Prepared in cooperation with the Bureau of Reclamation

Occurrence, Distribution, and Transport of Pesticides in Agricultural Irrigation-Return Flow from Four Drainage Basins in the Columbia Basin Project, Washington, 2002-04, and Comparison with Historical Data

Scientific Investigations Report 2006–5005

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

Cover: Photograph of Lind Coulee near Warden, Washington, about 1 mile west of State Route 17, looking downstream, July 2004.
(Photograph taken by Richard Wagner, U.S. Geological Survey.)

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By Richard J. Wagner, Lonna M. Frans, and Raegan L. Huffman

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Conversion Factors and Datums

Conversion Factors

Multiply	By	To obtain
acre	4,047	square meter
acre	0.001562	square mile
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
foot (ft)	0.3048	meter
inch (in.)	2.54	centimeter
liter (L)	33.82	ounce, fluid
mile (mi)	1.609	kilometer
pound, avoirdupois (lb)	0.4536	kilogram
square mile (mi^2)	2.590	square kilometer

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32.$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Datum

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD27) and North American Datum of 1983 (NAD83).

Occurrence, Distribution, and Transport of Pesticides in Agricultural Irrigation-Return Flow from Four Drainage Basins in the Columbia Basin Project, Washington, 2002-04, and Comparison with Historical Data

By Richard J. Wagner, Lonna M. Frans, and Raegan L. Huffman

Abstract

Water-quality samples were collected from sites in four irrigation return-flow drainage basins in the Columbia Basin Project from July 2002 through October 2004. Ten samples were collected throughout the irrigation season (generally April through October) and two samples were collected during the non-irrigation season. Samples were analyzed for temperature, pH, specific conductance, dissolved oxygen, major ions, trace elements, nutrients, and a suite of 107 pesticides and pesticide metabolites (pesticide transformation products) and to document the occurrence, distribution, and pesticides transport and pesticide metabolites.

The four drainage basins vary in size from 19 to 710 square miles. Percentage of agricultural cropland ranges from about 35 percent in Crab Creek drainage basin to a maximum of 75 percent in Lind Coulee drainage basin. More than 95 percent of cropland in Red Rock Coulee, Crab Creek, and Sand Hollow drainage basins is irrigated, whereas only 30 percent of cropland in Lind Coulee is irrigated.

Forty-two pesticides and five metabolites were detected in samples from the four irrigation return-flow drainage basins. The most compounds detected were in samples from Sand Hollow with 37, followed by Lind Coulee with 33, Red Rock Coulee with 30, and Crab Creek with 28. Herbicides were the most frequently detected pesticides, followed by insecticides, metabolites, and fungicides. Atrazine, bentazon, diuron, and 2,4-D were the most frequently detected herbicides and chlorpyrifos and azinphos-methyl were the most frequently detected insecticides.

A statistical comparison of pesticide concentrations in surface-water samples collected in the mid-1990s at Crab Creek and Sand Hollow with those collected in this study showed a statistically significant increase in concentrations for diuron and a statistically significant decrease for ethoprophos and atrazine in Crab Creek. Statistically significant increases were in concentrations of bromacil, diuron, and pendimethalin at Sand Hollow and statistically significant decreases were in concentrations of 2,6-diethylanaline, alachlor, atrazine, DCPA, and EPTC. A seasonal Kendall trend test on data from Lind Coulee indicated no statistically significant trends for any pesticide for 1994 through 2004.

A comparison of pesticide concentrations detected in this study with those detected in previous U.S. Geological Survey National Water-Quality Assessment studies of the Central Columbia Plateau, Yakima River basin, and national agricultural studies indicated that concentrations in this study generally were in the middle to lower end of the concentration spectrum for the most frequently detected herbicides and insecticides, but that the overall rate of detection was near the high end.

