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NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Factors Affecting the Occurrence and Distribution of Pesticides in the Yakima River Basin, Washington, 2000

Scientific Investigations Report 2007-5180

U.S. Department of the Interior
U.S. Geological Survey

Cover: Photograph of Union Gap and Toppenish Creek Basin, view to the north from Highway 97. (Photograph taken by Henry Ngan, June 20, 2001.)
Top Inset: Photograph of a cherry orchard near Granger, Washington. Orange-brown colored vegetation at the base of trees provides evidence of chemical control of vegetation. View to west. (Photograph taken by Henry M. Johnson, U.S. Geological Survey, May 4, 2005.)
Middle Inset: Photograph of pre-emergent agricultural chemical application near Toppenish, Washington. View is to the southwest. (Photograph taken by Lawrence H. Fisher, U.S. Geological Survey, March 14, 2005.)
Bottom Inset: Photograph of corn near Granger, Washington. (Photograph taken by Henry M. Johnson, U.S. Geological Survey, August 17, 2005.)

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By Henry M. Johnson

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Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (http://www.usgs.gov/). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (http://water.usgs.gov/nawqa). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991 to 2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (http://water.usgs.gov/nawqa/studyu.html).

In the second decade of the Program (2001–2012), a major focus is on regional assessments of water-quality conditions and trends. These regional assessments are based on major river basins and principal aquifers, which encompass larger regions of the country than the Study Units. Regional assessments extend the findings in the Study Units by filling critical gaps in characterizing the quality of surface water and ground water, and by determining status and trends at sites that have been consistently monitored for more than a decade. In addition, the regional assessments continue to build an understanding of how natural features and human activities affect water quality. Many of the regional assessments employ modeling and other scientific tools, developed on the basis of data collected at individual sites, to help extend knowledge of water quality to unmonitored, yet comparable areas within the regions. The models thereby enhance the value of our existing data and our understanding of the hydrologic system. In addition, the models are useful in evaluating various resource-management scenarios and in predicting how our actions, such as reducing or managing nonpoint and point sources of contamination, land conversion, and altering flow and (or) pumping regimes, are likely to affect water conditions within a region.

Other activities planned during the second decade include continuing national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology; and continuing national topical studies on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on stream ecosystems, and transport of contaminants to public-supply wells.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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Conversion Factors

Multiply	By	To obtain
centimeter (cm)	0.3937	inch (in.)
cubic meters per second (m^3/s)	35.31	cubic feet per second (ft^3/s)
gram (g)	0.03527	ounce, avoirdupois (oz)
gram per day (g/d)	0.03527	ounce per day (oz/d)
gram per hectare (g/ha)	0.01427	ounce per acre (oz/acre)
gram per year (g/yr)	0.03527	ounce per year (oz/yr)
hectare (ha)	2.471	acre
meter (m)	3.281	foot (ft)
square kilometer (km^2)	0.3861	square mile (mi^2)

Concentrations of chemical constituents in water are given in microgram per liter (µg/L).

Datums

Vertical coordinate information is referenced to the North American Vertical Datum 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum 1983 (NAD 83).

Projections are from the Lambert Conformal Conic (Oregon Lambert Projection).

Water-quality measurements used in this report:

µm	micrometer
µg/L	microgram per liter
mg/L	milligram per liter
mL/g	milliliter per gram

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Factors Affecting the Occurrence and Distribution of Pesticides in the Yakima River Basin, Washington, 2000

By Henry M. Johnson

Abstract

The Yakima River Basin is a major center of agricultural production. With a cultivated area of about 450,000 ha (hectares), the region is an important producer of tree fruit, grapes, hops, and dairy products as well as a variety of smaller production crops. To control pest insects, weeds, and fungal infections, about 146 pesticide active ingredients were applied in various formulations during the 2000 growing season. Forty-six streams or drains in the Yakima River Basin were sampled for pesticides in July and October of 2000. Water samples also were collected from 11 irrigation canals in July. The samples were analyzed for 75 of the pesticide active ingredients applied during the 2000 growing season—63 percent of the pesticides were detected. An additional 14 pesticide degradates were detected, including widespread occurrence of 2 degradates of DDT.

The most frequently detected herbicide was 2,4-D, which was used on a variety of crops and along rights-of-way. It was detected in 82 percent of the samples collected in July. The most frequently detected insecticide was azinphos-methyl, which was used primarily on tree fruit. It was detected in 37 percent of the samples collected in July. All occurrences of azinphos-methyl exceeded the Environmental Protection Agency recommended chronic concentration for the protection of aquatic organisms.

More than 90 percent of the July samples and 79 percent of the October samples contained two or more pesticides, with a median of nine in July and five in October. The most frequently occurring herbicides in mixtures were atrazine, 2,4-D, and the degradate deethylatrazine. The most frequently occurring insecticides in mixtures were azinphos-methyl, carbaryl, and *p,p'*-DDE (a degradate of DDT).

A greater number of pesticides and higher concentrations were found in July than in October, reflecting greater usage and water availability for transport during the summer growing and irrigation season. Most of the samples collected in October (baseflow conditions) contained at least one pesticide.

The mass ratio of instream pesticide load and application (pesticide loss) was used to explore spatial and temporal patterns of pesticide occurrence. Losses of pesticides with large organic carbon-water partitioning coefficients (K_{oc}) values, which adhere strongly to sediment and plant surfaces, were smallest in catchments where sprinkler and drip irrigation systems were widely used. In contrast, losses of pesticides with low K_{oc} values did not relate well with irrigation method.

Introduction

Degradation of the aquatic environment by agricultural activities is a major national concern (U.S. Environmental Protection Agency, 2002a). Pesticides are commonly detected in agricultural runoff and in waterways receiving that runoff (U.S. Geological Survey, 1999). Pesticides washed into the waterways can affect nontarget species—killing or inhibiting the growth of beneficial aquatic vegetation and insects, both of which are important to fish communities. Low concentrations of some pesticides interfere with fishes' ability to detect and avoid predators and with their homing capabilities (Arunachalam and Palanichamy, 1982; Sholtz and others, 2000), and have been implicated in the feminization of frogs (Hayes and others, 2002). Some pesticides accumulate in the tissues of aquatic invertebrates and fish and can pose a risk to people who consume them (Extension Toxicology Network, 1996; Rinella and others, 1993).

Several recent investigations of the occurrence and distribution of pesticides in the Yakima River Basin have been reported by the U.S. Geological Survey (USGS) and by the Washington Department of Ecology. The first basinwide assessment of pesticides was done by Johnson and others (1986) who reported on the occurrence of organochlorine pesticides in water, sediment, and fish from the Yakima River and its major tributaries. Rinella and others (1999) reported on the occurrence of pesticides in water, bed sediment, and biota at about 100 sites throughout the basin. Water-quality samples generally were collected from the Yakima River or from the mouths of tributaries. The occurrence of many current-use pesticides was reported in the study; however, most of the discussion is devoted to explaining the distribution and transport of historically used organochlorine pesticides.

Ebbert and Embrey (2002) reported the occurrence and distribution of historically and currently used pesticides and pesticide degradates from 34 sites on the Yakima River and mouths of tributaries. In addition to documenting the basinwide distribution of pesticides, Ebbert and Embrey documented the temporal variation of pesticide concentrations at three sites during the growing season.

This report builds on the work of these previous investigations, but differs in two significant ways. First, the focus of this report exclusively is on current-use pesticides, and second, most data were collected from small streams and drains rather than the Yakima River or major tributaries. Data for the study were collected as part of the USGS National Water-Quality Assessment (NAWQA) Program. The NAWQA Program monitors and periodically reports on national and regional trends in the quality of water and processes affecting the water-quality (for example, see U.S. Geological Survey, 1999; Gilliom and others, 2006). National and regional reports can be accessed at http://water.usgs.gov/nawqa.

Study Area

The Yakima River Basin is in south-central Washington State. The 15,940 km^2 basin lies in the rain shadow of the Cascade Range. Mean annual precipitation in the basin ranges from 350 cm in the mountains to less than 25 cm in the eastern lowlands. The western part of the basin is predominantly forested, whereas the eastern uplands are dominated by sagebrush and grasses. The lowlands in the central and eastern parts of the basin support the agricultural communities. The livelihood for many of the basin's 293,700 residents is based in some way on agriculture. Because arid conditions are prevalent in most of the river basin, irrigation is necessary for farming. During the growing season, a system of storage reservoirs and irrigation canals delivers water to about 450,000 ha of cultivated land. Water deliveries begin in mid-March and cease in mid-October. Further information on the geography, climate, and hydrology of the Yakima River Basin can be found in Rinella and others (1992; 1999).

Purpose and Scope

This report explains the observed distribution of agricultural pesticides at 57 streams, drains, and canals in the Yakima River Basin using information on chemical use, agricultural practices, chemical properties, and physical features of the catchments draining to the sampling sites. The sampled catchments are located throughout the Yakima River Basin, including Kittitas, Yakima, and Benton Counties (pl. 1). The sites were sampled two times during the calendar year 2000.

Study Design

The sampling network was designed to test two hypotheses about the movement of pesticides in the Yakima River Basin. First, that the use of sprinkler and drip irrigation reduces the transport of agricultural chemicals. Second, that there is a pattern in the occurrence of pesticides in streams and drains in the Yakima River Basin, and that pattern is a function of the type and timing of chemicals applied in the catchment, the physical properties of the chemicals, and the physical properties of the catchment.

The sampling network consists of 44 sites on streams or drains issuing from agricultural catchments, 2 sites on streams issuing from catchments with no canal water deliveries and no agricultural activities (except rangeland grazing), and 11 sites on irrigation-water delivery canals (table 1, pl. 1). All sites were sampled two times in 2000—once during the height of the irrigation season (July 10–July 20, hereinafter referred to as "July") and once shortly after the end of the irrigation season (October 30–November 2, hereinafter referred to as "October"). The July sampling was timed to assess water-quality conditions during the months when chemical use, water application, and runoff are highest. The October sampling was timed to assess water-quality conditions in the drains and streams when they are fed entirely by ground-water discharge and chemical use is low.

Twenty-eight of the 44 agricultural catchments contained a single dominant irrigation method—either rill or a mixture of sprinkler and drip (table 2). The remaining 16 agricultural catchments contained a mix of irrigation methods. Catchments ranged in size from 3 to 112,264 ha, however, the agricultural area[1] of the catchments was much smaller—ranging from 3 to 8,168 ha. The difference between total catchment area and agricultural area was greatest in large catchments, and was due to the presence of rangeland and forests upslope from the agricultural activities. The 11 canal sites were selected to approximate the quality of the water being delivered to the agricultural catchments in which samples were collected.

[1] For the purposes of this study, the agricultural area was defined as the area influenced by agricultural activities such as farming, dairies, and other infrastructure. It may include canals, roads, farmhouses and other noncrop areas.

Table 1. Sites sampled in the Yakima River Basin, Washington, 2000.

[Map reference numbers are shown on plate 1. **Abbreviations**: USGS, U.S. Geological Survey. Ag Drain, natural or dug waterway draining an area of agricultural activities]

Map reference No.	USGS station identification No.	Sampling site	Site type	County	Region
47	465631120234500	Drain at Sorenson Road	Ag Drain	Kittitas	Kittitas
48	465524120220500	Drain at Hamilton Road	Ag Drain	Kittitas	Kittitas
49	465204120182800	Badger Creek at Silica Road	Ag Drain	Kittitas	Kittitas
62	465428120213500	Badger Creek upstream of Wipple Wasteway	Ag Drain	Kittitas	Kittitas
84	465907120202800	Park Creek at Park Creek Road	Ag Drain	Kittitas	Kittitas
85	465918120193100	Drain at Park Creek Road	Ag Drain	Kittitas	Kittitas
95	465647120265700	Park Creek at South Ferguson Road	Ag Drain	Kittitas	Kittitas
96	465640120265700	Johnson Drain at South Ferguson Road	Ag Drain	Kittitas	Kittitas
108	465504120195600	KRD Canal at Wipple Spillway	Canal	Kittitas	Kittitas
114	465537120231500	Cascade Canal at Thrall Road	Canal	Kittitas	Kittitas
66	12484550	Umtanum Creek near mouth at Umtanum	Stream	Kittitas	Umtanum
2	463350120233000	Drain near Postma Road	Ag Drain	Yakima	Moxee
7	463258120222800	Drain at Faucher Road	Ag Drain	Yakima	Moxee
12	463245120205900	319 test site drain near Walters Road	Ag Drain	Yakima	Moxee
69	12500420	Moxee Drain at Birchfield Road near Union Gap	Ag Drain	Yakima	Moxee
97	463228120184400	Moxee Drain at Beane Road	Ag Drain	Yakima	Moxee
109	463223120184400	Roza Canal at Beane Road	Canal	Yakima	Moxee
115	463411120223900	Selah-Moxee Canal at Duffield Road	Canal	Yakima	Moxee
119	463349120380500	Yakima-Tieton Canal at Occidental Road	Canal	Yakima	Ahtanum-Wide Hollow
14	463343120385400	Drain at Draper Road	Ag Drain	Yakima	Ahtanum-Wide Hollow
99	463147120455700	Ahtanum Creek below Bachelor Creek	Ag Drain	Yakima	Ahtanum-Wide Hollow
107	463254120352800	Ahtanum Creek at 62nd Avenue	Ag Drain	Yakima	Ahtanum-Wide Hollow
26	462836120202600	Drain at Borquin Road	Ag Drain	Yakima	Buena-Zillah
27	462745120192400	Drain at Lombard Loop	Ag Drain	Yakima	Buena-Zillah
28	462603120174200	Drain at Hiland Drive	Ag Drain	Yakima	Buena-Zillah
120	462644120175000	Union Gap Canal at Blue Goose Road	Canal	Yakima	Buena-Zillah
59	462138120345900	Drain at Sunray Road	Ag Drain	Yakima	Toppenish
50	462053120055100	DR 2 near Outlook Fire Station	Ag Drain	Yakima	Granger
67	12505450	Granger Drain at Granger, Wash	Ag Drain	Yakima	Granger
92	462046120065600	DR 2 at Vanbelle Road	Ag Drain	Yakima	Granger
100	462023120075200	DR 2 at Yakima Valley Highway	Ag Drain	Yakima	Granger
101	462018120075200	JD 32.0 upstream of DR 2	Ag Drain	Yakima	Granger
135	462158120053200	Sunnyside Canal at North Outlook Road	Canal	Yakima	Granger
51	461254120051300	Drain at Colwash Road	Ag Drain	Yakima	Satus
74	12508500	Satus Creek below Dry Creek near Toppenish	Stream	Yakima	Satus
93	461644120084500	North Drain at Satus Longhouse Road	Ag Drain	Yakima	Satus
102	12508630	South Drain near Satus	Ag Drain	Yakima	Satus
113	461810120125200	West Lateral at Satus Pump Station Number 2	Canal	Yakima	Satus
29	462018120012000	JD 34.2 at Woodin Road	Ag Drain	Yakima	Sulphur
52	461809119494900	Drain at Snipes Road	Ag Drain	Benton	Sulphur
53	461716119504600	Drain at Evans Road	Ag Drain	Benton	Sulphur
63	461903119581400	DR 19 at Factory Road	Ag Drain	Yakima	Sulphur
103	461929119581200	JD 37.9 at East Edison Road	Ag Drain	Yakima	Sulphur
104	461700119595400	JD 43.9 at Mabton Sunnyside Road	Ag Drain	Yakima	Sulphur
110	462221119572500	Roza Canal at Ray Road	Canal	Yakima	Sulphur
112	461530119514200	Grandview Pump Lateral at McCreadie Road	Canal	Benton	Sulphur
116	461929119561500	Sunnyside Canal at East Edison Road	Canal	Yakima	Sulphur
54	461504119514100	JT DR 2 at Lemley Road	Ag Drain	Benton	Downstream of Sulphur
55	461717119460600	Spring Creek at Evans Road	Ag Drain	Benton	Downstream of Sulphur
56	461032119194900	Drain at Badger Road, Mile 8.8	Ag Drain	Benton	Downstream of Sulphur
57	461117119210500	Drain at Badger Road, Mile 7.3	Ag Drain	Benton	Downstream of Sulphur
58	461359119253500	Drain at Badger Road, Mile 1.8	Ag Drain	Benton	Downstream of Sulphur
83	461531119510300	Drain at Griffin Road	Ag Drain	Benton	Downstream of Sulphur
87	461141119510100	JD 51.4 at Yakima River	Ag Drain	Benton	Downstream of Sulphur
88	12509492	JD 52.8 at Wamba Road at Prosser	Ag Drain	Benton	Downstream of Sulphur
105	12509696	Spring Creek at Hanks Road near Prosser	Ag Drain	Benton	Downstream of Sulphur
106	461517119402500	Snipes Creek at McCreadie Road	Ag Drain	Benton	Downstream of Sulphur

Table 2. Area, irrigation methods, and crops for each catchment, Yakima River Basin, Washington, 2000.

