to censored data was used to estimate daily pesticide loads (Cohn and others, 1992). Pesticide loads for data with more than 50 percent censored data values were calculated by setting the censored data equal to either one-half or one-tenth the method detection limit, depending on the number of non-censored values and the value of the method detection limit.

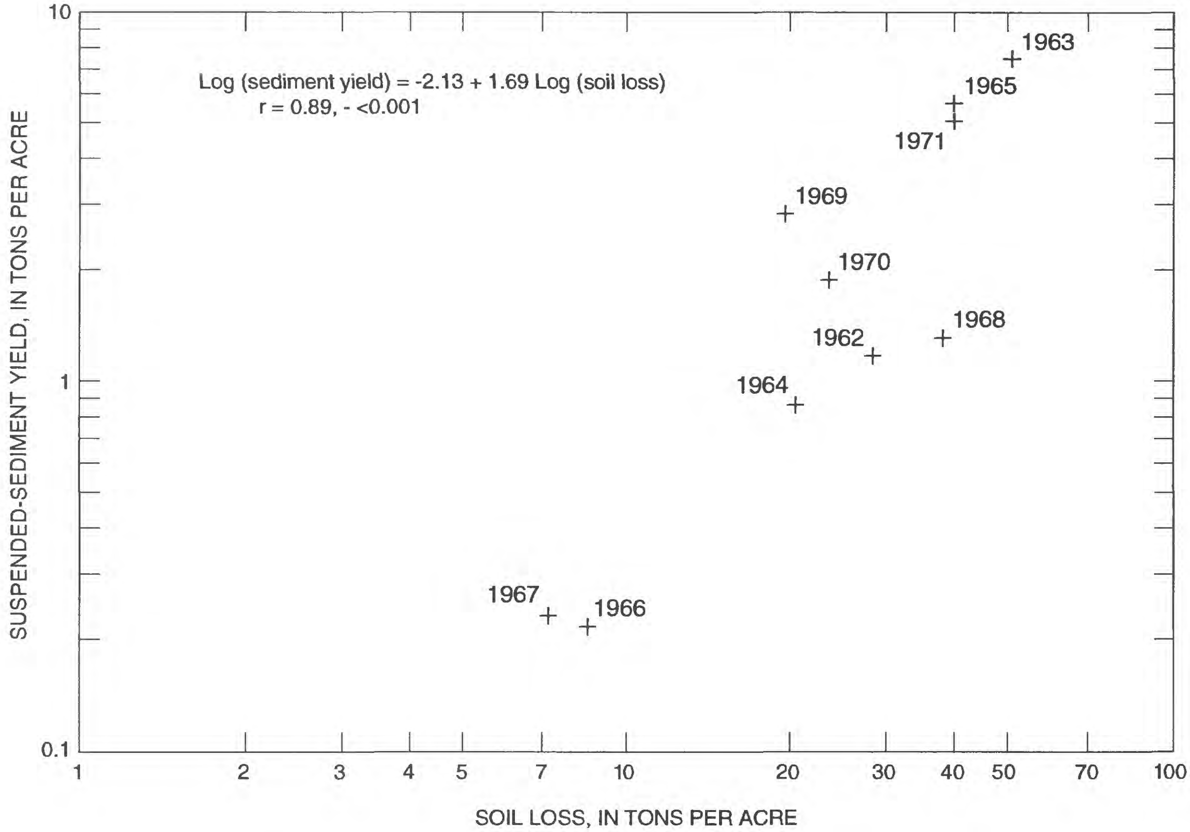

Figure 9. Relation of suspended sediment yield at Palouse River at Hooper, Washington, to soil loss from winter wheat fields in Whitman County, Washington, 1962-1971. Soil loss estimates by Kaiser (1967).

Loads for three pesticides frequently detected at Palouse River at Hooper plotted in relation to streamflow show large pesticide loads during storms in early 1995 while little or no pesticides are being transported during periods of low streamflow (fig. 10). Although samples for pesticides were not obtained as frequently during non-storm intervals, estimates for daily pesticide loads for 1993-95 also can be shown using the regression-based estimates (fig. 11). However, load estimates could be in error by as much as 50 percent, based on 95-percent confidence limits of the predicted load.

The average annual load for 12 of the pesticides detected at Palouse River at Hooper was compared with pesticide-use data for the Palouse subunit and is shown as a percentage of the amount applied (table 11). Loads for pesticides with application data, expressed as a percentage of the total applied pesticides, ranged from 0.03 to 0.16 percent and compared well with similar load calculations made by Larson and others (1995) for rivers in the Mississippi River drainage basin. Although pesticide use in the Mississippi River drainage basin is much greater than in the Palouse subunit, and the pesticide loads in the Mississippi ranged from less than 0.01 to 20 percent, the median values for pesticide loads in the Mississippi River drainage basin and the Palouse subunit are similar at 0.10 percent and 0.075 percent, respectively.

Although most pesticide transport occurs during storms, another pathway of pesticides to surface water is from ground water. During base-flow conditions from June through October, when there is generally little rain and no runoff, concentrations of atrazine, desethylatrazine, simazine, and triallate at Palouse River at Hooper ranged from the method detection limits to 0.17 µg/L, 0.005 µg/L, 0.021 µg/L, and 0.004 µg/L, respectively. Similar concentrations of these pesticides also were detected during base-flow conditions at PAL097, SFP002, and REB000. Streamflow during this period of time is nearly all from ground water, and the presence of these herbicides and metabolites in base flow is an indicator of potential contamination in the regional ground water. This hypothesis