Thirty-one of the 42 herbicides, insecticides, and fungicides detected in surface-water samples were applied to the major agricultural crops in the drainage basins, and 11 of the detected pesticides are sold for residential application. Eight of the pesticides detected in surface-water samples were not reported as having any agricultural or residential use. The overall pattern of pesticide use depends on which crops are grown in each drainage basin. Drainage basins with predominantly more orchards have higher amounts of insecticides applied, whereas basins with larger percentages of field crops tend to have more herbicides applied. Pesticide usage was most similar in Crab Creek and Sand Hollow, where the largest total amounts applied were the insecticides azinphos-methyl, carbaryl, and chlorpyrifos and the herbicide EPTC. In Red Rock Coulee basin, DCPA was the most heavily applied herbicide, followed by the fungicide chlorothalonil, the herbicide EPTC, and the insecticides chlorpyrifos and azinphos-methyl. In Lind Coulee, which has a large percentage of dryland agricultural area, the herbicides 2,4-D and EPTC were applied in the largest amount, followed by the fungicide chlorothalonil. The total amount of pesticides applied by residential homeowners and irrigation districts was negligible compared to total amounts applied to agricultural crops.

The State of Washington criterion of measuring water temperature by the 7-day average of the daily maximum temperatures was beyond the scope of this study, so water temperatures are only an indication of instantaneous temperatures at the time of sampling. Water temperature in 18 samples was greater than the State criterion of 16 degrees Celsius for salmon and trout spawning, core rearing, and migration: 7 in Red Rock Coulee, 5 in Crab Creek, 4 in Lind Coulee, and 2 in Sand Hollow. In 11 of these 18 samples, water temperature also was greater than the criterion of 17.5 degrees Celsius for salmon and trout spawning, non-core rearing, and migration. The State of Washington aquatic-life dissolved-oxygen criterion of 9.5 milligrams per liter for salmon and trout spawning, core rearing, and migration was exceeded eight times from June to early October: two times at Sand Hollow, three times at Red Rock Coulee, and three times at Crab Creek. The State of Washington aquatic-life pH criterion of 8.5 for fresh water was exceeded 12 times, 6 at Red Rock Coulee, 3 at Sand Hollow, 2 at Lind Coulee and 1 at Crab Creek. Concentrations of nitrate plus nitrite in two samples collected from Sand Hollow during the non-irrigation season exceeded the U.S. Environmental Protection Agency Maximum Contaminant Level for drinking water.

Concentrations of three insecticides and one herbicide exceeded U.S. Environmental Protection Agency or Canadian benchmark for the protection of freshwater aquatic life. Concentrations of the insecticide azinphos-methyl exceeded the aquatic-life benchmark at least once at each of the four sites. Concentrations in samples from Sand Hollow also exceeded the aquatic-life benchmark for chlorpyrifos, lindane, and dinoseb (0.041, 0.01, and 0.05 micrograms per liter, respectively). Water-quality benchmarks generally were exceeded in June and July, during the middle of the irrigation season, except the benchmark for dinoseb, which was exceeded in one sample during the non-irrigation season in February 2003.

Introduction

The National Marine Fisheries Service's (NMFS) 2000 Biological Opinion on the operation of the Federal Columbia River Power System (National Marine Fisheries Service, 2000) includes a recommendation to the Bureau of Reclamation to monitor water-quality characteristics of surface-water irrigation return flows to the Columbia River at various points in the Columbia Basin Project (CBP) in central Washington State. The presence of selected pesticides in these return flows at levels that may harm or adversely affect salmon and steelhead species listed for protection under the Endangered Species Act was of specific interest to NMFS.

In cooperation with the Bureau of Reclamation, the U.S. Geological Survey (USGS) included the sampling of surface water in four irrigation return-flow drainage basins in the CBP as an ancillary project to the second phase of the Central Columbia Plateau-Yakima (CCYK) National Water-Quality Assessment (NAWQA) Program. The NAWQA program uses procedures for sampling and analyzing pesticides and other analytes of interest in surface water that assures high-quality, representative data for many commonly used pesticides, and using these same methods for additional CBP sites is beneficial to assure data comparability.