[Map reference numbers are shown on plate 1]

Map reference No.	Catchment area (hectares)	Agricultural area of catchment (hectares)	Irrigation method in catchment (as percent of the agricultural area)				Crops grown in catchment (as percent of the agricultural area)				
			Rill	Drip	Sprinkler	Unirrigated	Hays, mint, small grains	Corn, asparagus, other vegetables	Orchards, vineyards, hops	Pasture	Uncropped
Kittitas Valley											
47	458	429	94	0	6	0	81	13	0	6	0
48	83	80	99	0	1	0	100	0	0	0	0
49	308	263	100	0	0	0	52	0	0	48	0
62	6,449	1,683	89	0	11	0	64	4	0	32	0
84	7,868	722	69	0	31	0	20	10	0	70	0
85	223	67	97	0	3	0	20	0	0	80	0
95	17,822	2,144	85	0	15	0	44	11	0	44	0
96	4,087	2,384	92	0	8	0	73	3	0	23	0
Mid Valley											
66	13,730	0	0	0	0	0	0	0	0	0	100
2	163	118	7	55	22	16	0	0	62	38	0
7	3	3	100	0	0	0	0	0	100	0	0
12	549	380	2	72	25	1	0	0	98	2	0
69	35,268	7,046	6	44	44	6	25	0	64	10	0
97	21,093	2,768	4	23	67	7	49	0	42	8	0
14	277	213	5	7	84	4	3	0	89	8	0
99	32,196	466	6	2	81	11	53	0	21	26	0
107	36,237	1,346	6	2	82	11	53	0	23	24	0
Lower Valley											
26	1,841	460	0	0	100	0	0	0	98	2	0
27	596	253	0	0	100	0	0	0	99	1	0
28	1,945	469	0	14	86	1	0	0	92	8	0
59	311	241	12	21	61	6	54	0	40	6	0
50	158	127	57	1	36	6	25	37	26	13	0
67	15,985	8,168	27	7	66	0	16	16	58	11	0
92	228	205	61	1	38	0	16	48	24	12	0
100	1,075	877	34	4	62	0	22	20	48	11	0
101	6,112	3,112	27	7	66	0	13	20	59	8	0
51	192	181	100	0	0	0	44	50	7	0	0
74	112,264	0	0	0	0	0	0	0	0	0	100
93	870	642	86	2	0	12	13	75	0	12	0
102	11,883	1,708	75	0	11	15	15	20	20	45	0
29	1,083	696	41	1	57	1	12	20	56	12	0
52	83	80	13	4	82	0	0	0	100	0	0
53	70	50	100	0	0	0	11	0	89	0	0
63	199	169	52	2	46	0	13	38	35	14	0
103	3,947	1,534	43	11	46	0	13	28	46	13	0
104	7,071	4,589	35	3	61	1	9	4	71	16	0
54	83	19	47	11	43	0	0	0	100	0	0
55	6,519	304	2	47	51	0	0	0	100	0	0
56	31	12	0	0	100	0	0	100	0	0	0
57	31	29	100	0	0	0	0	100	0	0	0
58	49	39	0	0	100	0	0	100	0	0	0
83	114	108	59	0	40	0	12	0	88	0	0
87	1,528	1,137	39	13	49	0	12	1	72	15	0
88	1,414	1,125	41	9	50	0	11	0	68	22	0
105	7,506	759	31	28	41	0	2	0	98	0	0
106	8,464	1,423	31	12	58	0	3	0	97	1	0

Methods

Stream discharge, water temperature, pH, dissolved oxygen concentration, specific conductance, and turbidity were measured on-site in the field to characterize water quality during sampling. Samples of water were collected for laboratory analyses of filtered (0.45 µm pore size) and unfiltered nutrients, filtered (0.7 µm pore size) pesticides, and suspended sediment. Samples also were collected for fecal-indicator bacteria analysis (Morace and McKenzie, 2002). During the October sampling period, samples for selected dissolved metals were collected (Fuhrer and others, 2004).

Field Procedures

Water-quality samples were collected by USGS personnel and representatives from Benton Conservation District, Kittitas Conservation District, Roza-Sunnyside Board of Joint Control, and South Yakima Conservation District as part of their routine sampling operations. The majority of the samples were collected by USGS personnel using procedures described in the following paragraphs.

Glass and fluorocarbon polymer (PFTE) equipment used to collect and process samples were cleaned with a 0.1 percent phosphate-free detergent solution, rinsed with tap water, rinsed with a 5 percent hydrochloric acid solution, rinsed with distilled water, and rinsed with pesticide-grade methanol. Metal equipment were cleaned similarly, but were not acid rinsed to prevent pitting and corrosion. Sampling equipment was either wrapped in clean aluminum foil or sealed in clean plastic bags and stored in a dust free environment prior to sample collection (U.S. Geological Survey, variously dated).

Due to the small size and unusual characteristics of many sites, dip samples frequently were collected; however, when conditions permitted, depth- and width-integrated samples were collected according to the protocols outlined in the USGS National Field Manual (U.S. Geological Survey, variously dated). When dip samples were collected, the sampling crew evaluated the site and modified or devised a technique to obtain a sample that was representative of the water at that site (U.S. Geological Survey, variously dated). Samples were collected by using a US DH-81 or US D-77 TM sampler (Edwards and Glysson, 1999), immersing sample bottles by hand in the stream or drain, or pumping water from the stream or drain using a pesticide-grade pump outfitted with a glass J-tube. Regardless of the collection method, an attempt was made to collect a depth- and width-integrated sample at all sites. Samples were collected into 3-liter PFTE bottles, 1-liter PFTE bottles, 1-liter narrow-mouth baked glass bottles or 1-liter wide-mouth baked glass bottles.

Water for pesticide analyses was pumped from its sampling vessel using flexible PFTE tubing connected to a valveless piston-metering pump. The water was filtered through a stainless-steel filtration unit containing a glass-fiber filter (0.7 µm pore diameter). The pumps and filters, and protocols for their use are described in the USGS National Field Manual (U.S. Geological Survey, variously dated). Samples were stored on ice and shipped within 36 hours of collection to the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado.

Laboratory Procedures

Pesticide samples were analyzed at the USGS NWQL. A total of 121 pesticides and pesticide degradates were analyzed by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring (Zaugg and others, 1995; Sandstrom and others, 2001). An additional 58 pesticides and pesticide degradates were analyzed by graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry (Furlong and others, 2001). A list of analytes is provided in appendix A.

Quality Control

Fifty-six samples were collected for quality control: 13 blank samples, 30 replicate samples, and 12 spike samples. With one exception, all blank water samples were free from pesticide residue. The fungicide myclobutanil was detected at 0.006 µg/L in one sample. This concentration is near the reporting level (RL) and was coded by the lab as an estimated value. This detection was very likely the result of carryover in contaminated equipment. The prior sample collected with the same equipment contained 4.74 µg/L of myclobutanil, which was the largest concentration of this compound detected in the study, exceeding the next largest by a factor of 50.

Replicate samples were used to evaluate lab and environmental variability. Most replicates were collected sequentially, and therefore recorded both sources of variability. Replicate samples were compared using the relative-percent difference (RPD) and absolute difference (AD) in the concentration of each analyte in the paired sample. The RPD was calculated as:

$$RPD = \frac{|R1 - R2|}{\left(\frac{R1 + R2}{2}\right)} \times 100,$$

where

$R1$ is sample 1, and

$R2$ is sample 2.

The distribution of RPD and AD values are shown in figure 1 for 93 analyte pairs for which these values could be calculated. The median RPD was 7.3 percent and the median AD was 0.001 µg/L. Five pairs exceeded the 95th percentile RPD value of 73.4 percent. In four of the five pairs, the greatest concentration was less than 2 times the RL, and in the fifth it was less than 2.5 times the RL.

RPD and AD could not be computed for 28 analyte pairs because the concentration in one of the two samples was not detected. In most samples, the one quantified concentration was near the RL for the analyte (fig. 2), and in all but two samples was less than two times the RL. The remaining two data points may reflect laboratory variability—since these data were collected, the RL for both of these analytes (methomyl and didealkylatrazine) has been increased. Using the current RLs, the methomyl sample would be 2.9 times the RL and the didealkylatrazine sample would be 1.5 times the RL. The nondetections in these 28 replicate pairs are interpreted as false negatives (reporting an analyte as not detected when it actually is in the water), due to the nearness to the RL. Three lines of evidence lend weight to this interpretation. First, only one pesticide was detected among blank samples, and it likely was the result of carryover contamination. Second, with the exception of chloramben, all of the analytes detected in replicates were found in at least one other environmental sample. Third, the method of setting the RL is designed to minimize false positives (quantifying an analyte when it is not present in the water); however, the tradeoff is that false negatives can be relatively common near the RL (Childress and others, 1999).

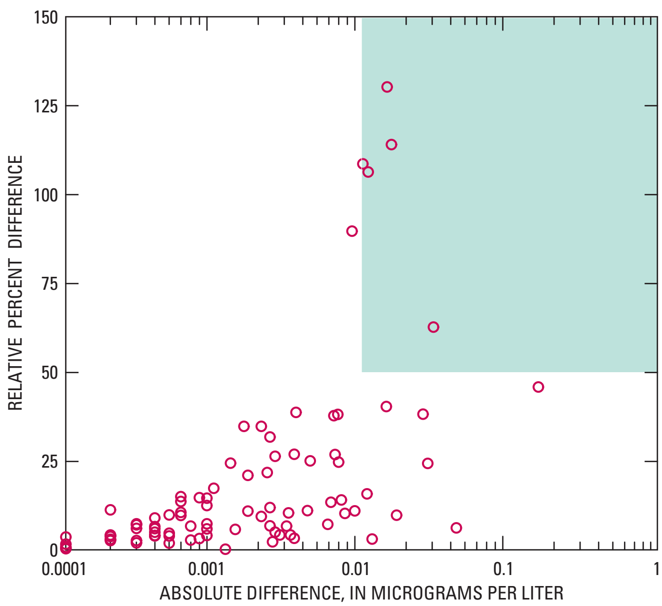

Figure 1. Relation between the absolute difference (AD) and relative percent difference (RPD) of environmental-replicate samples, Yakima River Basin, Washington, 2000. Shaded area is defined by sample pairs where the AD is greater than 0.01 µg/L and the RPD is greater than 50 percent. Samples that plot in this area are discussed in text.

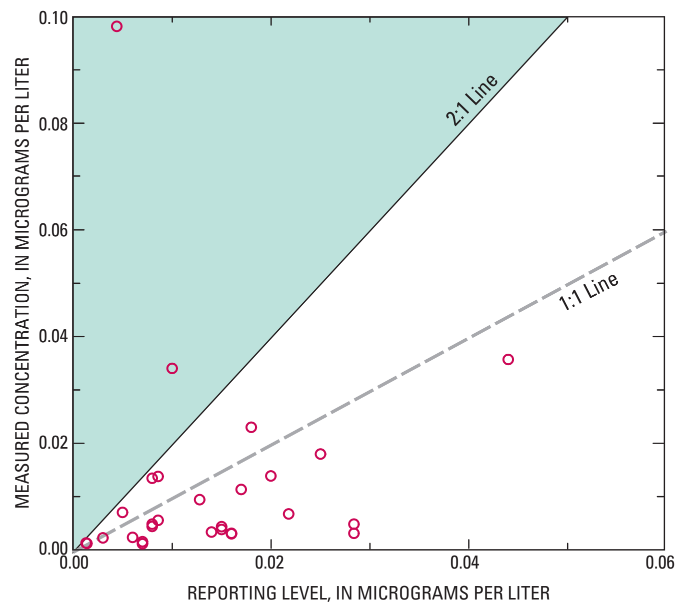

Figure 2. Relation between reporting level (RL) and measured concentration of environmental replicate samples where one of the two analyses was reported as a nondetection, Yakima River Basin, Washington. The shaded area is defined by samples having measured concentrations greater than two times the RL.

Pesticide recoveries from spiked samples of environmental water were compared to pesticide recoveries from laboratory-spiked organic-grade blank water samples, which routinely are conducted by NWQL (available online at http://bqs.usgs.gov/OBSP/). The range of recoveries from spiked environmental water was within the range of recoveries observed in samples of laboratory-spiked blank-water analyzed between February 1999 and December 2001 (fig. 3). The only anomalous recovery among the spiked environmental samples was for 1-naphthol from a sample spiked at South Drain on July 13, 2000. In this sample, the recovery of 100-percent 1-naphthol stands in stark contrast to three other spiked-environmental samples in which only 5–10 percent of the 1-naphthol was recovered. It also is atypical of laboratory-spiked blank water, which had a median recovery of 25 percent from 2001–03. The cause for the anomalously good recovery is unexplained.