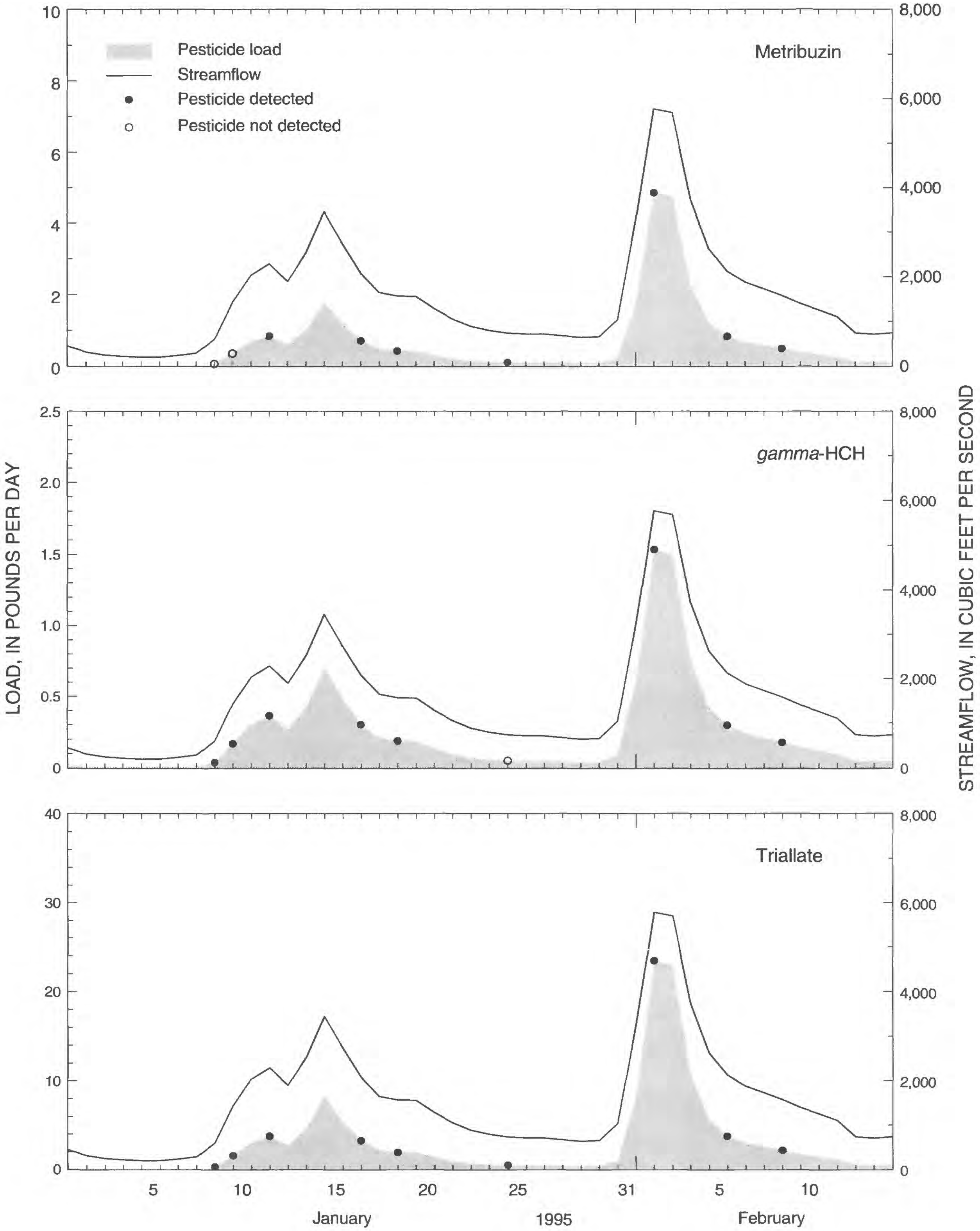

Figure 10. Storm loads for metribuzin, *gamma*-HCH, and triallate and corresponding streamflow at Palouse River at Hooper, Washington, January and February 1995.

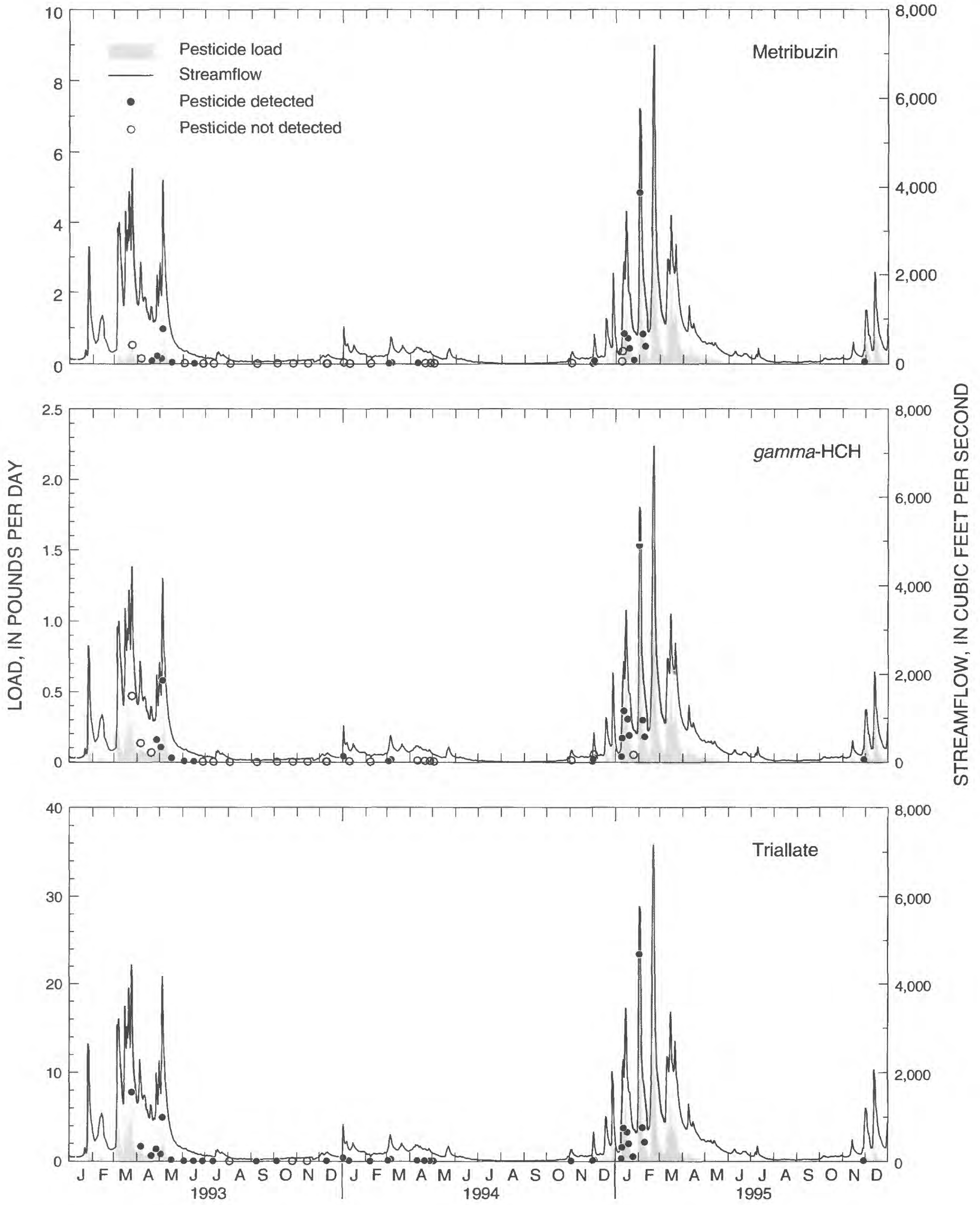

Figure 11. Daily loads for metribuzin, *gamma*-HCH, and triallate and corresponding streamflow at Palouse River at Hooper, Washington, 1993-1995.