Water-quality samples collected from streamflow-gaging station sites in the Crab Creek, Sand Hollow, Red Rock Coulee, and Lind Coulee drainage basins from July 2002 through October 2004 were analyzed for a suite of 107 pesticides and pesticide metabolites (pesticide transformation products), as well as concentrations of major ions, trace elements, and nutrients. The data were used to describe the occurrence, distribution, and transport of pesticides in agricultural irrigation return-flow water in the four irrigation-return flow drainage basins. Pesticide concentrations were compared with drinking-water standards and aquatic-life benchmarks, and pesticide detections in samples from the irrigation-return flows was compared with historical data and related to current pesticide use, land use, and other environmental factors.

Purpose and Scope

The purposes of this report are to (1) describe the occurrence, distribution, and transport of pesticides and pesticide metabolites in agricultural irrigation return-flow water in four drainage basins in the CBP; (2) describe the relation between pesticides detected in irrigation-return flows and current and historical pesticide use, land use, other environmental factors, and chemical properties of the pesticides; (3) discuss how measured pesticide concentrations compare with drinking-water standards and aquatic-life benchmarks; and (4) compare the results of this study with those from historical studies in the 1970s, 1990s, and the national NAWQA database. Four irrigation-return flow sites were sampled for pesticides 12 times from July 2002 through October 2004. Ten samples were collected throughout the irrigation season (generally April through October) and two samples were collected during the non-irrigation season.

Environmental Setting

The CBP is a multi-purpose project providing irrigation water to agricultural land in the Columbia River basin in central Washington (fig. 1). The CBP drainage area is more than 4,000 mi^2 and is bounded on the west by the Columbia River and on the south by the Snake River, and it extends east and north to include all lands considered

Figure 1. Locations of the four irrigation return-flow drainage basins and surface-water sampling sites, Columbia Basin Project, Washington.

economically irrigable from the project canal system (Bureau of Reclamation, 1982). Main geohydrologic units in the CBP are the Columbia Plateau River Basalt Group, extrusions of basalt lava that formed the Columbia Plateau between 6 and 16.5 million years ago, and the overlying deposits of unconsolidated sediment (Drost and others, 1990). Columbia Plateau River Basalt Group flows are estimated to be more than 14,000 ft thick near Pasco, Washington. Parts of the CBP also contain loess, a wind-deposited silt, and sand dunes typified by those at Potholes Reservoir.

Major land use and economy in the CBP is agriculture, followed by livestock production and food processing. The land is primarily rural, but five towns in the CBP area have populations greater than 5,000: Pasco, Othello, Moses Lake, Ephrata, and Quincy. Pasco is the largest town, with a population of about 32,000 (U.S. Census Bureau, 2004). Climate in the CBP is semiarid, with about 6 to 10 in. of annual precipitation, and air temperatures range from below freezing in winter to more than 38°C at times during summer.

The CBP has few natural perennial streams, and streamflow in the project area is augmented and indirectly regulated by seasonal delivery of irrigation water (generally April to October) to the area. Irrigation water is pumped from Lake Roosevelt, stored in Banks Lake, and distributed throughout the CBP by a network of re-regulation reservoirs and conveyance canals to irrigated lands. Surface-water drainages from irrigated lands lead to wasteway returns that create irrigation-return flows to major streams and rivers. The large quantities of irrigation water delivered to farm units in the CBP indirectly control the irrigation-return flow in the four drainage basins studied in the project area during the irrigation season (table 1). Water samples were collected at USGS streamflow-gaging stations in the study basins, and continuous streamflow data were available only for Crab Creek and Lind Coulee.