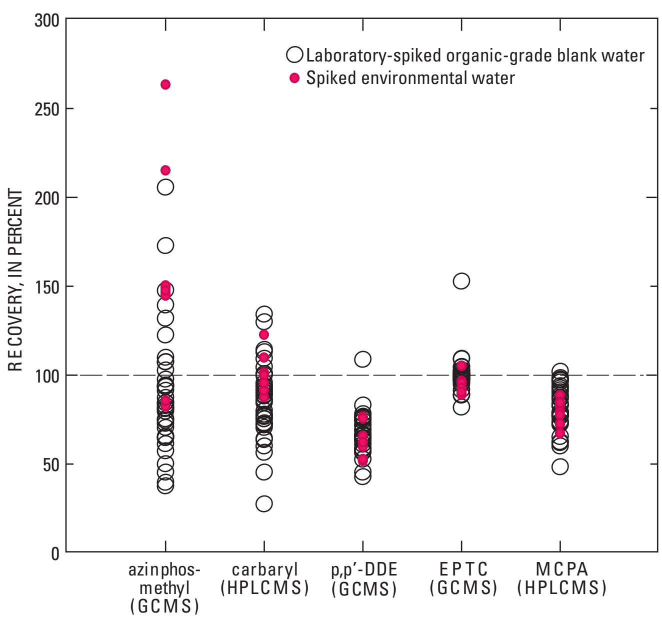

Figure 3. Selected recoveries of pesticide from laboratory-spiked organic-grade blank water and spiked environmental water, Yakima River Basin, Washington, 2000. Laboratory-spiked samples were analyzed between February 1999 and December 2001. The five pesticides shown were selected to represent typical variations in performance on the two analytical methods.

Nearly one-half (48 percent) of all spike recoveries were within 20 percent of the spiked concentration, and 83 percent of the spike recoveries were between 50 percent and 200 percent of the spiked concentration (fig. 4). Seventy-one percent of the spiked samples had recoveries of less than 100 percent, indicating that, taken as a whole, environmental-pesticide concentrations likely are to be slightly higher than reported by the laboratory. The degree to which pesticide concentrations might be lower than reported is modest—only 5 percent of the spiked samples had recoveries exceeding 150 percent and fewer than 2 percent of samples had recoveries exceeding 200 percent. Although a small percentage is affected by substantial overrecovery, there are three pesticides of moderate to high use in this group: azinphos-methyl, carbofuran, and terbacil. Most spike recoveries for these pesticides fall within the range of 50–200 percent and are not always overestimated. They are subject to occasional erratic recoveries for reasons that are not clear.

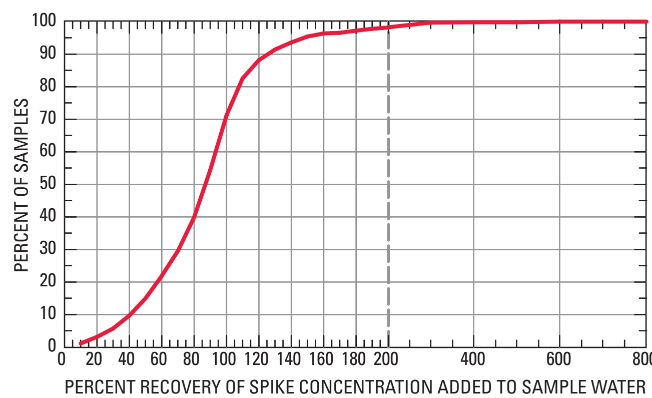

Figure 4. Frequency distribution of pesticide-spike recoveries in environmental waters, Yakima River Basin, Washington, July and October 2000.

Pesticide Occurrence and Distribution

An estimated 146 organic pesticides[2] were applied to crops in the Yakima River Basin during the 2000 growing season (table 3). Estimates were based on county-level agricultural statistics from the National Agricultural Statistics Service (NASS) and were verified and corrected in interviews with private crop chemical consultants and agriculture-extension agents in Kittitas, Yakima, and Benton Counties. Data on right-of-way applications were obtained from State and local transportation departments and irrigation districts. Details of the pesticide compilation are provided by Ebbert and Embrey (2002). Seventy-five of the 146 applied pesticides (51 percent) were analyzed for this study, and of these 75 pesticides, 47 were detected (63 percent). Only glyphosate (Roundup®, Rodeo®) was applied in large amounts, but not analyzed in this study. Pesticides that were applied but not often detected were applied in small quantities or have chemical properties that inhibit their transport to waterways, such as rapid degradation or a large soil organic carbon-water partitioning coefficient (K_{oc}). Summaries of detected pesticides and their concentrations in water samples are provided in table 4 and figure 5, respectively. Screened and unscreened summary statistics are presented for the reader (see Sidebar 1: Pesticide Reporting Levels).

Sidebar 1: Pesticide Reporting Levels

The minimum concentration reported by the NWQL varies from analyte to analyte. Pesticides routinely are detected below the established laboratory RL because the analytical methods are considered “information rich” and use multiple lines of evidence to identify and quantify an analyte (Childress and others, 1999). Analytes detected and reported below the RL are noted as such by the NWQL.

Comparisons among pesticides with different RLs can misrepresent the frequency and distribution of occurrence. Pesticides with lower RLs may seem to be distributed more widely or to be detected more frequently in the water than pesticides with a higher RL. For these types of comparisons, pesticide concentrations were screened at a concentration of 0.020 µg/L, which represents the lowest common RL for all pesticides that were detected. Unless specifically noted, data presented in this report are unscreened.

Samples were analyzed for 45 pesticides that had no record of application (table 5). Seven of these pesticides were detected. Their presence is a minor footnote to the larger picture of pesticides in the Yakima River Basin. These seven pesticides were rarely detected, and when they were, concentrations were near the laboratory RL. Application of some pesticides might be unrecorded because they were secondary ingredients in pesticide formulations, they were from supplies left over from previous seasons, or they were applied by a farmer who did not participate in the statistical survey. Two pesticides (dieldrin and dinoseb) are no longer registered for use in the United States, and the detection of these compounds is most likely of residuals from past use.

The most frequently detected pesticide during the July 2000 sampling was 2,4-D. Eighty-two percent of all samples collected contained 2,4-D at concentrations exceeding 0.02 µg/L. Three detections exceeded 1 µg/L, including two from canal-water samples in the Kittitas Valley. Although these concentrations are high in the context of this study, they are well below the U.S. Environmental Protection Agency (EPA) drinking water maximum contaminant level of 70 µg/L (the only available regulatory benchmark; U.S. Environmental Protection Agency, 2004a). Between 15 and 20 percent of all the 2,4-D used in catchments sampled for this study was applied to control weeds along road, canal, and drain rights-of-way. Because most of these rights-of-way were along flowing waterways, drift and overspray might result in the direct application to waterways.

The second most frequently detected pesticide in July 2000 (based on screened values) was the insecticide azinphos-methyl, which was found in 37 percent of the samples. Every occurrence of azinphos-methyl exceeded the chronic guidelines for the protection of aquatic organisms (0.01 µg/L) established by the EPA (U.S. Environmental Protection Agency, 2004b). In the Yakima River Basin, azinphos-methyl was used almost exclusively in tree-fruit orchards, where it was applied with airblast sprayers. Drift and overspray probably contributed to its widespread occurrence. In an environment similar to the Yakima River Basin, on a relative calm day late in the growing season, Schultz and others (2001) reported deposition rates of azinphos-methyl 15 m downwind of an orchard equal to 1.2 percent of the deposition rate in the orchard. They concluded that this was a best-case scenario. Spray drift deposited directly on water or on an adjacent field that is rill irrigated can facilitate its transport from the field of use. In addition, this author has observed runoff from a sprinkler-irrigated orchard flowing into roadside ditches or regional drains on two separate occasions at different sites. Anecdotal reports from farmers in the basin confirm that these observations were not isolated instances.

[2] Inorganic, petroleum, and biological controls also are used as pesticides in the Yakima River Basin, but are outside the scope of this report.

Table 3. Pesticides with a record of application in 2000, Yakima River Basin, Washington.

[**Bold** type indicates pesticide was detected at least once in 2000]

Analyzed		Not analyzed	
2,4-D[1]	**Hexazinone**	Abamectin	Ivermectin
2,4-D methyl ester	Imazaquin	Acephate	Kresoxim-methyl
2,4-DB	Imazethapyr	Acrolein	Mancozeb
Acetochlor	**Imidacloprid**	Amitraz	Mefenoxam
Alachlor	Iprodione	Azoxystrobin	Methamidophos
Aldicarb	**Lindane (*gamma*-HCH)**	Brodifacoum	Methoprene
Atrazine	**Linuron**	Butoxypolypropylene glycol	Methoxichlor
Azinphos-methyl	**Malathion**	Captan	Metiram
Bendiocarb	**MCPA**	Chlorethoxyfos	Moxidectin
Benomyl	**Metalaxyl**	Chlorophenoxy	Naled
Bentazon	Methidathion	Chlorosulfuron	Oxytetracycline
Bifenthrin	**Methomyl**	Clofentezine	Oxythioquinox
Bromacil	**Methyl-parathion**	Clomazone	Paraquat
Bromoxynil	**Metolachlor**	Coumaphos	Phosphamidon
Butylate	**Metribuzin**	Cyhexatin	Piperonyl butoxide
Carbaryl	**Metsulfuron-methyl**	Cymoxanil	Pirimiphos-methyl
Carbofuran	**Myclobutanil**	Dicofol	Polybutene
Chlorothalonil	**Norflurazon**	Diflubenzuron	Pyridaben
Chlorpyrifos	**Oryzalin**	Dimethenamid	Pyriporyfen
Clopyralid	Oxamyl	Dipropyl isocinchomeronate	Quizalofop-ethyl
Cyanazine	**Oxyfluorfen**	Dodine	Rimsulfuron
Cyfluthrin	**Pendimethalin**	Doramectin	Ronnel
lambda-Cyhalothrin	*cis*-Permethrin	Eprinomectin	Rotenone
Cypermethrin	Phorate	Esfenvalerate	Sethoxydim
Diazinon	**Phosmet**	Famphur	Spinosad
Dicamba	**Picloram**	Fenarimol	Tebuconazole
Dichlorvos	**Propargite**	Fenbutatin-oxide	Tetrachlorovinphos
Dimethoate	**Propiconazole**[4]	Fenvalerate	Thifensulfuron
Disulfoton	**Simazine**	Fluazifop-P-butyl	Thiram
Diuron	**Sulfometuron-methyl**	Flucythrinate	Triadimefon
EPTC	Tefluthrin	Flufenacet	Trichlorfon
Endosulfan[2]	**Terbacil**	Formetanate hydrochloride	Trifloyxstrobin
Ethalfluralin	Terbufos	Fosetyl-aluminum	Triflumizole
Ethion	Triallate	Glyphosate	Triphenyltin hydroxide
Ethoprophos	Tribenuron-methyl	Hexythiazox	Ziram
Fenthion	Triclopyr	Hydramethylnon	
Fonofos	**Trifluralin**		
alpha-HCH[3]			

[1]The 2,4-D analysis measures the acid form of this herbicide that primarily results from its application as an amine salt. However, some 2,4-D acid is formed from the hydrolysis of various 2,4-D esters, including 2,4-D methyl ester.

[2]The laboratory analyzes the individual components *alpha*-Endosulfan and *beta*-Endosulfan.

[3]*alpha*-HCH is both an impurity in lindane and a degradate of lindane.

[4]Only the *cis*- and *trans*-isomers were analyzed. Both were detected.

Table 4. Pesticide detection frequency in samples collected in July and October 2000, Yakima River Basin, Washington.

[**Abbreviations**: µg/L, microgram per liter; –, no detections]

Compound	July detection frequency (in percent)			October detection frequency (in percent)		
	Number of samples	Unscreened	Screened at 0.02 µg/L	Numer of samples	Unscreened	Screened at 0.02 µg/L
Parent pesticides						
2,4-D	51	84	82	33	12	3
2,4-D methyl ester	51	49	29	33	–	–
Acetochlor	51	14	2	33	–	–
Alachlor	51	16	4	33	3	–
Atrazine	51	82	27	33	70	15
Azinphos-methyl	51	37	37	33	–	–
Bentazon	51	35	14	33	30	18
Bifenthrin	51	2	–	33	–	–
Bromacil	51	14	8	33	33	12
Bromoxynil	51	10	4	33	–	–
Carbaryl	51	24	14	33	–	–
Carbofuran	51	–	–	33	3	3
Chlorpyrifos	51	12	2	33	–	–
Clopyralid	51	–	–	33	3	–
Cyanazine	51	2	–	33	–	–
Diazinon	51	2	2	33	–	–
Dicamba	51	20	18	33	–	–
Dieldrin	49	4	–	33	–	–
Dimethoate	51	4	2	33	–	–
Dinoseb	51	12	4	33	12	–
Disulfoton	51	2	–	33	–	–
Diuron	51	37	24	33	30	6
EPTC	49	41	4	28	4	–
Ethalfluralin	51	10	2	33	–	–
Fluometuron	51	2	–	33	–	–
gamma-HCH	51	2	–	33	–	–
Hexazinone	51	37	–	33	12	–
Imidacloprid	51	2	2	33	–	–
Linuron	51	–	–	33	3	–
Malathion	51	6	2	33	–	–
MCPA	51	2	2	33	–	–
MCPB	51	2	–	33	–	–
Metalaxyl	51	2	–	33	6	–
Methomyl	51	10	10	33	–	–
Methyl-parathion	51	2	2	33	–	–
Metolachlor	51	2	–	33	–	–
Metribuzin	51	2	–	33	–	–
Metsulfuron-methyl	51	8	4	33	–	–
Myclobutanil	51	33	12	33	6	–
Nicosulfuron	51	2	2	33	–	–
Norflurazon	51	25	4	33	30	3
Oryzalin	51	–	–	33	3	–
Oxyfluorfen	51	2	–	33	–	–
Pendimethalin	51	8	2	33	–	–
Phosmet	51	2	2	33	–	–
Picloram	51	4	4	33	–	–
Prometon	51	–	–	33	6	–
Propargite	50	6	2	33	–	–
cis-Propiconazole	51	2	–	33	–	–
trans-Propiconazole	51	2	–	33	–	–

Table 4. Pesticide detection frequency in samples collected in July and October 2000, Yakima River Basin, Washington.—Continued

[**Abbreviations**: µg/L, microgram per liter; –, no detections]

Compound	July detection frequency (in percent)			October detection frequency (in percent)		
	Number of samples	Unscreened	Screened at 0.02 µg/L	Numer of samples	Unscreened	Screened at 0.02 µg/L
Parent pesticides—Continued						
Simazine	51	22	6	33	36	6
Sulfometuron-methyl	51	2	–	33	–	–
Tebuthiuron	51	–	–	33	3	–
Terbacil	51	16	16	33	3	3
Trifluralin	51	20	–	33	–	–
Pesticide degradates						
1,4-Napthaquinone	51	4	4	33	–	–
1-Naphthol	51	18	6	33	–	–
2-(4-tert-butylphenoxy)-cyclohexanol	51	25	–	33	3	–
2-Hydroxyatrazine	51	16	8	33	39	–
3,4-Dichloroaniline	51	4	–	33	3	–
4,4'-Dichlorobenzophenone	51	14	–	33	–	–
p,p'-DDE	50	42	–	33	36	–
Deethylatrazine	51	80	22	33	82	27
Deisopropylatrazine	51	8	6	33	12	3
Didealkylatrazine	51	18	4	33	21	9
Disulfoton sulfone	51	16	10	33	–	–
Disulfoton sulfoxide	51	8	8	33	–	–
Endosulfan sulfate	51	14	–	33	–	–
Fenamiphos sulfoxide	51	4	2	33	–	–

Figure 5. Pesticide concentrations in samples collected in the Yakima River Basin, Washington, July and October 2000.