Table 11.--*Average annual pesticide load, annual pesticide load as a percentage of use, and pesticide runoff potential at Palouse River at Hooper, Washington, 1993-95*

[Average annual pesticide load is the mean of 1993-95; lbs/year, pounds per year; L, large; M, medium; S, small; --, no data]

Pesticide name	Average annual pesticide load (lbs/year)	Annual pesticide load as percentage of use[1]	Runoff potential[2]		
			Sorbed phase	Solution phase	Overall
Triallate	130	0.05	L	L	L
Diuron	[3]110	0.13	M	L	L
2,4-D	[3]28	0.03	S	M	S
MCPA	[4]28	0.08	M	M	L
Simazine	24	--	M	L	M
Prometon	21	--	M	L	L
Atrazine	18	--	M	L	M
Metribuzin	[3]18	0.16	S	L	M
gamma-HCH	[3]10	--	L	L	L
Tebuthiuron	[4]7	--	M	L	M
Desethylatrazine	4	--	--	--	--
DCPA	[3]2	0.03	L	M	L
EPTC	[3]2	--	S	M	M

[1] Pesticide use data are from Anderson and Gianessi (1995). Note that all values are less than 1 percent.

[2] Runoff potentials (Farm Chemicals Handbook '94, 1994) were developed from the U.S. Department of Agriculture Soil Conservation Service Pesticide Properties Database (Goss, 1992), based on pesticide properties of vapor pressure, half-life in soil, water solubility, and soil organic matter sorption coefficients.

[3] Pesticide load was calculated by setting censored data equal to one-half the method detection limit.

[4] Because of the high number of non-detections and relatively high method detection limit, pesticide load was calculated by setting censored data equal to one-tenth the method detection limit.

is supported by the detections of atrazine, desethylatrazine, and simazine in samples from public-supply wells that tap the regional ground water in the basalt aquifers. However, detection of some of these herbicides during base flow could also be explained by non-agricultural use of compounds and subsequent transport by surface-water runoff of domestic irrigation, summer rainstorms, or short ground-water flow paths.

Pathways of Pesticides to Ground Water

The predominant land use in the Palouse subunit is agriculture, and the use of chemicals to control weeds and pests is high. If pesticides leach into the ground water, they can be transported laterally or vertically. Nassar and Walters (1975) report that large quantities of ground water are available in most parts of the Palouse subunit, and that all sources of public-supply water are from ground water. Several of the larger public-supply water sources (the cities of Pullman, Wash., Moscow, Idaho, and Colfax, Wash., for example) are located in or near the Palouse River or South Fork Palouse River drainage channels, and the large amounts of water pumped have drawn down the hydraulic head, increasing the gradient from the land surface to the wells.

Several mechanisms support possible transport of contaminants into the ground-water system: (1) poor well construction and open-hole basalt well construction; (2) preferential pathways into the surficial loess aquifer and the deeper basalt aquifers; (3) river leakage; and (4) bank storage and reversal of the normal hydraulic gradient toward the river during flood-stage conditions.

Well construction, location of the screened (or open) interval, and the lithology of the finished well are important factors that possibly affect the concentration of pesticides, VOCs, major ions, and nutrients in ground water sampled from the three well types (shallow monitoring, domestic, and deeper public-supply wells). Freezing and thawing cycles, for example, can destroy the integrity of the annular seal of a well, providing a preferential pathway for surface runoff to the ground water. Poor construction of the annular seal also can provide a pathway for pesticides into the ground water. It is a common practice to install casing only in the surficial overburden and to complete wells drilled in basalt as open holes. Domestic wells with known depth and construction details in this study, for example, have a median depth of 100 feet, yet the median cased depth is 36 feet, leaving a median length of 67 feet uncased. Uncased or partially-cased wells in which hydrostatic head decreases with depth can allow water to move from higher aquifers to lower aquifers, and considerable amounts of water may drain from shallow aquifers to deeper aquifers (Nassar and Walters, 1975). Thus, pesticides which have migrated to the surficial ground-water system may be rapidly transported to deeper aquifers by leakage in uncased wells.

A second potential mechanism for transport of pesticides into the ground water is preferential pathways by macropore flow in the surficial loess and by flow through cracks and fissures in the basalt. This can occur in the surficial loess by macropore flow in subsurface soils or lateral transport of water along soil horizons. Macropores in the loess deposits are tubular openings in the subsurface soil matrix with a minimum diameter ranging from 30 to 3,000 micrometers; these openings are formed by root penetration and decay or by organisms that live in the soil. Williams and Allman (1969) have observed 10-fold increases in saturated hydraulic conductivity due to macropores in loess soils. The potential for pesticide transport by macropore flow is offset, however, by higher sorption and mineralization characteristics of macropore surfaces (Mallawatantri and others, 1994). Lum and others (1990) estimated recharge to the ground-water system of the South Fork Palouse River drainage basin of about 3 inches per year, primarily from infiltration of precipitation through the surficial loess. This compares well with the tritium profile data from which O'Brien and Keller (1993) calculated average linear pore-water velocities that range from less than 1 inch to about 6 inches per year. The loess soils are considered relatively impermeable, but Russel (1897) noted the presence of "innumerable minute and almost capillary tubes" transversing the subsoil from top to bottom. Williams and Allman (1969) performed a series of infiltration tests to examine factors affecting water movement through loess soils and observed unusually high infiltration rates of 3 to 4 inches per hour. Several of the infiltration sites were excavated and revealed numerous tubular openings that extended to depths greater than 30 feet. The tests by Williams and Allman were performed under a steady-state condition during which a layer of water 1/2-inch deep was maintained within the infiltrometer during the test. They further observed that where loess is heavily cultivated, the surficial layers establish a limit on infiltration capacity and result in severe erosion; erosion is minimal on areas covered by alfalfa or grasses and infiltration capacity is at a maximum. O'Brien and Keller (1993) also described very fine to coarse macropores throughout soil samples from their investigations at three loess locations; and though their findings show that most ground-water movement occurs in the loess matrix, they suggest that a portion of ground water moves laterally and through vertical macropores. In addition to macropore and lateral flow, repeated freezing and thawing cycles can create structural voids or cracks in the surficial loess that can provide transport pathways for pesticides dissolved in surface-water runoff. Preferential pathways in surficial loess through macropores or ground fractures from repeated freezing and thawing cycles may explain the detections of pesticides in monitoring wells installed in the surficial loess aquifer.