Crab Creek irrigation-return drainage basin covers 296 mi^2, and water samples were collected at gaging station 12472600, near Beverly (fig. 1). Before water was diverted from Lake Roosevelt for irrigation, Crab Creek was one of the few perennial streams in the CBP and flowed from the northeastern Columbia Plateau, about 3 mi east of Reardan, southwest to where it empties into the Columbia River near Beverly, Washington. Drifting sand dunes impounded Crab Creek and created Moses Lake, the largest natural lake in the CBP (Walters and Grolier, 1960). Construction of O'Sullivan Dam formed Potholes Reservoir, creating a central point in the CBP for storage of excess canal water, natural runoff, and irrigation-return flow and redistribution of water for irrigation reuse in the southern part of the CBP. The entire length of Crab Creek drains 4,840 mi^2, but Moses Lake and Potholes Reservoir hydrologically separate the stream into Upper Crab Creek, the stretch from the headwaters to Moses Lake, and Lower Crab Creek, the stretch from O'Sullivan Dam to the mouth that includes the Crab Creek study basin. Potholes Reservoir has no perennial outlet to Lower Crab Creek, and most water in Lower Crab Creek comes from Goose Lake Wasteway. Hansen and others (1994) calculated average ground-water discharge to Lower Crab Creek as 76.3 ft^3/s prior to irrigation development and 145.1 ft^3/s for 1983–85. Therefore, water at the Crab Creek site near Beverly is directly affected by ground-water seepage from Potholes Reservoir and from tributary inflow downstream of O'Sullivan Dam.

Sand Hollow drains the western flanks of Royal Slope and flows west, emptying into the Columbia River across from Vantage, Washington. Sand Hollow irrigation-return drainage basin covers 60 mi^2 and represents a drainage basin of varied agricultural land uses that is irrigated primarily by surface water. The first water sample from Sand Hollow during this study was collected at S Road SW at gaging station 12464606 (fig. 1). Historical data were collected at this site by NAWQA during the 1990s. The drainage area at this site is 43 mi^2. All subsequent samples for this study were collected at the mouth at gaging station 12464607 (fig. 1), where one water sample was collected by the USGS in 1991 and sediment samples were collected in 1992. Although a minor tributary flows into Sand Hollow in the 3 mi between S Road SW and the mouth, land use is the same for the entire basin and data from both sampling sites are treated as one for data analysis in this study.

Table 1. Physical and land-use characteristics of the four irrigation return-flow drainage basins sampled for pesticides, Columbia Basin Project, Washington, July 2002 to October 2004.

[USGS, U.S. Geological Survey; ft^3/s, cubic feet per second; mi^2, square mile; S, south; Rd, Road; SW, Southwest; SR, State Route; >, greater than]

Irrigation return-flow basin	Sampling site		Short name	Number of samples	Streamflow at time of sampling (ft^3/s)			Drainage area (mi^2)	Harvested cropland area (mi^2)	Percentage of harvested cropland	Percentage of irrigated cropland
	USGS gaging station No. and name				Median	Minimum	Maximum				
Crab Creek	12472600	Crab Creek near Beverly	Crab Creek	12	214	129	331	[1]296	103	35	>95
Lind Coulee	12471400	Lind Coulee Wasteway at SR 17, near Warden	Lind Coulee	12	255	58	355	710	533	75	30
Red Rock Coulee	12472520	Red Rock Coulee near Smyrna	Red Rock Coulee	12	71.5	43	114	19	9	47	>95
Sand Hollow	12464606	Sand Hollow at S Rd SW, near Vantage	Sand Hollow at S Rd	1	79	79	79	43	36	70	>95
	12464607	Sand Hollow at mouth, near Vantage	Sand Hollow	11	94	23	141	60	42	84	>95

[1]Drainage area is for Lower Crab Creek; the entire Crab Creek drainage area is 4,840 mi^2.