Table 5. Pesticides for which samples were analyzed during this study, but with no record of application in the Yakima River Basin, Washington, in 2000.

[**Bold** type indicates pesticide was detected at least once in 2000]

Acifluorfen	Neburon
Benfluralin	**Nicosulfuron**
Bensulfuron-methyl	Parathion
Chloramben methyl ester	Pebulate
Chlorimuron-ethyl	Profenofos
Cycloate	**Prometon**
Dacthal	Prometryn
Dichlorprop	Propachlor
Dicrotophos	Propanil
Dieldrin	Propetamphos
Dimethomorph[1]	Propham
Dinoseb	Propoxur
Diphenamid	Propyzamide
Fenamiphos	Siduron
Fenuron	Sulfotepp
Flumetralin	Sulprofos
Flumetsulam	Tebupirimphos
Fluometuron	**Tebuthiuron**
Isofenphos	Temephos
MCPB	Terbuthylazine
Methiocarb	Thiobencarb
Molinate	Tribuphos
Napropamide	

[1]Two isomers of dimethomorph were analyzed, designated (E)-dimethomorph and (Z)-dimethomorph.

Pesticide Mixtures

More than 90 percent of the July samples and 79 percent of the October samples contained at least two pesticides or degradates (fig. 6). In July, the median number of chemicals in a mixture was 9, and the maximum was 26. In October, the median number of chemicals in a mixture was 5, and the maximum was 13. The most frequently occurring herbicides in mixtures were atrazine, 2,4-D, and the degradate deethylatrazine. The most frequently occurring insecticides in mixtures were azinphos-methyl, carbaryl, and *p,p'*-DDE (a degradate of DDT).

Research to understand the impact of mixtures of pesticides on human health and aquatic life is in its early stages (Mileson 1999/2000; Richardson and others, 2001). For some pesticide mixtures, test organisms in laboratory studies are affected by the compounds in the mix as if they were exposed to each compound individually (additive effect)—the total toxicity to the test organisms is represented as the toxicity due to compound 1 plus the toxicity due to compound 2 plus the toxicity due to compound 3, and so on. For other mixtures, test organisms respond as if they were exposed to lower concentrations of both compounds; that is, the mixture is less toxic than the summation of the individual compounds (antagonistic or protective effect). The opposite effect also has been observed—mixtures of some pesticides are more toxic than their individual components (synergistic effect) (Danish Veterinary and Food Administration, 2003).

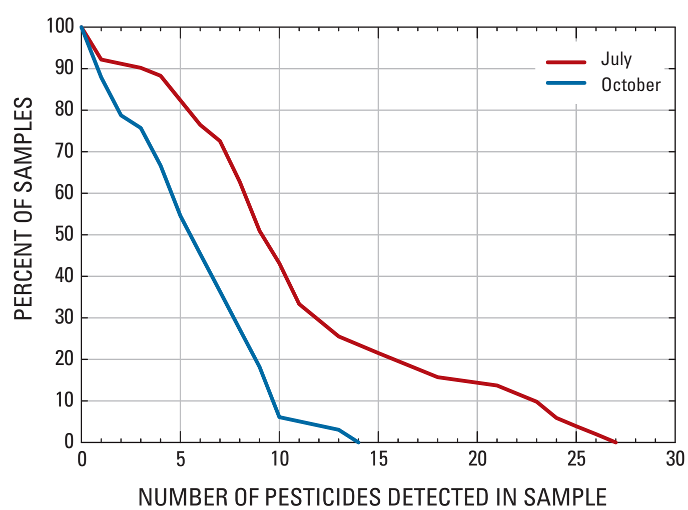

Figure 6. Frequency of detecting multiple pesticides in a sample, Yakima River Basin, Washington, 2000.

The EPA has taken the initial steps to regulate mixtures of pesticides by conducting exposure and risk assessments for groups of chemicals having a common mode of toxicity. The first of these assessments has been completed for the organophosphate insecticides, which include azinphos-methyl and diazinon (U.S. Environmental Protection Agency, 2002b). Additional cumulative risk assessments are in progress for N-methyl carbamate, triazine, and chloroacetanilide pesticides. Changes in pesticide handling and application required by these risk assessments are designed to protect human health, but also could help reduce environmental contamination. Guidelines to protect aquatic life, however, remain based on single chemical exposures and, for reasons already noted, probably do not reflect the actual toxicity when multiple pesticides are present. In addition, existing guidelines are based on mortality from direct toxicity and do not consider behavioral (Sholtz and others, 2000) and physiological changes (Hayes and others, 2006) that are detrimental to the reproduction and survival of an organism.

Pesticide Degradates

In addition to the analyses for parent pesticides, samples were analyzed for 54 pesticide degradates (table 6). Degradates are important because many maintain pesticidal action. Some pesticides, such as diazinon, produce a degradate that is more toxic than the parent (Agency for Toxic Substances and Disease Registry, 1996). Understanding and monitoring degradates can provide insight into the pathways through which pesticides are transported into waterways. During this study, 14 degradates were detected among the July and October samples. Four triazine herbicide degradates (deethylatrazine, deisopropylatrazine, deethyldeisopropylatrazine, and 2-hydroxy-atrazine) were among the most commonly detected. Degradates of the insecticides carbaryl (1-naphthol and 1,4-naphthoquinone) and DDT (*p,p'*-DDE and 4,4'-dichlorobenzophenone) also were detected regularly in water samples. DDT was used widely in the Yakima River Basin prior to its cancellation in 1972.

Table 6. Pesticide degradates for which samples were analyzed during this study, Yakima River Basin, Washington.

[**Bold** type indicates the compound was detected at least once in 2000]

Parent product applied		Parent product not applied
3-(4-chlorophenyl)-1-methyl urea	**Deisopropylatrazine**	2,5-Dichloroaniline
1,4-Naphthaquinone	**Didealkylatrazine**	3-Trifluoromethyl-aniline
1-Naphthol	**Disulfoton sulfone**	4-Chlorobenzylmethyl sulfone
2-(4-tert-butylphenoxy)-cyclohexanol	**Disulfoton sulfoxide**	**4,4'-Dichlorobenzophenone**[1]
2,6-Diethylaniline	Endosulfan ether	Dacthal monoacid
2-[2-Ethyl-6-methylphenyl) amino]-1-propanol	**Endosulfan sulfate**	Fenamiphos sulfone
2-Amino-N-isopropylbenzamide	Ethion monoxon	**Fenamiphos sulfoxide**
2-Chloro-2,6-diethyl-acetanilide	Fenthion sulfoxide	***p,p'*-DDE** [1]
2-Ethyl-6-methylaniline	Fonofos oxygen analog	Paraoxon-ethyl
2-Hydroxyatrazine	Malaoxon	Tebupirimphos oxygen analogue
3,4-Dichloroaniline	Methomyl oxime	
3,5-Dichloroaniline	*cis*-Methyl-3-(2,2-dichloro-vinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate	
3-Hydroxycarbofuran	*trans*-Methyl-3-(2,2-dichloro-vinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate	
3-Ketocarbofuran	O-Ethyl-O-methyl-S-propylphosphorothioate	
3-Phenoxybenzyl alcohol	Oxamyl oxime	
4-(Hydroxymethyl) pendimethalin	Paraoxon-methyl	
4-Chloro-2-methylphenol	Phorate oxon	
Aldicarb sulfone	Phosmet oxon	
Aldicarb sulfoxide	TCPSA ethyl ester	
Azinphos-methyl oxon	Tefluthrin metabolite [R 119364]	
Chlorpyrifos oxon	Tefluthrin metabolite [R 152912]	
Deethylatrazine	Terbufos-O-analogue sulfone	

[1]Degradate of DDT (dichlorodiphenyltrichloroethane). Prior to its cancellation in 1972, DDT was widely applied in the Yakima River Basin.

Spatial Distribution

The Yakima River Basin has three large, distinct agricultural areas with about 450,000 ha in cultivation: the Kittitas Valley, the Mid Valley, and the Lower Valley (fig. 7). The Kittitas Valley is the most northern of the agricultural areas. Most of the farmland in this region is devoted to raising timothy hay. Other hays, small grains, sweet corn, potatoes, and apples also are grown in this area. The Mid Valley agricultural area surrounds the city of Yakima.

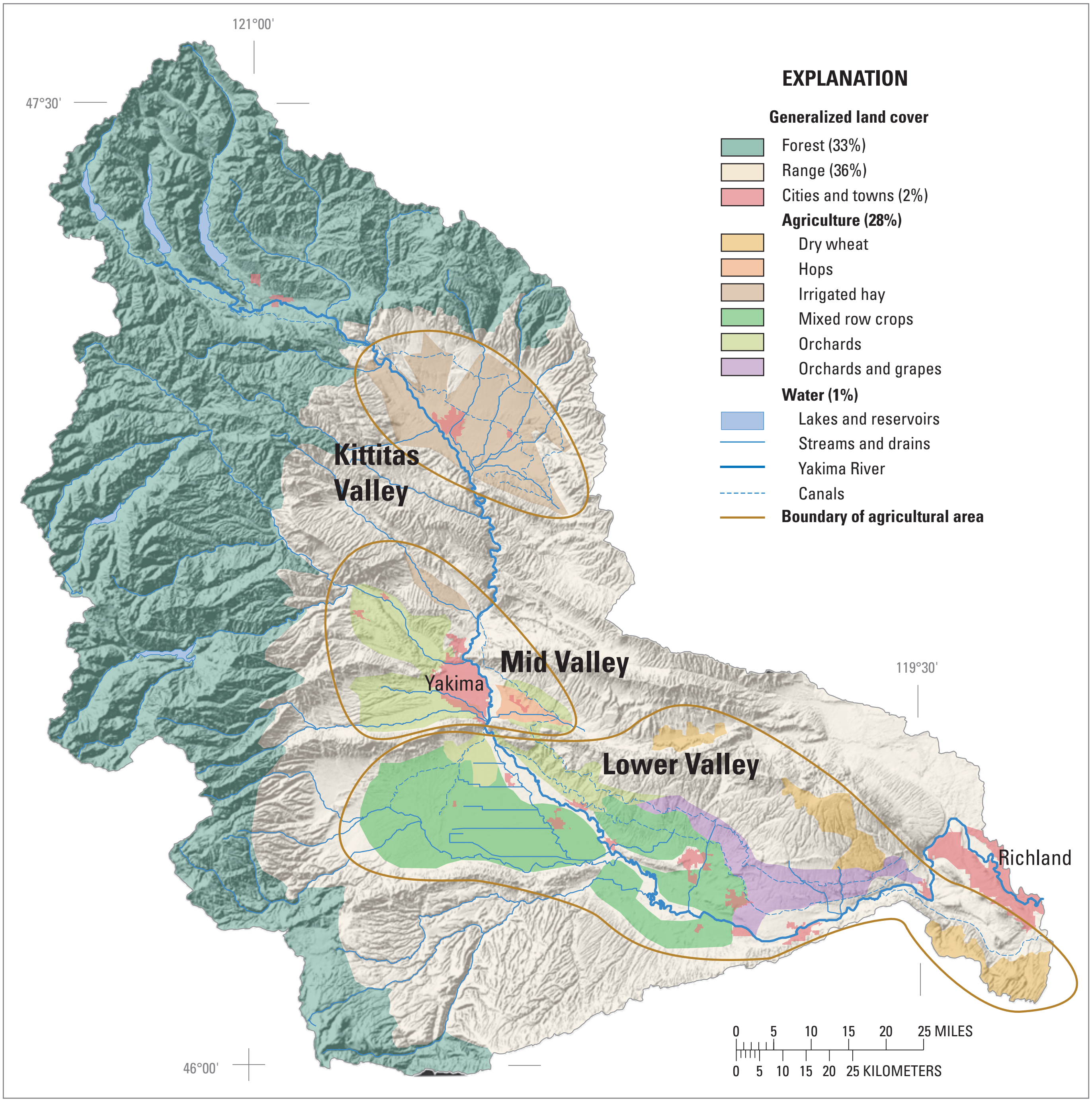

Figure 7. Land cover of the Yakima River Basin, Washington, 2001. (Source: Fuhrer and others, 2004.)

Hops and fruit orchards (primarily apples and pears) are the major crops produced in this part of the Yakima River Basin. The Lower Valley begins south of the city of Yakima and extends to Richland, and is the largest of the three agricultural areas. A large variety of crops are grown in this region, including tree-fruit orchards (apples, pears, cherries, nectarines, apricots), juice grapes, wine grapes, feed corn, alfalfa hay, hops, asparagus, mint, sweet corn, potatoes, and onions, along with a variety of other minor crops. In addition, more than 250,000 cattle are raised for milk and beef in this area and are an important part of the agricultural landscape.

The spatial distribution of pesticide detections in the Yakima River Basin is summarized in table 7. Sites in the Kittitas Valley were dominated by detections of herbicide and herbicide degradates. Sites in the Mid Valley and Lower Valley contained complex mixtures of herbicides, fungicides, insecticides, and degradates, which reflect differences in crop patterns noted above.

Table 7. Number of pesticides detected in water samples from sites sampled in July and October 2000, Yakima River Basin, Washington.