Preferential pathways in the basalt can transport pesticides either laterally, from upper to lower aquifers, or directly from the surface. Three domestic wells that contained trace concentrations of VOCs, for example, are completed in fractured, porous basalt that can provide preferential pathways for pesticide transport. Additionally, these three domestic wells (LE14, LE16, and LE22) have less than 30 feet of loess overburden and also are located in river drainage basins or areas in which the surficial geology consists of basalt or granitic outcrops (figs. 2 and 6). The three domestic wells and four public-supply wells that contained pesticides also are completed in fractured basalt. The surficial loess overburden that covers most of the Palouse subunit is broken by outcrops of basalt along the southern border (fig. 2); in this area, in the Union Flat drainage basin, pesticides were detected in four of the public-supply wells (SU13, SU16, SU17, and SU18). Samples from three of the four public-supply wells with detections of atrazine also contained desethylatrazine whereas samples from the two monitoring wells with detections of atrazine contained no desethylatrazine.

This suggests that water in the deeper public-supply wells has had a longer residence time and that the source of desethylatrazine may be inflow from longer flow paths, which allowed atrazine to degrade.

River leakage is a potential mechanism for transport of pesticides to ground water in some areas and at some times. According to Nelson (1991), nearly all streams in the Palouse subunit tend to gain streamflow; however, the Palouse River between Colfax and Winona is a losing reach. Greene and others (1997) describe a mass balance of chloride and water discharges of the Palouse River and show that ground-water discharge and river leakage are in dynamic flux along reaches of the Palouse River between Colfax and Winona, gaining at times and losing at others. The authors conclude that loss of orthophosphate and dilution of chloride represent the net effects of gains and losses along the reach, with the losses exceeding the gains. The Palouse River drains a large agricultural region of Whitman County, and samples of surface water routinely contain low concentrations of pesticides. For example, 44 samples from March 1993 through November 1995 from Palouse River at Hooper (PAL018) contained a median of 6 pesticide detections per sample, ranging from a low of 1 detection during base-flow conditions to a high of 18 detections during spring when herbicides are commonly applied. River leakage from the Palouse River along this particular reach therefore provides a source of dissolved pesticides for infiltration directly into the deeper basalt aquifers.

Transport of pesticides to ground water during flood-stage conditions allows two mechanisms to operate: (1) pesticides applied to fields, pastures, roadsides, and other streamside areas that normally are dry become available for transport by surface-water runoff; and (2) the increase in river stage can reverse the normal hydraulic gradient and induce streamflow into the adjacent aquifer. The first mechanism may simply transport pesticides downstream, but the second mechanism can result in pesticide infiltration into adjacent aquifers. Receding flood waters may also leave saturated soils or ponded water, which is likely to leach to ground water. As noted by Barbash and Resek (1996), pesticide concentrations generally are greater in surface water than in ground water in regions dominated by agricultural land use; however, during periods of runoff, substantial increases in pesticide concentrations also have been observed in ground water drawn from alluvial aquifers in agricultural areas. Freeze and Cherry (1979) observed that in the upper reaches of a watershed, subsurface contributions to streamflow aid in the buildup of the flood wave in a natural stream; but in lower stream reaches a different type of ground water-streamflow interaction occurs, known as bank storage, which often attenuates the flood wave. As river stage increases with the arriving flood wave, flow may be induced into the stream banks, and as the stage declines, the flow is reversed. But during periods of heavy rainfall or snowmelt, Squillace (1996) observed that surface-water runoff can increase river stage and temporarily reverse the normal ground-water gradient toward the river. River water moves into the adjacent aquifer, and as the river recedes, the normal hydraulic gradient is reestablished. Thus, flood-stage conditions may also provide a transport pathway of pesticides into the ground water.

SUMMARY

One surface-water site was sampled monthly or more frequently for pesticides for 1 year, and 10 additional sites were sampled for pesticides during storms, periods of pesticide applications, or periods of low flow to describe the occurrence and mass transport of pesticides in surface water. Thirty different pesticides were found in surface water of the Palouse subunit, primarily during storm runoff. In addition, 34 shallow monitoring wells and 19 deeper wells were sampled to examine the effects of land use, pesticide use, and other environmental factors on the occurrence and distribution of pesticides in ground water. Six pesticides, one pesticide metabolite, and seven volatile organic compounds (VOCs) were detected in 28 percent of the ground-water samples. Only ground water was sampled for VOCs. No pesticides were detected in ground water (the primary source of drinking water) at concentrations that exceed drinking water standards, whereas three pesticides were detected in surface water at concentrations that exceed the freshwater-chronic criteria for the protection of aquatic life; concentrations of two pesticides exceed the U.S. Environmental Protection Agency risk-specific dose health advisory for drinking water associated with a 1 in a million cancer risk.

Most pesticides detected in surface-water samples were herbicides; only seven insecticides and two insecticide metabolites were detected. Ten of the 20 most frequently applied pesticides in the Palouse subunit were detected in surface-water samples, but none of these pesticides were detected in ground water. Samples from all surface-water sites except the Palouse River at Laird Park (located in the forested headwaters of the Palouse River) had detections of one or more pesticides. Atrazine and triallate were the pesticides detected most frequently in surface water of the Palouse subunit. Timing of rainfall soon after the application of agricultural pesticides to fields is the most significant environmental factor in relation to pesticide detections in surface water; the thickness of the loess overburden and preferential pathways in the loess or basalt are the most significant factors that relate to detections of pesticides or VOCs in ground water. Pesticides or VOCs were detected in all types of ground-water systems sampled (monitoring wells installed at the water table, shallow domestic wells, and deeper public-supply wells). Atrazine and desethylatrazine were the most commonly detected organic compounds in ground water. Although many of the pesticides detected in surface and ground water are applied for agricultural purposes, roadside applications and domestic use also may be significant sources of pesticides.

Runoff from storms and snowmelt is the primary mode of pesticide transport during winter and spring. The amount of pesticides lost from fields and transported to surface water depends on the physical and chemical properties of the pesticide, the weather, the type of soil, topography, and agricultural practices. Pesticides, either dissolved in water or sorbed to soil particles, can be transported from agricultural fields to surface water if rainfall, rate of application, and field conditions are appropriate.