Red Rock Coulee drains about 19 mi^2 of irrigated agricultural land, beginning near the eastern boundary of Grant County, just north of Royal Lake, and flowing west to Red Rock Lake (fig. 1). Red Rock Coulee flows out of Red Rock Lake, passes through a culvert beneath county road E SW, flows south about 2.5 mi before crossing beneath county road E SW again, and continues another mile before emptying into Crab Creek. During this study, samples were collected from Red Rock Coulee downstream of the second culvert at gaging station 12472520, but during the NAWQA program, in 1994, one sample was collected about 1 mi upstream.

The headwaters of Lind Coulee combine with the flow of several smaller coulees south of Ritzville, and the main branch flows east through the town of Lind before joining with Weber Coulee and flowing another 5 mi to empty into Potholes Reservoir. Weber Coulee combines the flow from Bauer Coulee and Farrier Coulee, and the entire Lind Coulee basin drains about 710 mi^2. Samples from Lind Coulee were collected at gaging station 12471400, about 1 mi downstream of the State Highway 17 crossing.

Agriculture crop acreage in the four irrigation-return flow drainage basins varies from year to year. Orchards usually are a long-term crop, but many field crops are rotated frequently. One primary rotation in the CBP is between alfalfa, corn, and potatoes. Estimates of agricultural acreage for 2003 in the four irrigation-return flow basins were used to describe the agricultural land use during this study (table 2; Patricia Daly, Franklin County Conservation District, written commun., 2004). Percentage of agricultural harvested cropland varies from year to year, but ranged from 35 percent in Crab Creek basin to a maximum of 75 percent in Lind Coulee basin during this study. Harvested cropland was 47 percent in Red Rock Coulee basin and 70 percent in Sand Hollow basin during the current study. Most agricultural cropland in Red Rock Coulee, Sand Hollow, and Crab Creek drainage basins is irrigated, but only 30 percent of the crop acreage in Lind Coulee is irrigated (table 1). Alfalfa is the largest percentage of crop acreage in Crab Creek drainage basin, followed by orchards and irrigated wheat. Peas, corn, and potatoes are nearly 20 percent of crop acreage in the Crab Creek drainage basin (table 2). Nearly one-third of the crop acreage in Lind Coulee is in dryland wheat, and more than one-third of the acreage is fallow land. Minor percentages of the acreage in Lind Coulee drainage basin are in alfalfa, potatoes, and peas. The largest percentage of crop acreage in Red Rock Coulee drainage basin is alfalfa, followed by onions and orchards. Peas and irrigated wheat make up about 15 percent of the total agricultural acreage. The largest percentage of crop acreage in Sand Hollow also is alfalfa, followed by orchards. Peas and irrigated wheat make up about 30 percent of the total agricultural acreage, followed by minor percentages of grass, potatoes, and mint.

Table 2. Crop acreage estimates in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, 2003.

[Data for crop-acreage estimates provided by Franklin County Conservation District (Patricia Daly, written commun., 2004). **Percentage of crop acreage:** may not add to 100 percent due to rounding. <, less than]

Crop	Acres	Percentage of crop acreage
	Crab Creek	
Alfalfa	24,292	37
Orchard	13,999	21
Wheat (irrigated)	6,662	10
Pea	5,172	8
Corn	3,666	6
Potato	3,600	5
Unclassified	2,598	4
Grass	1,814	3
Onion	1,603	2
Wheat (dryland)	1,189	2
Mint	983	1
Timothy	162	<1
Fallow	98	<1
	Lind Coulee	
Fallow	119,929	35
Wheat (dryland)	116,713	34
Wheat (irrigated)	33,835	10
Alfalfa	17,899	5
Potato	15,238	4
Unclassified	13,646	4
Corn	9,667	3
Pea	8,074	2
Orchard	4,206	1
Onion	1,183	<1
Grass	686	<1
	Red Rock Coulee	
Alfalfa	3,345	57
Onion	682	12
Orchard	536	9
Wheat (irrigated)	449	8
Pea	428	7
Potato	129	2
Corn	122	2
Unclassified	116	2
Grass	105	2
	Sand Hollow	
Alfalfa	7,610	28
Orchard	4,746	18
Pea	4,091	15
Wheat (irrigated)	4,001	15
Grass	2,378	9
Potato	1,216	5
Mint	1,070	4
Corn	602	2
Unclassified	601	2
Fallow	181	1
Wheat (dryland)	164	1
Onion	125	<1