[Map reference numbers are shown on plate 1. **Abbreviations**: H, herbicides; I, insectides; F, fungicides; D, pesticide degradates; –, no detections]

Region	Map reference No.	July				October			
		H	I	F	D	H	I	F	D
Kittitas Valley									
Kittitas	47	5	–	–	3	1	–	–	2
Kittitas	48	3	–	–	3	1	–	–	2
Kittitas	49	3	–	–	1	–	–	–	1
Kittitas	62	6	1	–	3	*Not sampled*			
Kittitas	84	3	–	–	1	–	–	–	2
Kittitas	85	3	–	–	2	1	–	–	–
Kittitas	95	7	–	–	2	2	–	–	2
Kittitas	96	11	–	–	2	2	–	–	2
Kittitas	108	3	–	–	–	*Dry*			
Kittitas	114	5	–	–	2	*Dry*			
Mid Valley									
Umtanum	66	–	–	–	1	–	–	–	–
Moxee	2	2	1	–	1	2	1	–	1
Moxee	12	7	–	1	2	1	–	–	–
Moxee	69	3	1	1	4	4	–	–	2
Moxee	97	5	–	1	3	1	–	–	2
Moxee	109	5	–	–	2	*Dry*			
Moxee	115	2	1	–	2	*Dry*			
Ahtanum-Wide Hollow	14	2	2	1	2	*Dry*			
Ahtanum-Wide Hollow	99	–	–	–	–	–	–	–	–
Ahtanum-Wide Hollow	107	–	–	–	–	–	–	–	–
Ahtanum-Wide Hollow	119	–	–	–	–	*Dry*			
Lower Valley									
Buena-Zillah	26	2	1	1	4	*Dry*			
Buena-Zillah	27	8	1	–	2	3	–	–	2
Buena-Zillah	28	3	2	1	5	*Dry*			
Buena-Zillah	120	2	3	1	4	*Dry*			
Toppenish	59	*Dry*				*Dry*			
Granger	50	7	2	–	5	5	–	–	3
Granger	67	9	1	–	5	4	–	–	4
Granger	92	10	2	–	3	2	–	–	2
Granger	100	12	3	–	3	2	–	–	3
Granger	101	17	2	–	5	5	–	–	4
Granger	135	5	1	–	1	*Dry*			
Satus	51	13	2	1	9	*Dry*			
Satus	74	–	–	–	–	–	–	–	–
Satus	93	15	2	–	6	5	–	–	2

Table 7. Number of pesticides detected in water samples from sites sampled in July and October 2000, Yakima River Basin, Washington.—Continued

[Map reference numbers are shown on plate 1. **Abbreviations**: H, herbicides; I, insecticides; F, fungicides; D, pesticide degradates; –, no detections]

Region	Map reference No.	July				October			
		H	I	F	D	H	I	F	D
Lower Valley—Continued									
Satus	102	14	2	1	4	6	–	–	3
Satus	113	14	3	1	5	*Dry*			
Sulphur	29	13	6	–	7	9	–	–	4
Sulphur	52	*Dry*				*Dry*			
Sulphur	53	6	1	3	2	*Dry*			
Sulphur	63	11	–	–	4	7	–	–	3
Sulphur	103	5	–	–	5	3	–	–	4
Sulphur	104	9	3	1	8	5	–	–	1
Sulphur	110	4	1	–	1	*Dry*			
Sulphur	112	4	2	–	2	*Dry*			
Sulphur	116	3	1	–	1	*Dry*			
Downstream of Sulphur	54	6	2	2	2	3	–	2	4
Downstream of Sulphur	55	4	1	1	2	4	–	–	1
Downstream of Sulphur	56	*Dry*				*Dry*			
Downstream of Sulphur	57	*Dry*				*Dry*			
Downstream of Sulphur	58	*Dry*				*Dry*			
Downstream of Sulphur	83	4	1	–	2	*Dry*			
Downstream of Sulphur	87	5	2	1	1	4	–	1	3
Downstream of Sulphur	88	5	1	1	1	6	1	–	2
Downstream of Sulphur	105	6	1	1	2	3	–	–	3
Downstream of Sulphur	106	4	2	–	2	5	–	1	1

Temporal Distribution

With few exceptions, samples collected in July contained more pesticides than samples collected in October (table 7). In addition, the number of pesticides detected in July was larger (63 pesticides and degradates) compared with October (27 pesticides and degradates; table 4). Concentrations of pesticides generally were greater in July than in October or they were comparable between the two samples. Rarely were concentrations greater in October. These observations are consistent with greater pesticide use during the growing season and the availability of water to transport them off the plants and fields to which they were applied.

It is notable however, that most of the samples collected in October did contain at least one pesticide (82 percent contained deethylatrazine and 70 percent contained atrazine). Few insecticides or insecticide degradates were detected in October. In mid-October 2000, the irrigation canals were drained, and at most sites, the water in the streams and drains at the time of sampling was entirely ground-water discharge, which occurs either as seepage directly into open-channel drains and streams or as seepage into onfield and regional tile drains. It is possible, however, that a few sites might have been receiving water from onfarm storage ponds that were being drained at the end of the season. The incidence of pesticide detections after mid-October suggests there is widespread, low-level contamination of the shallow ground water in agricultural areas of the Yakima River Basin. Subsequent investigations in the Lower Valley have provided additional information about the role of ground water in pesticide transport (Capel and others, 2004; Steele and others, in press, 2007).

Based on the limited data available, it seems unlikely that insecticides are distributed widely in the ground water. However, chronic, low-level exposure to a mixture of herbicides and their degradation products is likely for residents drinking from shallow wells in some parts of the Yakima River Basin. The effects of long-term exposure to low-level herbicide concentrations have not been well studied, in part because widespread herbicide use dates only to the 1960s, and chronic health effects often take decades to manifest themselves. The few studies available in the literature suggest a potential link between long-term, drinking water exposure to herbicide exposure and increased incidences of cancer (Kettles and others, 1997; Van Leeuwen and others, 1999) and retarded fetal development (Munger and others, 1997). All three studies acknowledge their limitations and urge additional studies to verify the preliminary findings.

Pesticide-Transport Processes

Many factors affect the mobility of pesticides in the environment, such as the manner, amount, frequency, and timing of application; the method of irrigation; the chemical properties of the pesticide; soil properties; land slope; and proximity to flowing water. The poor relation between application rates and detection frequency[2] from the July 2000 sampling (fig. 8) illustrates the end result of a multitude of contingencies that determine the fate of a pesticide after it is applied. Some pesticides, such as the insecticides azinphos-methyl and chlorpyrifos, were detected less often than expected solely on the basis of their application rates. Conversely, some pesticides, such as the herbicide atrazine, were detected more frequently than expected. Among the universe of possibilities, two factors explained a large part of the variation observed in samples collected from small agricultural catchments in July 2000: the K_{oc} value (see Sidebar 2: Organic Carbon-Water Partitioning Coefficient, K_{oc}) and the method of irrigation. The K_{oc} value for each pesticide (U.S. Department of Agriculture, 2005) is included in figure 8. Pesticides with a high K_{oc} value were detected at a lower frequency than might be expected for their application amounts; whereas, pesticides with a low K_{oc} value were often detected at a higher frequency than might be expected for their application amounts. This general pattern was not observed with other pesticide physical properties such as solubility, half life, or volatility.

[2] Detection frequencies presented in figure 8 are calculated from concentration data screened at 0.02 µg/L because comparisons are being made between pesticides (for unscreened frequencies, refer to table 4).

Sidebar 2: Organic Carbon-Water Partitioning Coefficient, K_{oc}

When a pesticide is first applied, most of it is bound to soil or plant surfaces. When irrigation water or rain reaches a treated field, a portion of the pesticide dissolves into the water. The amount of pesticide that dissolves in the water is controlled by a property of the pesticide called its organic carbon-water partitioning coefficient, or K_{oc}. A pesticide with a large K_{oc} value will remain largely bound to the soil or plant material and only a small amount will dissolve in the water. Conversely, a pesticide with a small K_{oc} value will detach more readily from the soil or plant material and dissolve in the water. The maximum amount of pesticide that will dissolve in the water is limited by the solubility of the pesticide. K_{oc} values for currently used pesticides range from less than 10 (dicamba, clopyralid) to more than 100,000 (bifenthrin, oxyfluorfen).

In most soils, the fraction of organic material is small compared with the inorganic mineral fraction (sand and clay), however, this small fraction of organic material is responsible for most of the pesticide retention capacity of soils. Soils with more organic material potentially can retain more pesticides than soils with a lesser amount. The organic-matter content of soils from catchments in this study ranged from 0.4 to 1.2 percent by weight (mean = 0.57, standard deviation = 0.22), which is low compared to other agricultural soils in the United States (typically around 5 percent organic-matter content [Brady and Weil, 2002]). There was no discernible difference in the instream pesticide concentrations or pesticide losses due to differences in soil organic matter at the sites in this study; however, this may have been due to the resolution of the soils data available for the Yakima River Basin at the time of this study.

Further study of figure 8 shows some exceptions to this generality. For example, the K_{oc} values for the herbicides simazine and atrazine are similar, yet atrazine is detected more frequently than simazine despite less usage. Most simazine use is in orchards and vineyards, many of which use sprinkler or drip irrigation; whereas, most atrazine use is on corn, which mostly is rill irrigated. Thus, knowledge of the irrigation method in addition to the K_{oc} values provides more insight into pesticide movement than the K_{oc} values alone.

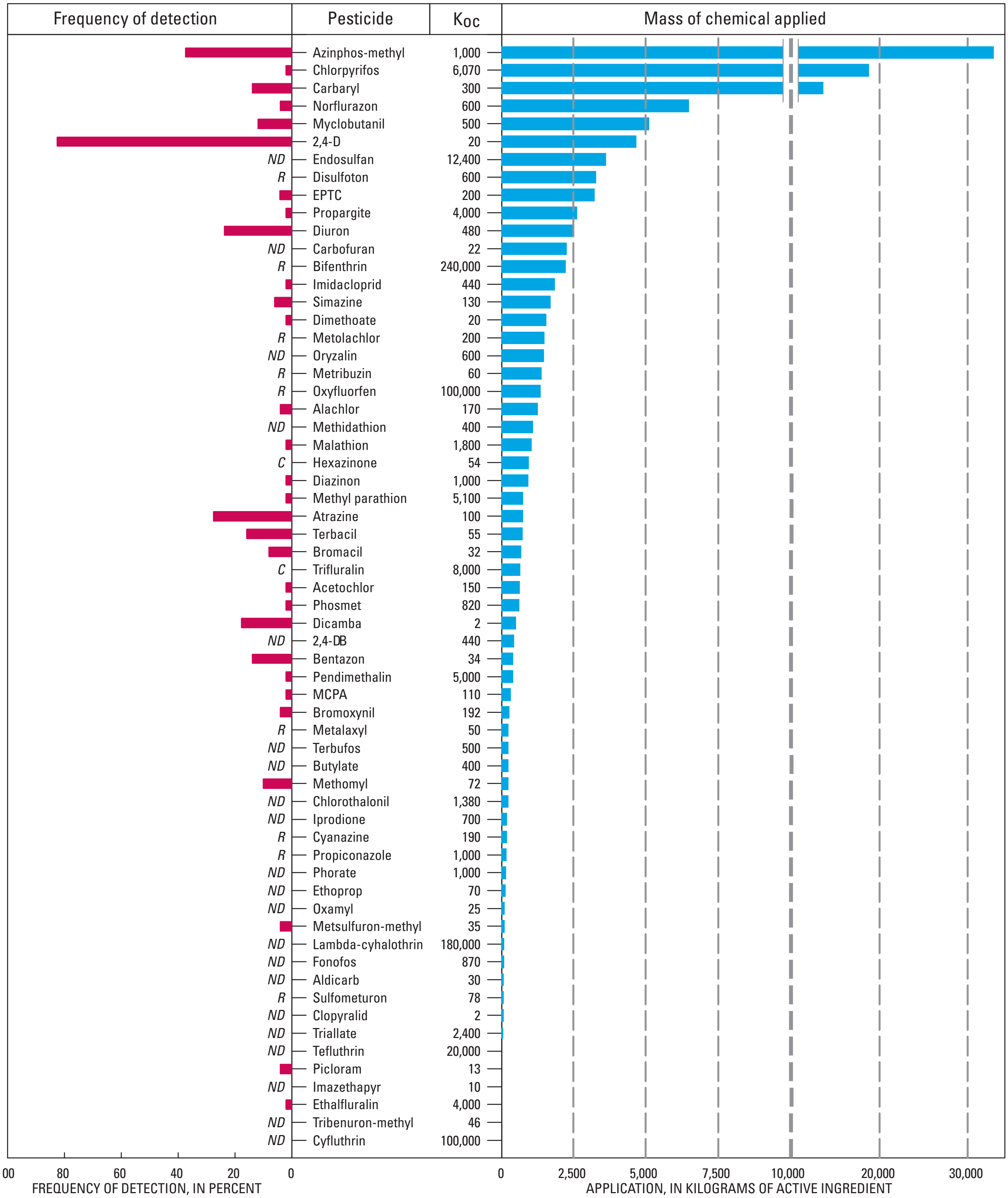

Figure 8. Comparison of frequency of pesticide detections in July 2000 and estimates of pesticide applications during the 2000 growing season, Yakima River Basin, Washington. Frequencies were determined using pesticide concentrations screened at 0.02 µg/L (*C*, commonly detected below screening value; *R*, rarely detected below screening value; *ND*, not detected). Organic carbon-water partitioning coefficient (K_{oc}) values were obtained from the U.S. Department of Agriculture WIN-PST program (http://www.wsi.nrcs.usda.gov/products/W2Q/pest/winpst.html), accessed Sept. 24, 2007). K_{oc} values are reported in milliliters per gram.

Pesticide Loss—Calculation

One method to quantify the relation between pesticide applications and detections is to calculate the pesticide loss, which is a ratio of the mass of pesticide in the stream to the mass applied. Besides compressing application and detection data into a single value, the advantage of a mass-based loss statistic is that the data are normalized to catchment size and stream flow, and, therefore, comparison among catchments can be made readily. For additional examples of the use of pesticide loss statistics refer to Larson and others (1997) and references therein.

Using estimated pesticide-application data for 2000 and the pesticide concentrations and discharge from July 2000, the pesticide loss was calculated for each pesticide in each catchment. Because the contributing area to a canal is indeterminate, samples from canals are excluded from this part of the analysis. The pesticide loss was calculated as follows:

For each catchment, y, and for each pesticide detected, x,

$$\text{Pesticide Loss}_{xy} = \log\left(\frac{\text{daily mass of pesticide x in water sample from catchment } y \text{ (g/d)}}{\text{annual mass of pesticide } x \text{ applied in catchment } y \text{ (g/yr)}}\right),$$

where

$$\text{mass of pesticide in water sample from catchment } y = Q_y \times C_{xy} \times k,$$

where

Q_y is instantaneous discharge, in cubic meters per second,

C_{xy} is pesticide concentration, in micrograms per liter, and

k is 86.4, units conversion constant ($m^3 \rightarrow L$; $s \rightarrow d$; $\mu g \rightarrow g$),

and

$$\text{mass of pesticide applied in catchment} = \sum_{i=1}^{n} R_i * A_i,$$

where

R_i is rate of application for crop i, in grams per hectare per year, and

A_i is area of crop i in catchment, in hectares.

Because the loss values span nearly eight orders of magnitude, the common log (base 10) of the resulting value was used. The units conversion factor scales the calculated runoff mass to a daily value, *that is,* the instantaneous mass measured at the time of sampling is considered to be representative of the daily mass moving through that waterway. The applied mass is calculated using only applications expected to have been made through the end of July.

Large annual variations in pesticide concentrations have been measured in streams and drains of the Yakima River Basin by various studies conducted since the late 1980s (Rinella and others, 1999; Ebbert and Embrey, 2002; U.S. Geological Survey, 2007). The pesticide losses calculated and discussed herein represent the concentration measured once at each site during a 2-week period in July 2000. Despite the limited temporal nature of this data set, meaningful insights into pesticide-transport processes are possible due to the large spatial coverage and the large number of pesticides analyzed.

Pesticide Loss—Implications for Pesticide Transport

The calculated pesticide losses are shown in figure 9. The loss data are arranged along the x-axis in order of increasing K_{oc} value. At higher K_{oc} values there are fewer high-loss values and more low-loss values. The amount of variation of losses for any single pesticide is considerable, ranging up to five orders of magnitude. This relation is quantitatively depicted in figure 10 by substituting the K_{oc} value for pesticide along the x-axis. Despite large variability, a highly significant ($p < 0.0001$) negative correlation between K_{oc} and pesticide loss was observed. Larger pesticide losses were associated with pesticides having low K_{oc} values compared with pesticides having high K_{oc} values. In other words, for pesticides with low K_{oc} values, a larger fraction of the applied pesticide was transported off the field and into waterways.