Pesticides that are soluble in water are also subject to infiltration to the ground water and further transport by advection and hydrodynamic dispersion. Several mechanisms support possible transport of pesticides into the ground-water system: (1) poor well construction and open-hole basalt well construction; (2) preferential pathways into the surficial loess aquifer and the deeper basalt aquifers; (3) river leakage; and (4) bank storage and reversal of the normal hydraulic gradient toward the river.

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Appendix A1.--*Maximum concentrations of pesticides and volatile organic compounds in blank samples*
[µg/L, micrograms per liter; F, field; E, equipment; FP, field processing; --, no data]

Pesticide or volatile organic compound	Type of blank	Number of samples	Number of detections	Maximum concentration (µg/L)
		Results of surface-water blanks		
Atrazine	F	8	2	0.007
	E	4	1	0.003
	FP	1	1	0.003
Simazine	F	8	2	0.009
	E	4	1	E0.004
	FP	1	1	E0.004
		Results of ground-water blanks		
Chloroform	F	2	1	0.2
	E	2	0	--
Methylene-chloride	F	2	1	0.6
	E	2	--	--
Toluene	F	2	1	0.3
	E	2	0	--

E Concentration reported is less than the method detection limit.

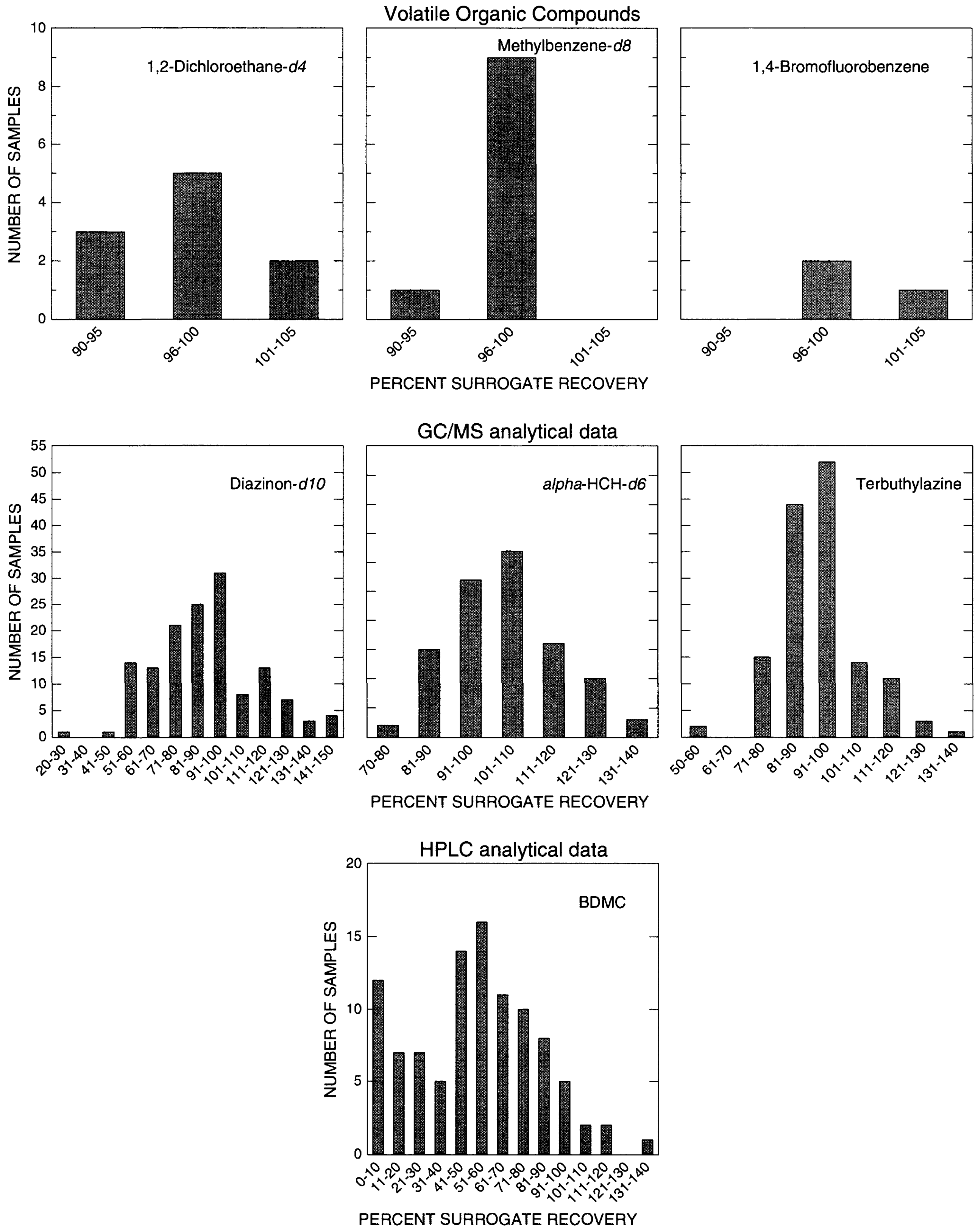

Figure A1. Percent surrogate recoveries for volatile organic compounds, gas chromatography mass spectrometry (GC/MS) analytical method, and high-performance liquid chromatography (HPLC) analytical method.

Appendix A2.--*Concentrations and precision data for pesticide and volatile organic compound replicate samples*

[VOC, volatile organic compound; µg/L, micrograms per liter; <, less than; --, could not be calculated]