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Methods

Surface-water samples were collected from four irrigation return-flow drainage basins and analyzed for pesticides and pesticide metabolites, major ions, trace elements, and nutrients (table 3). The pesticides were selected by the NAWQA program (Gilliom and others, 1995) from a list of about 400 pesticides most commonly used in the United States (Gianessi and Puffer, 1991, 1992a, 1992b). Each pesticide was selected on the basis of the following factors: a national use of more than 8,000 lb of active ingredient annually; inclusion in the analytical schedules of other Federal monitoring or survey programs; toxicity; leachability; and its ability to be trapped and extracted from the appropriate solid-phase-concentrating matrix. Samples for analysis of pesticides and major ions were collected and submitted to the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colo., the samples for pesticides were analyzed using either gas-chromatography/mass spectrometry (GC/MS) or high-performance liquid chromatography/mass spectrometry (HPLC/MS), depending on the physical characteristics of the target analytes. Samples for nutrient analysis were sent to the Bureau of Reclamation laboratory in Boise, Idaho.

Field Methods

The sampling site in each drainage basin was visited 10 times during the irritation season and 2 times during the non-irrigation season from July 2002 to October 2004. During each visit, water temperature, pH, dissolved oxygen (DO) concentrations, and specific conductance were measured and water samples were collected for analysis of pesticides, major ions, trace elements, and nutrients. The first sample from Sand Hollow drainage basin was collected from the bridge at S Road SW and all subsequent samples were collected from the mouth of Sand Hollow before it empties into the Columbia River. One DO measurement was removed from the data set because of a faulty sensor. Samples representative of flow in the stream cross section were obtained by collecting depth-integrated subsamples at equally spaced verticals across the stream using a US DH-81 sampler as described by Edwards and Glysson (1999) and Wilde and others (1999a). The sampler holds a 1- or 3-L Teflon® bottle, and all parts of the sampler coming in contact with the water sample are made of Teflon®. Subsamples were composited and split using a Teflon® churn splitter (Wilde and others, 2004). From June through August 2002, the Teflon® churn was not available, so a polyethylene churn splitter was used. Subsamples for analysis of inorganic analytes were collected and split out using the churn. Samples for pesticides were collected directly into a 3-L Teflon® bottle from each section of the stream and were not composited into the polyethylene churn. Water samples for pesticides were drawn from the Teflon® churn splitter (after August 2002) and filtered through a 0.7-µm baked glass-fiber filter into 1-L baked glass bottles, stored at less than 4°C, and shipped to the NWQL within 24 hours. Samples for major ions and nutrients were drawn from the churn splitter and filtered or preserved, if necessary. Subsamples for analysis of filtered nutrients were pumped through a disposable 0.45-µm filter cartridge into opaque polyethylene bottles and chilled to less than 4°C. Samples for analysis of unfiltered nutrients were collected in translucent polyethylene bottles and preserved with sulfuric acid to a pH less than 2. Samples for analysis of major ions also were filtered through a 0.45-µm filter cartridge, and samples for analysis of cations, iron, and manganese were acidified with nitric acid to a pH less than 2. Samples were shipped on ice to the NWQL for pesticide and major ions analysis, and samples were shipped to the Bureau of Reclamation Boise laboratory for nutrients analysis. All equipment used to collect and process samples was cleaned with a 0.2-percent non-phosphate detergent, soaked in a 5-percent hydrochloric acid solution, and rinsed with deionized water, as described in Wilde (2004). Equipment used to filter the pesticide samples was additionally rinsed with pesticide-grade methanol and pesticide-free reagent water. All cleaned equipment was placed in doubled plastic bags and stored in a dust-free environment prior to sample collection.