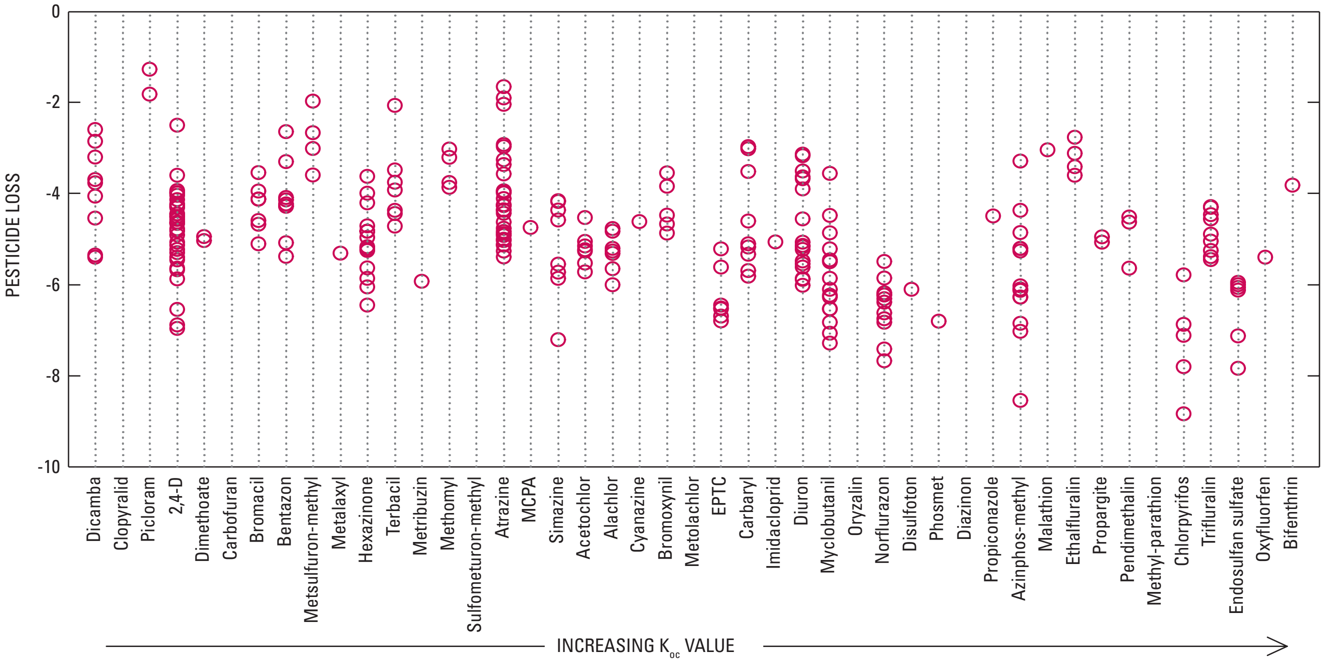

Figure 9. Pesticides and losses arranged in order of increasing organic carbon-water partitioning coefficient (K_{oc}) value, Yakima River Basin, Washington, 2000. The loss generally decreases as the K_{oc} value increases, although the variability for a single pesticide is large.

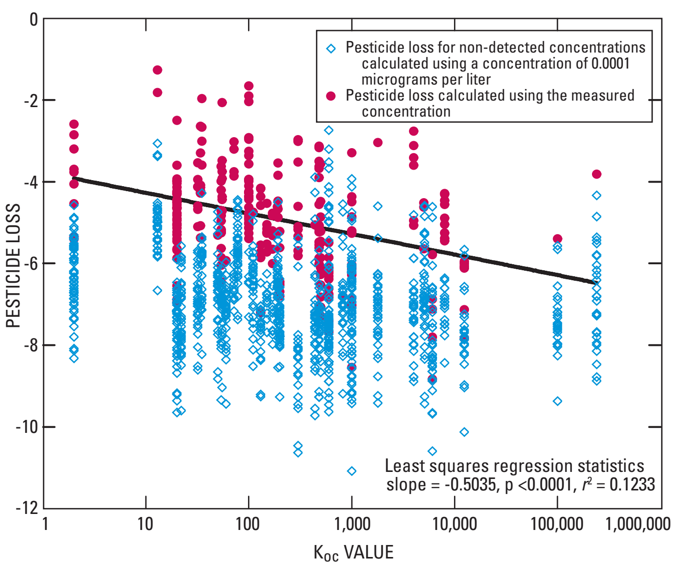

Figure 10. Relation between pesticide organic carbon-water partitioning coefficient (K_{oc}) value and pesticide loss, Yakima River Basin, Washington, 2000. Hypothetical pesticide losses were calculated for sites where a pesticide was reported to have been used, but where concentrations were below the detection level. A concentration of 0.0001 microgram per liter was used to calculate the hypothetical losses. Line shows the ordinary least-squares regression fit through losses of detected pesticides.

More than one-half of the potential-loss values could not be calculated because the pesticide was not detected at the site. In some cases, the pesticide truly may not be present. In most cases, the more likely scenario is that it was present, but at a concentration below the detection limit of the laboratory. To better assess the full range of potential-loss values, a small, but nonzero concentration was assumed to be present in waters with no detections. A concentration of 0.0001 µg/L was chosen, which is approximately one order of magnitude smaller than the lowest RL. The results of this exercise are presented in figure 10. A similar trend of decreasing loss with increasing K_{oc} is apparent in the loss values estimated for nondetected concentrations.

The relations presented in figures 9 and 10 are weak considering the large variability in the loss values for any given K_{oc} value. To attempt to improve the relations, additional explanatory variables were considered in the analysis, including solubility, soil half-life, soil-clay content, soil erosivity, soil organic-matter content, soil permeability, catchment area, catchment slope, irrigation method, and crop type. Among these, only irrigation method provided further insight into the relations observed in figures 9 and 10.

Figure 11 shows the relation between pesticide loss and the percent of the catchment using sprinkler or drip irrigation. A clear pattern emerges when losses are grouped by K_{oc} value. Losses of pesticides with K_{oc} values greater than or equal to 300 were assigned to the “high” group, and less than 300 were assigned to the “low” group.

Losses of pesticides with high K_{oc} values

Losses of pesticides with high K_{oc} values declined as the percentage of sprinkler and drip irrigation increases (fig. 11). This relation is due to both the sorptive nature of the pesticides and to a reduction in sediment washed from fields in catchments with widespread use of sprinkler and drip irrigation. Because of a greater affinity to soil and other organic material, pesticides with high K_{oc} values are more likely to have a longer residence time at the place of application, which increases the time for physical and biological processes to degrade the chemicals. Onfield residence time is further increased by the use of sprinkler or drip irrigation, which produce little or no sediment-bearing runoff (fig. 12) compared with rill irrigation.

Despite the significant positive correlation between suspended sediment and loss of high K_{oc} pesticides (fig. 13), a negligible fraction of most pesticides is sorbed to the suspended sediment measured in the stream. Squillace and Thurman (1992) calculated that 99 percent of the atrazine is transported in the dissolved phase, even at relatively high concentrations of suspended sediment (700 mg/L). Their result was corroborated by laboratory analyses that demonstrated no analytical difference between the concentration of atrazine in a centrifuged sample and the concentration of total atrazine in unfiltered, uncentrifuged water. For the purposes of this report, atrazine is considered to have a low K_{oc} value (around 100 mL/g); however, Ebbert and Kim (1998) calculated the theoretical

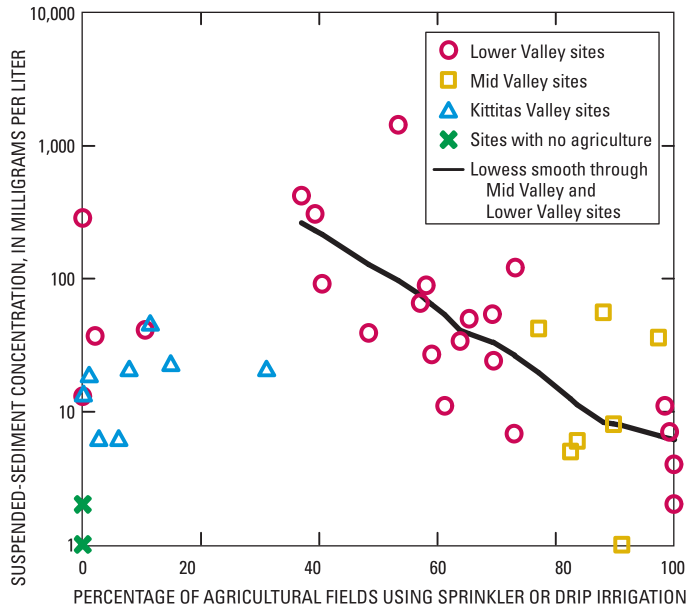

Figure 12. Relation between percentage of sprinkler or drip irrigation used in catchment and suspended-sediment concentrations, Yakima River Basin, Washington, 2000. Suspended-sediment concentrations tend to decrease with increasing use of sprinkler or drip irrigation at most sites in the Mid Valley and Lower Valley. Suspended-sediment concentrations are lower at Kittitas Valley sites considering the low use of sprinkler or drip irrigation.

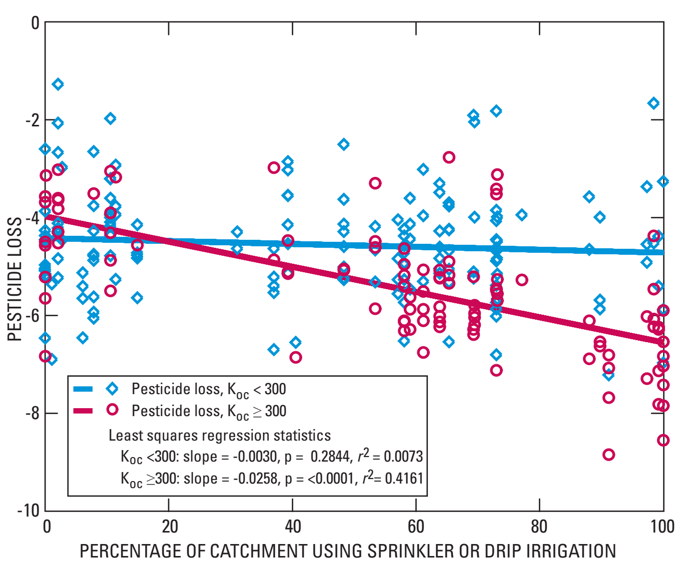

Figure 11. Relation between pesticide loss and irrigation method, Yakima River Basin, Washington, 2000. Lines shown are ordinary least-squares regression fits through points of the same color.

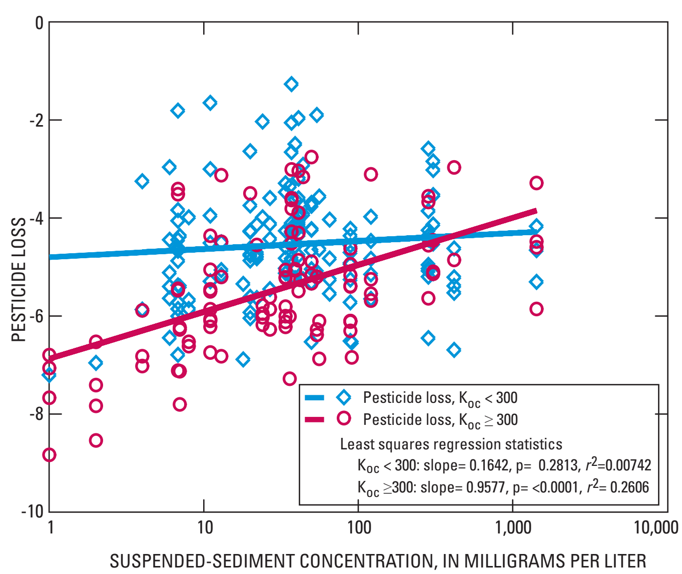

Figure 13. Relation between suspended-sediment concentration and pesticide loss, Yakima River Basin, Washington, 2000. Lines shown are ordinary least-squares regression fits through points of the same color.

dissolved fraction for a hypothetical pesticide with a moderately high K_{oc} value (20,000 mL/g) and determined that it also should occur primarily in the dissolved phase (97 percent). Rinella and others (1999) calculated the fraction of total pesticide expected to occur in the dissolved phase for a range of K_{oc} values (5,000–4,000,000 mL/g) and suspended-sediment concentrations (0–1000 mg/L) of known organic-carbon content in Yakima River Basin waterways. On the basis of the results of Rinella and others (1999), most pesticides with high K_{oc} values currently used in the Yakima River Basin should occur primarily in the dissolved phase. Major exceptions include pyrethroid insecticides and oxyfluorfen, a diphenyl ether herbicide, which have K_{oc} values greater than about 100,000 mL/g. At suspended-sediment concentrations commonly measured in streams and drains in the Yakima River Basin, up to one-half of the total mass of these pesticides with K_{oc} values exceeding 100,000 mL/g might be sorbed to suspended sediment.

The important relation between suspended sediment and pesticides is not at the scale of the stream or drain, but rather at the field scale where soil is first entrained and suspended by surface irrigation. It is here where significant desorption from soil particles occurs due a change in soil to water ratio. Equilibrium partitioning favors desorption of even high K_{oc} compounds from the soil, a process described in detail by Squillace and Thurman (1992) for atrazine in the Midwest United States, but applicable to the desorption of all pesticides. The observed relation between suspended sediment and pesticide loss is largely an effect of the irrigation method rather than a direct relation between the suspended sediment in the waterway and the pesticide loss (see Sidebar 3: Relation Between Irrigation Method and Suspended-Sediment Concentration). The implication for managing rill-irrigated fields is subtle, but important. Most farmers who use rill irrigation on their fields in the Yakima River Basin employ one or more sediment-control measures on their property. Measures that prevent sediment suspension during irrigation such as mulching furrows or the use of polyacrylamide (PAM) likely are to be more effective at preventing pesticides from leaving the field compared to sediment-control measures that prevent the off-farm migration of sediment-laden tail water such as grass-filter strips or sediment-retention ponds.

One final group of data has relevance to the issue of movement of high K_{oc} pesticides. As was noted earlier in the text, water collected from drains and streams during the October 2000 sampling was a good surrogate for the chemistry of the shallow ground-water system. With the exception of the DDT degradate, *p,p´*-DDE, all pesticides detected during this sampling had K_{oc} values less than or equal to 600 (table 8). Of the 27 detected pesticides, 19 had K_{oc} values less than 300. Pesticides with K_{oc} greater than 300 were infrequently detected or occurred at low concentrations. This pattern of occurrence suggests that pesticides with high K_{oc} values are being degraded or they are bound tightly to the soil and are not flushed routinely into the shallow ground water. All of the highly toxic pesticides included in this study had K_{oc} values greater than 300, and therefore widespread ground-water contamination by this group of pesticides is unlikely.