Pesticide or VOC target analyte	Concentration in replicates (µg/L)	Relative percent difference
Concentrations of Replicate Data Greater than the Method Detection Limit		
Atrazine	0.047 0.047	0.0
	0.007 0.007	0.0
	<0.001 <0.001	0.0
Desethylatrazine	^{E}0.004 ^{E}0.004	0.0
	<0.002 <0.002	0.0
	<0.002 <0.002	0.0
Dieldrin	0.003 <0.001	--
	<0.001 <0.001	0.0
	<0.001 <0.001	0.0
gamma-HCH	0.011 0.008	31.6
	<0.004 <0.004	0.0
	<0.004 <0.004	0.0
Prometon	^{E}0.007 ^{E}0.01	35.3
	^{E}0.008 ^{E}0.011	31.6
	<0.018 <0.018	0.0
Simazine	0.011 0.011	0.0
	0.007 0.008	13.3
	<0.005 <0.005	0.0
Tebuthiuron	^{E}0.007 <0.01	--
	<0.01 <0.01	0.0
	<0.01 <0.01	0.0
Triallate	0.003 0.003	0.0
	0.023 0.024	4.3
	<0.001 <0.001	0.0
Diuron	^{E}0.02 0.03	40.0
	<0.02 <0.02	0.0
	<0.02 <0.02	0.0
Concentrations of Replicate Data Less than the Method Detection Limit		
2,4-D	<0.15	0.0
2,4-DB	<0.24	0.0
2,4,5-T	<0.035	0.0
2,4,5-TP	<0.021	0.0
3-Hydroxy-carbofuran	<0.014	0.0
Acifluorfen	<0.035	0.0
Alachlor	<0.002	0.0
Aldicarb	<0.55	0.0
Aldicarb sulfone	<0.10	0.0
Aldicarb sulfoxide	<0.021	0.0
Azinphos-methyl	<0.001	0.0
Benfluralin	<0.002	0.0
Bentazon	<0.014	0.0
Bromacil	<0.035	0.0
Bromoxynil	<0.035	0.0
Carbaryl	<0.008	0.0
Carbofuran	<0.12	0.0

Appendix A2.--*Concentrations and precision data for pesticide and volatile organic compound replicate samples*--Continued

Pesticide or VOC target analyte	Concentration in replicates (µg/L)	Relative percent difference
Concentrations of Replicate Data Less than the Method Detection Limit--continued		
Chloramben	<0.42	0.0
Chlorothalonil	<0.48	0.0
Clopyralid	<0.23	0.0
Cyanazine	<0.004	0.0
Dacthal, mono-acid	<0.017	0.0
Dicamba	<0.035	0.0
Dichlobenil	<1.2	0.0
Dichlorprop	<0.032	0.0
Dinoseb	<0.035	0.0
DNOC	<0.42	0.0
Fenuron	<0.013	0.0
Fluometuron	<0.035	0.0
Linuron	<0.018	0.0
MCPA	<0.17	0.0
MCPB	<0.14	0.0
Methiocarb	<0.026	0.0
Methomyl	<0.017	0.0
Neburon	<0.015	0.0
Norflurazon	<0.024	0.0
Oryzalin	<0.31	0.0
Oxamyl	<0.018	0.0
Picloram	<0.05	0.0
Propham	<0.035	0.0
Propoxur	<0.035	0.0
Triclopyr	<0.25	0.0
1,1-Dichloroethane	<0.2	0.0
1,1-Dichloroethene	<0.2	0.0
1,1-Dichloropropene	<0.2	0.0
1,2-Dibromo-3-chloropropane	<1.0	0.0
1,2-Dibromoethane	<0.2	0.0
1,2-Dichlorobenzene	<0.2	0.0
1,2-Dichloroethane	<0.2	0.0
cis-1,2-Dichloroethene	<0.2	0.0
trans-1,2-Dichloroethene	<0.2	0.0
1,2-Dichloropropane	<0.2	0.0
1,3-Dichlorobenzene	<0.2	0.0
1,3-Dichloropropane	<0.2	0.0
cis-1,3-Dichloropropene	<0.2	0.0
trans-1,3-Dichloropropene	<0.2	0.0
1,4-Dichlorobenzene	<0.2	0.0
2,2-Dichloropropane	<0.2	0.0
2-Chloro-1-methylbenzene	<0.2	0.0
4-Chloro-1-methylbenzene	<0.2	0.0
1,1,1-Trichloroethane	<0.2	0.0
1,1,2-Trichloroethane	<0.2	0.0
1,2,3-Trichlorobenzene	<0.2	0.0
1,2,3-Trichloropropane	<0.2	0.0
1,2,4-Trichlorobenzene	<0.2	0.0
1,2,4-Trimethylbenzene	<0.2	0.0
1,3,5-Trimethylbenzene	<0.2	0.0
1,1,1,2-Tetrachloroethane	<0.2	0.0
1,1,2,2-Tetrachloroethane		
1,1,2-Trichloro-1,2,2-trifluoroethane	<0.2	0.0
Benzene	<0.2	0.0
Bromobenzene	<0.2	0.0
Bromochloromethane	<0.2	0.0
Bromodichloromethane	<0.2	0.0
Bromomethane	<0.2	0.0
n-Butylbenzene	<0.2	0.0
sec-Butylbenzene	<0.2	0.0
tert-Butylbenzene	<0.2	0.0
Chlorobenzene	<0.2	0.0
Chloroethane	<0.2	0.0
Chloroethene	<0.2	0.0
Chloromethane	<0.2	0.0
Dibromochloromethane	<0.2	0.0
Dibromomethane	<0.2	0.0
Dichlorodifluoromethane	<0.2	0.0
Dichloromethane	<0.2	0.0
Ethylbenzene	<0.2	0.0
Hexachlorobutadiene	<0.2	0.0
Isopropyl benzene	<0.2	0.0
p-Isopropyltoluene	<0.2	0.0
Methyl *tert*-butyl ether	<0.2	0.0
Napthalene	<0.2	0.0
n-Propylbenzene	<0.2	0.0
Styrene	<0.2	0.0
Tetrachloroethene	<0.2	0.0
Tetrachloromethane	<0.2	0.0
Toluene	<0.2	0.0
Tribromomethane	<0.2	0.0
Trichloroethene	<0.2	0.0
Trichlorofluoromethane	<0.2	0.0
Trichloromethane	<0.2	0.0
Xylenes (total)	<0.2	0.0

[E] Concentration reported is less than the method detection limit.

Appendix A3.--*Summary of percent mean recoveries from field-matrix- and laboratory-reagent-spike pesticide and volatile organic compound analyses*

[VOC, volatile organic compound; SD, standard deviation of the mean recovery; --, no data; laboratory-reagent spikes were analyzed at the National Water Quality Laboratory from December 1993 to March 1994]