Table 3. Inorganic and organic analytes and schedules, analytical methods, and references.

[**Abbreviations**: °C, degrees Celsius; CAS, Chemical Abstract Services; IC, ion-chromatography; ASF, automated-segment flow; ISE, ion-selective electrode; ICP, inductively coupled plasma; SPE, solid-phase extraction; GC/MS, gas-chromatography/mass spectrometry; HPLC/MS, high-performance liquid chromatography/mass spectrometry; USEPA, U.S. Environmental Protection Agency]

Analyte or schedule	CAS registry No.	Analytical method	Analytical method reference
Inorganic compounds			
Calcium	7440-70-2	ICP	Fishman, 1993
Chloride	16887-00-6	IC	Fishman and Friedman, 1989
Fluoride[1]	16984-48-8	ASF ISE	Fishman and Friedman, 1989
Iron	7439-89-6	ICP	Fishman, 1993
Magnesium	7439-95-4	ICP	Fishman, 1993
Manganese	7439-96-5	ICP	Fishman, 1993
Potassium[2]	7440-09-7	ICP	American Public Health Association and others, 1998
Residue, 180°C		Gravimetric	Fishman and Friedman, 1989
Silica	7631-86-9	Colorimetry, ASF, molybdate blue	Fishman and Friedman, 1989
Sodium	7440-23-5	ICP	Fishman, 1993
Sulfate	14808-79-8	IC	Fishman and Friedman, 1989
Ammonia as N		ISE, USEPA Method 350.3	U.S. Environmental Protection Agency, 1979
Ammonia plus organic nitrogen as N	7727-37-9	Total Kjeldahl Nitrogen, (colorimetric, semi-automatic), USEPA Method 351.2	U.S. Environmental Protetection Agency, 1993
Nitrite plus nitrate as N		Nitrate-Nitrite Nitrogen by colorimetry, USEPA Method 353.2	U.S. Environmental Protetection Agency, 1993
Orthophosphorus as P		Phosphorus, all forms (colorimetric, automatic, ascorbic), USEPA Method 365.1	U.S. Environmental Protetection Agency, 1993
Phosphorus as P		Phosphorus, all forms (colorimetric, automatic, ascorbic), USEPA Method 365.1	U.S. Environmental Protetection Agency, 1993
Organic compounds			
Schedule 2001	Various (see table 4)	SPE technology and GC/MS	Zaugg and others, 1995; Lindley and others (1996); and Madsen and others (2003)
Schedule 2060	Various (see table 4)	SPE technology and HPLC/MS	Furlong and others (2001)

[1]Analyzed by manual ISE method (Fishman and Friedman, 1989) from July 2002 through April 2003.
[2]Analyzed by flame atomic absorption (Faires, 1993) prior to May 2003.

Laboratory Methods

Samples for a broad spectrum of pesticides were analyzed at the NWQL using either gas chromatography/mass spectrometry (GC/MS) or high-performance liquid chromatography/mass spectrometry (HPLC/MS) techniques (table 4). Compounds that were sufficiently volatile and thermally stable for gas chromatography were analyzed by GC/MS, as described by Zaugg and others (1995), Lindley and others (1996), and Madsen and others (2003); the remaining pesticides were analyzed by HPLC/MS, as described by Furlong and others (2001).

The USGS NWQL collects water-quality control data on a continuing basis for method evaluation and to determine long-term method detection levels (LT-MDLs) and laboratory reporting levels (LRLs). Concentrations are reported as less than the LRL for samples in which the analyte was not detected or failed to meet necessary identification criteria. Analytes detected at concentrations lower than the lowest calibration standard or between the LT-MDL and the LRL and that pass identification criteria are reported with a remark code of “E”. In addition, some analytes generally have low or variable recovery and routinely are reported with an “E” remark code.