Sidebar 3: Relation between Irrigation Method And Suspended-Sediment Concentration

Suspended-sediment concentrations decreased with increasing use of sprinkler or drip irrigation at sites in the Mid Valley and Lower Valley. However, the trend was apparent only among sites where the sprinkler or drip was used in more than about 40 percent of the catchment. At smaller percentages of sprinkler or drip use, there is no relation between suspended-sediment concentration and irrigation method, although the data are sparse, and may be an artifact of the time sampling, onfarm sediment-management practices, or dilution by large inputs of canal spill or ground water.

In contrast to the relation observed among sites in the Mid Valley and Lower Valley, sites in the Kittitas Valley had no relation with irrigation practices and relatively low suspended-sediment concentrations, despite the fact that farms in this region have not widely adopted sprinkler- or drip-irrigation methods. Low suspended-sediment concentrations in the Kittitas Valley are most likely a result of the extensive fields of timothy hay for which the region is known. Timothy hay is a multiyear crop and establishes dense networks of roots near the surface that help retain soil despite the use of rill irrigation.

Losses of Pesticides with Low K_{oc} Values

There was no significant relation (p = 0.2844) between method of irrigation and losses of low K_{oc} pesticides (fig. 11) in data collected for this study. The lack of a strong association with irrigation method might be due to several confounding issues. First, many pesticides with low K_{oc} values are pre-plant or pre-emergent herbicides, and typically are applied between late April and early June. By mid-July, a large portion of the mass already may have been washed off the fields, thereby weakening the ability of this study to detect a relation with irrigation method. Although pesticides with low K_{oc} values do not strongly sorb to the soil, the use of rill irrigation is still expected to more readily transport these pesticides to streams and drains because the travel time through the soil and ground-water systems is orders of magnitude longer than overland flow. Second, in some catchments, the irrigation water delivered to the field already contains measurable amounts of pesticides (table 9), and most of these pesticides have low K_{oc} values. A lack of information about irrigation-water deliveries prior to and at the time of sampling precludes any attempt to estimate the importance of this source. Pesticides might be introduced to canal water in several ways, including discharge of field runoff directly into canals, drift, overspray, or atmospheric deposition. The third issue confounding the interpretation of the low K_{oc} group of pesticide-loss data is related to right-of-way applications. Herbicides used for weed control along rights-of-way include 2,4-D, diuron, bromacil, sulfometuron, and dicamba, and all except diuron are classified in the low K_{oc} group. Most rights-of-way in the study catchments were along alignments of roads, canals, and drains. The use of herbicides on rights-of-way in close proximity to intermittent or perennial waterways increases the likelihood that this group of herbicides will be detected in the region's surface water. Assessing the prevalence and importance of this issue was not within the scope of this project, but it may have contributed to the lack of trend among the low K_{oc} pesticides.

Table 8. Pesticides detected in stream and drain samples during the October–November 2000 sampling and K_{oc} values, Yakima River Basin, Washington.

[Pesticide concentrations were screened at 0.020 micrograms per liter (µg/L). Number of samples, 33. **Abbreviations**: K_{oc}, organic carbon-water partitioning coefficient; mL/g, milliliters per gram; P, pesticide detected one or more times below screening level; >, greater than; <, less than]

Compound	Number of detections	K_{oc} (mL/g)
Parent pesticides		
Clopyralid	P	2
2,4-D	1	20
Carbofuran	1	22
Dinoseb	P	30
Bromacil	4	32
Bentazon	6	34
Metalaxyl	P	50
Hexazinone	P	54
Terbacil	1	55
Tebuthiuron	P	80
Atrazine	5	100
Simazine	2	130
Prometon	P	150
Alachlor	P	170
EPTC	P	200
Linuron	P	400
Diuron	2	480
Myclobutanil	P	500
Norflurazon	1	600
Oryzalin	P	600
Pesticide degradates		
2-(4-tert-butylphenoxy)-cyclohexanol	P	< 300
Deethylatrazine	9	< 300
Deisopropylatrazine	1	< 300
Didealkylatrazine	3	< 300
3,4-Dichloroaniline	P	> 300
2-Hydroxyatrazine	P	> 300
p,p´-DDE	P	50000

Table 9. Pesticides detected in canal samples collected during July 2000 sampling and K_{oc} values, Yakima River Basin, Washington.

[Pesticide concentrations screened at a common level of 0.020 micrograms per liter (µg/L). Pesticide degradates are grouped with their parent compounds, indented, and italicized. Number of samples, 11. **Abbreviations**: K_{oc}, organic carbon-water partitioning coefficient; mL/g, milliliter per gram; >, greater than]

Compound	Number of detections	K_{oc} (mL/g)
Dicamba	1	2
2,4-D	9	20
Dinoseb	1	30
Terbacil	1	55
Methomyl	1	72
2,4-D methyl ester	1	97
Atrazine	2	100
2-*Hydroxyatrazine*	1	>300
Carbaryl	1	300
Diuron	2	480
Disulfoton	0	600
Disulfoton sulfoxide	1	104
Disulfoton sulfone	1	122
Azinphos-methyl	3	1,000
Diazinon	1	1,000
Methyl-parathion	1	5,100

Summary and Conclusions

The effort to maximize production and protect agricultural commodities leads to high pesticide usage throughout the Yakima River Basin. Despite the massive amounts applied, instream concentrations of most chemicals are small compared to other intensely cultivated areas of the United States, for example the Midwest Corn Belt. Heat and aridity in the Yakima River Basin makes irrigation a necessity, and routine operation of the region's irrigation system results in large amounts of relatively uncontaminated water being returned to drains and streams during the summer. This is not to imply that the system is wasteful (most farms and irrigation districts are conscientious in their water use), but rather that the volume of water being applied to farmland throughout the basin provides a large amount of dilution relative to the total mass of pesticides applied in the region.

Forty-seven pesticides and 14 pesticide degradates were detected in the streams, drains, and canals sampled during this study. The herbicide 2,4-D was the most frequently detected pesticide in this study, occurring in 82 percent of the samples collected in July 2000 and in 3 percent of the samples collected in October 2000 (based on concentration values screened at 0.02 µg/L). In the Yakima River Basin, it is used on a variety of crops, to control weeds along rights-of-way, and is an ingredient in several products sold for use by homeowners. In 2000, it was the 6th most heavily applied pesticide (by mass of active ingredient) to agricultural land and rights of way. The second most frequently detected pesticide was azinphos-methyl (based on concentration values screened at 0.02 µg/L). Like 2,4-D, azinphos-methyl is widely used in the Yakima River Basin, and was the most heavily applied pesticide in 2000. Despite greater use, the detection frequency of azinphos-methyl was less than half that of 2,4-D. The disparity illustrates the importance of understanding the myriad factors that affect pesticide occurrence in the aquatic environment, including soil-half life, time of use, K_{oc}, irrigation method, proximity of place of use to flowing water, and numerous others.

In this study, irrigation method and K_{oc} were identified as the best predictors of the mass of pesticide in a stream or drain relative to the amount of pesticide applied in the catchment it drains. Pesticide loss was defined as the ratio of instream mass to applied mass. Among pesticides with large K_{oc} values, pesticide loss was significantly correlated with irrigation method – large values of pesticide loss were associated with a large percentage of the agricultural land in the catchment using rill-irrigation. Properly functioning sprinkler and drip irrigation systems virtually eliminate irrigation-related soil erosion, and therefore, the mobilization of sediment-bound pesticides. Among pesticides with small K_{oc} values, there was no significant correlation between pesticide loss and irrigation method, possibly due to the timing of sampling or the transport of pesticides through the ground water system.

Samples of waters collected during base flow conditions in October provide evidence of widespread, low-level contamination of shallow ground water with pesticides and pesticide degradates. Most of the samples collected in October contained at least one pesticide, and most compounds detected were herbicides or their degradates. Concentrations in October tended to be lower than concentrations in July. In general, the pesticides detected in October had small K_{oc} values, consistent with interpretations of the pesticide loss relations. More work is needed to understand the extent to which the shallow ground water is contaminated with pesticides and the processes controlling the transport and attenuation of these chemicals.

Acknowledgments

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Organizations

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Appendix A. Pesticides and Pesticide Degradates Analyzed for This Study, Yakima River Basin, Washington

[Reporting levels represent the value at which an undetected compound is reported as less than. If detected and quantifiable, a compound will be reported less than this value and flagged in the database with an "E" (estimated). Reporting units are in micrograms per liter. **Abbreviations**: GCMS, capillary-column gas chromatography/mass spectrometry with selected ion monitoring; HPLCMS, high performance liquid chromatography/mass spectrometry; USGS, U.S. Geological Survey; –, not applicable]

Compound	Use	Chemical class	Parent pesticide	Laboratory method	USGS Parameter code	USGS Laboratory schedule	Reporting level
Detected pesticides							
1,4-Naphthoquinone	Degradate	Quinone	Napropamide, Carbaryl	GCMS	61611	9002	0.008
1-Naphthol	Degradate	Phenol	Carbaryl, Napropamide	GCMS	49295	9002	.036
2-(4-tert-butylphenoxy)-cyclohexanol	Degradate	Aliphatic alcohol	Propargite	GCMS	61637	9002	.004
2,4-D	Herbicide	Chlorophenoxy acid	–	HPLCMS	39732	9060	.022
2,4-D methyl ester	Herbicide	Chlorophenoxy acid ester	–	HPLCMS	50470	9060	.009
2-Hydroxyatrazine	Degradate	Triazine	Atrazine	HPLCMS	50355	9060	.008
3,4-Dichloroaniline	Degradate	Aniline	Diuron, Linuron, Neburon, Propanil	GCMS	61625	9002	.002
4,4'-Dichlorobenzophenone	Degradate	Organochlorine	DDT, Dicofol	GCMS	61631	9002	.001
Acetochlor	Herbicide	Chloroacetanilide	–	GCMS	49260	2001	.002
Alachlor	Herbicide	Chloroacetanilide	–	GCMS	46342	2001	.001
Atrazine	Herbicide	Triazine	–	GCMS	39632	2001	.004
Azinphos-methyl	Insecticide	Organothiophosphate	–	GCMS	82686	2001	.020
Bentazon	Herbicide	Benzothiadiazole	–	HPLCMS	38711	9060	.011
Bifenthrin	Insecticide	Pyrethroid	–	GCMS	61580	9002	.001
Bromacil	Herbicide	Uracil	–	HPLCMS	04029	9060	.033
Bromoxynil	Herbicide	Benzonitrile	–	HPLCMS	49311	9060	.017
Carbaryl	Insecticide	Carbamate	–	HPLCMS	49310	9060	.028
Carbofuran	Insecticide	Carbamate	–	GCMS	82674	2001	.010
Chlorpyrifos	Insecticide	Organothiophosphate	–	GCMS	38933	2001	.003
Clopyralid	Herbicide	Pyridine	–	HPLCMS	49305	9060	.014
Cyanazine	Herbicide	Triazine	–	GCMS	04041	2001	.009
p,p'-DDE	Degradate	Organochlorine	DDT	GCMS	34653	2001	.001
Deethylatrazine	Degradate	Triazine	Atrazine	GCMS	04040	2001	.003
Deisopropylatrazine	Degradate	Triazine	Atrazine, Cyanazine, Simazine	HPLCMS	04038	9060	.044
Diazinon	Insecticide	Organothiophosphate	–	GCMS	39572	2001	.003
Dicamba	Herbicide	Benzoic acid	–	HPLCMS	38442	9060	.013
Didealkylatrazine	Degradate	Triazine	Atrazine, Cyanazine, Simazine	HPLCMS	04039	9060	.010
Dieldrin	Insecticide	Organochlorine	–	GCMS	39381	2001	.005
Dimethoate	Insecticide	Organothiophosphate	–	GCMS	82662	9002	.001
Dinoseb	Herbicide	Nitrophenol	–	HPLCMS	49301	9060	.012
Disulfoton	Insecticide	Organothiophosphate	–	GCMS	82677	2001	.011
Disulfoton sulfone	Degradate	Organothiophosphate	Disulfoton	GCMS	61640	9002	.003
Disulfoton sulfoxide	Degradate	Organothiophosphate	Disulfoton	GCMS	61641	9002	.001
Diuron	Herbicide	Phenylurea	–	HPLCMS	49300	9060	.015
Endosulfan sulfate	Degradate	Organochlorine	*alpha*-Endosulfan, *beta*-Endosulfan	GCMS	61590	9002	.002

Appendix A. Pesticides and pesticide degradates analyzed for study, Yakima River Basin, Washington.—Continued

[Reporting levels represent the value at which an undetected compound is reported as less than. If detected and quantifiable, a compound will be reported less than this value and flagged in the database with an "E" (estimated). Reporting units are in micrograms per liter. **Abbreviations**: GCMS, capillary-column gas chromatography/mass spectrometry with selected ion monitoring; HPLCMS, high performance liquid chromatography/mass spectrometry; USGS, U.S. Geological Survey; –, not applicable]