	Field-matrix spikes			Laboratory-reagent spikes		
VOC or target analyte	Mean recovery (percent)	SD recovery (percent)	Number of samples	Mean recovery (percent)	SD recovery (percent)	Number of samples
	Gas Chromatography/Mass Spectrometry analytical method					
Alachlor	105	26	4	122	16	31
Atrazine	96	28	4	104	17	31
Azinphos-methyl[1]	204	30	4	86	30	31
Benfluralin	59	7	4	94	12	31
Butylate	83	9	4	107	12	31
Carbaryl[1,2]	203	54	4	69	41	31
Carbofuran[1,2]	218	53	4	105	44	31
Chlorpyrifos	98	23	4	107	17	31
Cyanazine	114	36	4	116	22	31
DCPA	104	18	4	110	17	31
p,p'-DDE	54	7	4	82	7	31
Desethylatrazine[1]	28	7	4	30	6	31
Diazinon	82	14	4	115	18	31
Dieldrin	81	9	4	115	14	31
2,6-Diethylanaline	79	10	4	100	13	31
Disulfoton	86	13	4	119	46	31
EPTC	85	10	4	107	14	31
Ethalfluralin	71	7	4	104	18	31
Ethoprop	88	14	4	109	14	31
Fonofos	76	16	4	99	16	31
alpha-HCH	92	20	4	112	14	31
gamma-HCH	94	27	4	110	13	31
Linuron[2]	101	17	4	118	20	31
Malathion	89	12	4	116	14	31
Methyl parathion	107	34	4	112	22	31
Metolachlor	111	25	4	133	19	31
Metribuzin	71	14	4	86	17	31
Molinate	87	11	4	112	13	31
Napropamide	88	11	4	129	15	31
Parathion	99	33	4	114	13	31
Pebulate	83	11	4	106	13	31
Pendimethalin	63	6	4	88	24	31
cis-Permethrin	35	10	4	32	15	31
Phorate	70	11	4	94	18	31
Prometon	97	22	4	109	19	31
Pronamide	81	20	4	100	22	31

Appendix A3.--*Summary of percent mean recoveries from field-matrix- and laboratory-reagent-spike pesticide and volatile organic compound analyses--Continued*

VOC or target analyte	Field-matrix spikes			Laboratory-reagent spikes		
	Mean recovery (percent)	SD recovery (percent)	Number of samples	Mean recovery (percent)	SD recovery (percent)	Number of samples
	Gas Chromatography/Mass Spectrometry analytical method--continued					
Propachlor	92	13	4	108	12	31
Propanil	96	17	4	106	17	31
Propargite	96	26	4	155	17	31
Simazine	90	21	4	93	15	31
Tebuthiuron	79	34	4	106	48	31
Terbacil[1]	139	27	4	96	46	31
Terbufos	85	6	4	114	27	31
Thiobencarb	91	13	4	121	17	31
Triallate	87	18	4	110	12	31
Trifluralin	61	7	4	97	12	31
	High-Performance Liquid Chromatography analytical method					
2,4-D	46	13	4	64	20	29
2,4-DB	24	9	4	40	22	31
2,4,5-T	31	--	1	82	26	31
2,4,5-TP[3]	49	6	4	73	23	32
3-Hydroxy-carbofuran[3,4]	--	--	0	97	30	28
Acifluorfen[4]	--	--	0	71	24	32
Aldicarb[3,5]	12	0	2	93	32	22
Aldicarb sulfone[3,5]	--	--	0	64	32	28
Aldicarb sulfoxide	91	81	4	143	30	27
Bentazon	41	10	4	72	26	31
Bromacil	44	15	4	119	28	27
Bromoxynil	46	9	4	77	24	31
Carbaryl[2,3,5]	21	20	3	83	35	28
Carbofuran[2,3]	33	18	4	107	26	27
Chloramben[4]	--	--	0	74	24	29
Chlorothalonil[4,6]	--	--	0	19	14	18
Clopyralid[4]	--	--	0	54	28	30
Dacthal, mono-acid[4]	--	--	0	70	28	32
Dicamba	25	12	4	61	27	31
Dichlobenil[4,6]	--	--	0	59	32	29
Dichlorprop	47	11	4	76	26	32
Dinoseb	35	10	4	71	20	29
Diuron	40	4	4	84	27	28
DNOC[6]	45	11	4	32	20	25

Appendix A3.--*Summary of percent mean recoveries from field-matrix- and laboratory-reagent-spike pesticide and volatile organic compound analyses--Continued*

	Field-matrix spikes			Laboratory-reagent spikes		
VOC or target analyte	Mean recovery (percent)	SD recovery (percent)	Number of samples	Mean recovery (percent)	SD recovery (percent)	Number of samples
High-Performance Liquid Chromatography analytical method--continued						
Fenuron	35	7	4	105	22	29
Fluometuron	36	8	2	104	24	29
Linuron[2]	72	8	4	113	29	17
MCPA	38	13	4	57	23	32
MCPB[4]	--	--	0	34	21	29
Methiocarb[3,5]	12	11	3	100	31	17
Methomyl	40	16	4	109	25	29
Neburon	40	6	4	91	32	29
Norflurazon[4]	--	--	0	101	31	27
Oryzalin[4]	--	--	0	88	27	27
Oxamyl[3,5]	9	13	4	82	31	24
Picloram[3]	44	18	4	47	22	27
Propham	67	10	4	96	26	28
Propoxur	29	15	4	123	28	15
Triclopyr[3,4]	--	--	0	70	24	31
Volatile Organic Compound analytical method						
1,1-Dichloroethane[4]	--	--	0	95	3	16
1,1-Dichloroethene	116	22	2	94	4	16
1,1-Dichloropropene[4]	--	--	0	106	3	16
1,2-Dibromo-3-chloropropane[4]	--	--	0	90	9	16
1,2-Dibromoethane[4]	--	--	0	99	4	16
1,2-Dichlorobenzene[4]	--	--	0	98	6	16
1,2-Dichloroethane	164	13	2	100	4	16
cis-1,2-Dichloroethene[4]	--	--	0	94	3	16
trans-1,2-Dichloroethene[4]	--	--	0	97	4	16
1,2-Dichloropropane[4]	--	--	0	97	4	16
1,3-Dichlorobenzene[4]	--	--	0	97	5	16
1,3-Dichloropropane[4]	--	--	0	98	5	16
cis-1,3-Dichloropropene[4]	--	--	0	105	5	16
trans-1,3-Dichloropropene[4]	--	--	0	105	5	16
1,4-Dichlorobenzene	167	13	2	97	6	16
2,2-Dichloropropane[4]	--	--	0	95	6	16
2-Chloro-1-methylbenzene[4]	--	--	0	100	5	16
4-Chloro-1-methylbenzene[4]	--	--	0	100	5	16

Appendix A3.--*Summary of percent mean recoveries from field-matrix- and laboratory-reagent-spike pesticide and volatile organic compound analyses--Continued*