Compound	Use	Chemical class	Parent pesticide	Laboratory method	USGS		Reporting level
					Parameter code	Laboratory schedule	
Detected pesticides—Continued							
EPTC	Herbicide	Thiocarbamate	–	GCMS	82668	2001	.001
Ethalfluralin	Herbicide	Dinitroaniline	–	GCMS	82663	2001	.005
Fenamiphos sulfoxide	Degradate	Organophosphate	Fenamiphos	GCMS	61646	9002	.000
Fluometuron	Herbicide	Phenylurea	–	HPLCMS	38811	9060	.031
gamma-HCH	Insecticide	Organochlorine	–	GCMS	39341	2001	0.002
Hexazinone	Herbicide	Triazinone	–	GCMS	04025	9002	.002
Imidacloprid	Insecticide	Chloro-Nicotinyl	–	HPLCMS	61695	9060	.007
Linuron	Herbicide	Phenylurea	–	HPLCMS	38478	9060	.014
Malathion	Insecticide	Organothiophosphate	–	GCMS	39532	2001	.014
MCPA	Herbicide	Chlorophenoxy acid	–	HPLCMS	38482	9060	.016
MCPB	Herbicide	Chlorophenoxy acid	–	HPLCMS	38487	9060	.015
Metalaxyl	Fungicide	Benzenoid	–	GCMS	61596	9002	.002
Methomyl	Insecticide	Carbamate	–	HPLCMS	49296	9060	.004
Methyl-parathion	Insecticide	Organothiophosphate	–	GCMS	82667	2001	.003
Metolachlor	Herbicide	Chloroacetanilide	–	GCMS	39415	2001	.006
Metribuzin	Herbicide	Triazinone	–	GCMS	82630	2001	.003
Metsulfuron-methyl	Herbicide	Sulfonylurea	–	HPLCMS	61697	9060	.025
Myclobutanil	Fungicide	Triazole	–	GCMS	61599	9002	.001
Nicosulfuron	Herbicide	Sulfonylurea	–	HPLCMS	50364	9060	.013
Norflurazon	Herbicide	Pyridazinone	–	HPLCMS	49293	9060	.016
Oryzalin	Herbicide	Dinitroaniline	–	HPLCMS	49292	9060	.018
Oxyfluorfen	Herbicide	Diphenyl ether	–	GCMS	61600	9002	.002
Pendimethalin	Herbicide	Dinitroaniline	–	GCMS	82683	2001	.005
Phosmet	Insecticide	Organothiophosphate	–	GCMS	61601	9002	.001
Picloram	Herbicide	Pyridine	–	HPLCMS	49291	9060	.020
Prometon	Herbicide	Triazine	–	GCMS	04037	2001	.007
Propargite	Acaricide	Sulfite ester	–	GCMS	82685	2001	.011
cis-Propiconazole	Fungicide	Triazole	–	GCMS	79846	9002	.001
trans-Propiconazole	Fungicide	Triazole	–	GCMS	79847	9002	.001
Simazine	Herbicide	Triazine	–	GCMS	04035	2001	.006
Sulfometuron-methyl	Herbicide	Sulfonylurea	–	HPLCMS	50337	9060	.009
Tebuthiuron	Herbicide	Thiadiazole	–	GCMS	82670	2001	.008
Terbacil	Herbicide	Uracil	–	GCMS	82665	2001	.017
Trifluralin	Herbicide	Dinitroaniline	–	GCMS	82661	2001	.005
Pesticides not detected							
2,4-DB	Herbicide	Chlorophenoxy acid	–	HPLCMS	38746	9060	0.016
2,5-Dichloroaniline	Degradate	Aniline	Chloramben	GCMS	61614	9002	.009
2,6-Diethylaniline	Degradate	Aniline	Alachlor	GCMS	82660	2001	.003
2-[(2-Ethyl-6-methylphenyl)amino]-1-propanol	Degradate	Aniline, aliphatic alcohol	Metolachlor	GCMS	61615	9002	.058
2-Amino-N-isopropylbenzamide	Degradate	Amide	Bentazon	GCMS	61617	9002	.001
2-Chloro-2,6-diethylacetanilide	Degradate	Chloroacetanilide	Alachlor	GCMS	61618	9002	.002

Appendix A. Pesticides and pesticide degradates analyzed for study, Yakima River Basin, Washington.—Continued

[Reporting levels represent the value at which an undetected compound is reported as less than. If detected and quantifiable, a compound will be reported less than this value and flagged in the database with an "E" (estimated). Reporting units are in micrograms per liter. **Abbreviations**: GCMS, capillary-column gas chromatography/mass spectrometry with selected ion monitoring; HPLCMS, high performance liquid chromatography/mass spectrometry; USGS, U.S. Geological Survey; –, not applicable]

Compound	Use	Chemical class	Parent pesticide	Laboratory method	USGS		Reporting level
					Parameter code	Laboratory schedule	
Pesticides not detected—Continued							
2-Ethyl-6-methylaniline	Degradate	Aniline	Metolachlor	GCMS	61620	9002	.002
3-(4-chlorophenyl)-1-methyl urea	Degradate	Phenylurea	Monuron, Neburon, Linuron, Diuron	HPLCMS	61692	9060	.024
3,5-Dichloroaniline	Degradate	Aniline	Iprodione	GCMS	61627	9002	.002
3-Hydroxycarbofuran	Degradate	Carbamate	Carbofuran	HPLCMS	49308	9060	.006
3-Ketocarbofuran	Degradate	Carbamate	Carbofuran	HPLCMS	50295	9060	1.500
3-Phenoxybenzyl alcohol	Degradate	Diphenyl ether	Permethrin	GCMS	61629	9002	.013
3-Trifluoromethyl-aniline	Degradate	Aniline	Fluometuron	GCMS	61630	9002	0.002
4-(Hydroxymethyl)pendime thalin	Degradate	Dinitroaniline	Pendimethalin	GCMS	61665	9002	.046
4-Chloro-2-methylphenol	Degradate	Phenol	MCPA, MCPB	GCMS	61633	9002	.001
4-Chlorobenzylmethyl sulfone	Degradate	Sulfone	Thiobencarb	GCMS	61634	9002	.008
Acifluorfen	Herbicide	Diphenyl ether	–	HPLCMS	49315	9060	.007
Aldicarb	Insecticide	Carbamate	–	HPLCMS	49312	9060	.040
Aldicarb sulfone	Degradate	Sulfone	Aldicarb	HPLCMS	49313	9060	.020
Aldicarb sulfoxide	Degradate	Sulfoxide	Aldicarb	HPLCMS	49314	9060	.008
Azinphos-methyl oxon	Degradate	Organothiophosphate	Azinphos-methyl	GCMS	61635	9002	.001
Bendiocarb	Insecticide	Carbamate	–	HPLCMS	50299	9060	.025
Benfluralin	Herbicide	Dinitroaniline	–	GCMS	82673	2001	.005
Benomyl	Fungicide	Benzimidazole	–	HPLCMS	50300	9060	.004
Bensulfuron-methyl	Herbicide	Sulfonylurea	–	HPLCMS	61693	9060	.016
Butylate	Herbicide	Thiocarbamate	–	GCMS	04028	2001	.002
Carbofuran	Insecticide	Benzimidazole	–	HPLCMS	49309	9060	.006
Chloramben methyl ester	Herbicide	Chlorophenoxy acid	–	HPLCMS	61188	9060	.018
Chlorimuron ethyl	Herbicide	Sulfonylurea	–	HPLCMS	50306	9060	.010
Chlorothalonil	Fungicide	Chloronitrile	–	HPLCMS	49306	9060	.035
Chlorpyrifos oxon	Degradate	Organophosphate	Chlorpyrifos	GCMS	61636	9002	.010
Cycloate	Herbicide	Thiocarbamate	–	GCMS	04031	9002	.002
Cyfluthrin	Insecticide	Pyrethroid	–	GCMS	61585	9002	.001
lambda-Cyhalothrin	Insecticide	Pyrethroid	–	GCMS	61595	9002	.001
Cypermethrin	Insecticide	Pyrethroid	–	GCMS	61586	9002	.001
Dacthal	Herbicide	Alkyl Phthalate	–	GCMS	82682	2001	.002
Dacthal monoacid	Degradate	Alkyl Phthalate	Dacthal	HPLCMS	49304	9060	.012
Dichlorprop	Herbicide	Chlorophenoxy acid	–	HPLCMS	49302	9060	.014
Dichlorvos	Insecticide, Fumigant, Degradate	Organophosphate	Naled	GCMS	38775	9002	.003
Dicrotophos	Insecticide	Organophosphate	–	GCMS	38454	9002	.017
(E)-Dimethomorph	Fungicide	Morpholine	–	GCMS	79844	9002	.002
(Z)-Dimethomorph	Fungicide	Morpholine	–	GCMS	79845	9002	.003
Diphenamid	Herbicide	Amide	–	HPLCMS	04033	9060	.026
alpha-Endosulfan	Insecticide	Organochlorine	–	GCMS	34362	9002	.001
beta-Endosulfan	Insecticide	Organochlorine	–	GCMS	34357	9002	.004
Endosulfan ether	Degradate	Organochlorine	*alpha*-Endosulfan, *beta*-Endosulfan	GCMS	61642	9002	.002
Ethion	Insecticide	Organothiophosphate	–	GCMS	82346	9002	.001
Ethion monoxon	Degradate	Organophosphorus	Ethion	GCMS	61644	9002	.007
Ethoprop	Insecticide	Organothiophosphate	–	GCMS	82672	2001	.002

Appendix A. Pesticides and pesticide degradates analyzed for study, Yakima River Basin, Washington.—Continued

[Reporting levels represent the value at which an undetected compound is reported as less than. If detected and quantifiable, a compound will be reported less than this value and flagged in the database with an "E" (estimated). Reporting units are in micrograms per liter. **Abbreviations**: GCMS, capillary-column gas chromatography/mass spectrometry with selected ion monitoring; HPLCMS, high performance liquid chromatography/mass spectrometry; USGS, U.S. Geological Survey; –, not applicable]

Compound	Use	Chemical class	Parent pesticide	Laboratory method	USGS Parameter code	USGS Laboratory schedule	Reporting level
Pesticides not detected—Continued							
Fenamiphos	Nematocide	Organophosphorus	–	GCMS	61591	9002	.015
Fenamiphos sulfone	Degradate	Organophosphorus	Fenamiphos	GCMS	61645	9002	.001
Fenthion	Insecticide	Organothiophosphate	–	GCMS	38801	9002	.005
Fenthion sulfoxide	Degradate	Organothiophosphate	Fenthion	GCMS	61647	9002	.002
Fenuron	Herbicide	Phenylurea	–	HPLCMS	49297	9060	.032
Flumetralin	Plant Growth Regulator	Dinitroaniline	–	GCMS	61592	9002	0.001
Flumetsulam	Herbicide	Sulfonamide	–	HPLCMS	61694	9060	.011
Fonofos	Insecticide	Organophosphorus	–	GCMS	04095	2001	.001
Fonofos oxygen analog	Degradate	Organophosphorus	Fonofos	GCMS	61649	9002	.001
alpha-HCH	Insecticide, Degradate	Organochlorine	*gamma*-HCH	GCMS	34253	2001	.002
Imazaquin	Herbicide	Imidazolinone	–	HPLCMS	50356	9060	.016
Imazethapyr	Herbicide	Imidazolinone	–	HPLCMS	50407	9060	.017
Iprodione	Fungicide	Dicarboximide	–	GCMS	61593	9002	.746
Isofenphos	Insecticide	Organothiophosphate	–	GCMS	61594	9002	.001
Malaoxon	Degradate	Organothiophosphate	Malathion	GCMS	61652	9002	.001
Methidathion	Insecticide	Organothiophosphate	–	GCMS	61598	9002	.001
Methiocarb	Insecticide	Carbamate	–	HPLCMS	38501	9060	.008
Methomyl oxime	Degradate	Oxime	Methomyl	HPLCMS	61696	9060	.011
cis-Methyl-3-(2,2-dichlorovinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate	Degradate	Aliphatic acid ester	Cyfluthrin	GCMS	79842	9002	.005
trans-Methyl-3-(2,2-dichlorovinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate	Degradate	Aliphatic acid ester	Cyfluthrin	GCMS	79843	9002	.008
Molinate	Herbicide	Thiocarbamate	–	GCMS	82671	2001	.001
Napropamide	Herbicide	Amide	–	GCMS	82684	2001	.003
Neburon	Herbicide	Phenylurea	–	HPLCMS	49294	9060	.012
O-Ethyl-O-methyl-S-propylphosphorothioate	Degradate	Organothiophosphate	Ethoprophos	GCMS	61660	9002	.003
Oxamyl	Insecticide	Carbamate	–	HPLCMS	38866	9060	.012
Oxamyl oxime	Degradate	Oxime	Oxamyl	HPLCMS	50410	9060	.013
Paraoxon-ethyl	Insecticide, Degradate	Organothiophosphate	Parathion	GCMS	61663	9002	.002
Paraoxon-methyl	Degradate	Organothiophosphate	Methyl-parathion	GCMS	61664	9002	.010
Parathion	Insecticide	Organothiophosphate	–	GCMS	39542	2001	.003
Pebulate	Herbicide	Thiocarbamate	–	GCMS	82669	2001	.001
cis-Permethrin	Insecticide	Pyrethroid	–	GCMS	82687	2001	.003
Phorate	Insecticide	Organothiophosphate	–	GCMS	82664	2001	.006
Phorate oxon	Degradate	Organothiophosphate	Phorate	GCMS	61666	9002	.008
Phosmet oxon	Degradate	Organothiophosphate	Phosmet	GCMS	61668	9002	.009
Profenofos	Insecticide	Organothiophosphate	–	GCMS	61603	9002	.001
Prometryn	Herbicide	Triazine	–	GCMS	04036	9002	.002

Appendix A. Pesticides and pesticide degradates analyzed for study, Yakima River Basin, Washington.—Continued

[Reporting levels represent the value at which an undetected compound is reported as less than. If detected and quantifiable, a compound will be reported less than this value and flagged in the database with an "E" (estimated). Reporting units are in micrograms per liter. **Abbreviations**: GCMS, capillary-column gas chromatography/mass spectrometry with selected ion monitoring; HPLCMS, high performance liquid chromatography/mass spectrometry; USGS, U.S. Geological Survey; –, not applicable]

Compound	Use	Chemical class	Parent pesticide	Laboratory method	USGS Parameter code	USGS Laboratory schedule	Reporting level
Pesticides not detected—Continued							
Pronamide	Herbicide	Amide	–	GCMS	82676	2001	.002
Propachlor	Herbicide	Chloroacetanilide	–	GCMS	04024	2001	.005
Propanil	Herbicide	Anilide	–	GCMS	82679	2001	.005
Propetamphos	Insecticide	Organothiophosphate	–	GCMS	61604	9002	.001
Propham	Herbicide	Carbamate	–	HPLCMS	49236	9060	.010
Propiconazole	Fungicide	Triazole	–	HPLCMS	50471	9060	.021
Propoxur	Insecticide	Carbamate	–	HPLCMS	38538	9060	.008
Siduron	Herbicide	Phenylurea	–	HPLCMS	38548	9060	0.017
Sulfotepp	Insecticide	Organothiophosphate	–	GCMS	61605	9002	.001
Sulprofos	Insecticide	Organothiophosphate	–	GCMS	38716	9002	.002
TCPSA ethyl ester	Degradate	Sulfonic acid ester	Triallate	GCMS	61670	9002	.020
Tebupirimfos	Insecticide	Organothiophosphate	–	GCMS	61602	9002	.002
Tebupirimfos oxygen analogue	Degradate	Organothiophosphate	Tebupirimfos	GCMS	61669	9002	.002
Tefluthrin	Insecticide	Pyrethroid	–	GCMS	61606	9002	.001
Tefluthrin metabolite [R 119364]	Degradate	Pyrethroid	Tefluthrin	GCMS	61671	9002	.003
Tefluthrin metabolite [R 152912]	Degradate	Pyrethroid	Tefluthrin	GCMS	61672	9002	.003
Temephos	Insecticide	Organothiophosphate	–	GCMS	61607	9002	.036
Terbufos	Insecticide	Organothiophosphate	–	GCMS	82675	2001	.009
Terbufos oxygen analogue sulfone	Degradate	Organothiophosphate	Terbufos	GCMS	61674	9002	.018
Terbuthylazine	Herbicide	Triazine	–	GCMS	04022	9002	.005
Thiobencarb	Herbicide	Thiocarbamate	–	GCMS	82681	2001	.002
Triallate	Herbicide	Thiocarbamate	–	GCMS	82678	2001	.001
Tribenuron-methyl	Herbicide	Sulfonylurea	–	HPLCMS	61159	9060	.009
Tribuphos	Defoliant	Organothiophosphate	–	GCMS	61610	9002	.001
Triclopyr	Herbicide	Pyridine	–	HPLCMS	49235	9060	.022

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