	Field-matrix spikes			Laboratory-reagent spikes		
VOC or target analyte	Mean recovery (percent)	SD recovery (percent)	Number of samples	Mean recovery (percent)	SD recovery (percent)	Number of samples
	<u>Volatile Organic Compound analytical method--continued</u>					
1,1,1-Trichloroethane	140	21	2	100	4	16
1,1,2-Trichloroethane[4]	--	--	0	98	6	16
1,2,3-Trichlorobenzene[4]	--	--	0	98	5	16
1,2,3-Trichloropropane[4]	--	--	0	97	6	16
1,2,4-Trichlorobenzene[4]	--	--	0	100	5	16
1,2,4-Trimethylbenzene[4]	--	--	0	101	6	16
1,3,5-Trimethylbenzene[4]	--	--	0	100	5	16
1,1,1,2-Tetrachloroethane[4]	--	--	0	100	6	16
1,1,2,2-Tetrachloroethane[4]	--	--	0	97	5	16
1,1,2-Trichloro-1,2,2-trifluoroethane[4]	--	--	0	95	4	16
Benzene[4]	--	--	0	95	3	16
Bromobenzene[4]	--	--	0	100	5	16
Bromochloromethane[4]	--	--	0	99	4	16
Bromodichloromethane	147	22	2	96	4	16
Bromomethane[4]	--	--	0	100	10	16
n-Butylbenzene[4]	--	--	0	99	5	16
sec-Butylbenzene[4]	--	--	0	100	5	16
tert-Butylbenzene[4]	--	--	0	101	5	16
Chlorobenzene[4]	--	--	0	97	6	16
Chloroethane[4]	--	--	0	99	9	16
Chlorodifluoromethane[4]	--	--	0	--	--	0
Chloroethene	70	12	2	89	11	16
Chloromethane[4]	--	--	0	98	15	16
Dibromochloromethane	150	26	2	96	6	16
Dibromomethane[4]	--	--	0	97	4	16
Dichlorodifluoromethane[4]	--	--	0	98	29	16
Dichloromethane[4]	--	--	0	98	4	16
Ethylbenzene	133	19	2	96	6	16
Hexachlorobutadiene[4]	--	--	0	102	6	16
Isopropyl benzene[4]	--	--	0	100	5	16
p-Isopropyltoluene[4]	--	--	0	102	5	16
Methyl *tert*-butyl ether	165	9	2	95	6	16
Napthalene[4]	--	--	0	100	6	16
n-Propylbenzene[4]	--	--	0	102	5	16
Styrene[4]	--	--	0	100	7	16

Appendix A3.--*Summary of percent mean recoveries from field-matrix- and laboratory-reagent-spike pesticide and volatile organic compound analyses--Continued*

VOC or target analyte	Field-matrix spikes Mean recovery (percent)	Field-matrix spikes SD recovery (percent)	Field-matrix spikes Number of samples	Laboratory-reagent spikes Mean recovery (percent)	Laboratory-reagent spikes SD recovery (percent)	Laboratory-reagent spikes Number of samples
			Volatile Organic Compound analytical method--continued			
Tetrachloroethene	106	19	2	96	6	16
Tetrachloromethane	132	32	2	98	4	16
Toluene[4]	--	--	0	96	3	16
Tribromomethane	142	24	2	98	9	16
Trichloroethene	140	17	2	99	3	16
Trichlorofluoromethane[4]	--	--	0	93	6	16
Trichloromethane[4]	--	--	0	96	4	16
Xylenes (total)[4]	--	--	0	99	6	16

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[1] Concentrations for these pesticides are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction (Zaugg and others, 1995).

[2] Analyzed by both gas chromatography/mass spectrometry and high-performance liquid chromatography methods.

[3] Pesticide target analyte may degrade if spike mixture and/or sample is not kept chilled at less than 4 degrees Celsius.

[4] Analyte not included in field-matrix spike mixture.

[5] Field-matrix spike analyte selected for qualitative reporting based on poor overall recovery and precision.

[6] Pesticide target analyte selected for qualitative reporting or removal from method schedule based on poor overall recovery and precision (NAWQA/NWQL Quality Assurance Committee for the Schedule 2050/2051 Pesticide Analysis Method, written commun., 1995).

Appendix A4.--*Concentrations of pesticides that exceed drinking water standards or guidelines*

[μg/L, micrograms per liter; <, less than; RSD health advisory, U.S. Environmental Protection Agency (USEPA) risk-specific health advisory for drinking water associated with a 10^{-6} cancer risk (see table 3). Health advisories are from Nowell and Resek (1994) and USEPA (1996). See table 5 for site names. **Concentrations in bold exceed the drinking water health advisories (see table 3)]**

Site code	Station number	Date	Dieldrin (μg/L)	*alpha* HCH (μg/L)	*gamma* HCH (μg/L)
	Samples with concentrations that exceed the RSD health advisory				
PAR000	13346990	4-20-94	<0.001	<0.002	**0.045**
SFP002	13349200	4-12-94	<0.001	<0.002	**0.047**
		4-20-94	<0.001	<0.002	**0.028**
PAL018	13351000	4-27-93	**0.01**	<0.002	**0.029**
		5-05-93	**0.01**	<0.002	**0.027**
		6-03-93	<0.001	**0.007**	0.008
		1-02-94	<0.001	<0.002	**0.036**
		1-09-94	<0.001	<0.002	**0.029**
		1-10-94	<0.001	<0.002	**0.066**
		1-12-94	**0.006**	<0.002	**0.081**
		2-02-94	<0.001	<0.002	**0.053**
		2-02-94	<0.001	<0.002	**0.046**

Appendix A5.--*Concentrations of pesticides that exceed aquatic-life water-quality criteria*

[µg/L, micrograms per liter; <, less than; aquatic-life criteria are U.S. Environmental Protection Agency freshwater-chronic criteria for the protection of aquatic life (see table 3). Aquatic-life criteria and health advisories are from Nowell and Resek (1994). See table 5 for site names. **Concentrations in bold exceed the aquatic-life water-quality criteria** (see table 3)]

Site code	Station number	Date	Triallate (µg/L)	Diazinon (µg/L)	*gamma* HCH (µg/L)
		Samples with concentrations that exceed the aquatic-life criteria			
PAL097	13346000	7-24-95	0.006	**0.021**	<0.004
PAR000	13346990	4-20-94	0.06	**0.270**	0.045
SFP002	13349200	4-26-94	0.083	**0.045**	<0.004
		7-24-95	0.007	**0.069**	<0.004
PAL018	13351000	4-27-93	**0.41**	<0.002	0.029
		5-05-93	**0.26**	<0.002	0.029
		12-10-93	0.013	**0.012**	<0.004
		1-02-94	**0.49**	<0.002	0.036
		1-12-95	**0.33**	<0.002	**0.081**

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