Table 4. Pesticide target analytes, laboratory reporting levels, drinking water standards or guidelines, and aquatic-life benchmarks.

[If laboratory reporting level changed during the study, the most frequently used level is indicated. **Pesticide target analyte:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-triazine; GC/MS, gas chromatography/mass spectrometry; HPLC/MS, high-performance liquid chromatography/mass spectrometry. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Drinking-water standards and guidelines:** Maximum contaminant levels for drinking water from U.S. Environmental Protection Agency (2004a). **Freshwater aquatic-life benchmark:** From U.S. Environmental Protection Agency (2004b), unless otherwise footnoted. **Abbreviations:** CAS, Chemical Abstracts Service; µg/L, microgram per liter; –, no data or not available; *, interim values (Canadian Council of Resource and Environment Ministers, 1997)]

Pesticide target analyte	Trade or common name(s)	Type of pesticide	CAS registry No.	Laboratory reporting level (µg/L)	Drinking-water standard or guideline (µg/L)	Freshwater aquatic-life benchmark (µg/L)
Gas Chromatography/Mass Spectrometry analytical data						
Acetochlor	Acenit, Sacenid	H	34256-82-1	0.006	–	–
Alachlor	Lasso	H	15972-60-8	.005	2	–
Atrazine[1]	Aatrexx	H	1912-24-9	.007	3	[3]1.8
Azinphos-methyl[2]	Guthion	I	86-50-0	.05	–	.01
Benfluralin	Balan, Benefin	H	1861-40-1	.010	–	–
Butylate	Sutran +, Genate Plus	H	2008-41-5	.004	[4]400	–
Carbaryl[1,2]	Sevin, Savit	I	63-25-2	.041	[4]700	[3].20
Carbofuran[1,2]	Furadan	I	1563-66-2	.02	40	[3]1.8
CIAT[1,2]	none	T	6190-65-4	.006	–	–
Chlorpyrifos	Lorsban	I	2921-88-2	.005	[4]20	.041
Cyanazine	Bladex	H	21725-46-2	.018	[4]1	[3]2.0
DCPA	Dacthal	H	1861-32-1	.003	[4]70	–
4,4'-DDE	none	T	72-55-9	.003	1	.001
Desulfinylfipronil	none	T	–	.012	–	–
Desulfinylfipronil amide	none	T	–	.029	–	–
Diazinon	several	I	333-41-5	.005	[4].6	[5].08
Dieldrin	Panoram D-31	I	60-57-1	.009	[6].02	.056
2,6-Diethylanaline	none	T	579-66-8	.006	–	–
Disulfoton	Di-Syston	I	298-04-4	.021	[4].3	–
EPTC	Eptam, Eradicane	H	759-94-4	.004	–	–
Ethalfluralin	Sonalan, Curbit EC	H	55283-68-6	.009	–	–
Ethoprophos	Mocap	I	13194-48-4	.005	–	–
Fipronil	Regent	I	120068-37-3	.016	–	–
Fipronil sulfide	none	T	120067-83-6	.013	–	–
Fipronil sulfone	none	T	120068-36-2	.024	–	–
Fonofos	Dyfonate	I	944-22-9	.003	[4]10	–
alpha-HCH	none	I	319-84-6	.005	[7].06	–
gamma-HCH	Lindane	I	58-89-9	.004	.2	[3].01
Linuron[1]	Lorox, Linex	H	330-55-2	.035	–	[3]7*
Malathion	several	I	121-75-5	.027	[4]100	0.1
Methyl parathion	Penncap-M	I	298-00-0	.015	32	–
Metolachlor[3]	Dual, Pennant	H	51218-45-2	.013	[4]100	[3]7.8*
Metribuzin	Lexone, Sencor	H	21087-64-9	.006	[4]200	[3]1*
Molinate	Ordram	H	2212-67-1	.003	–	–
Napropamide	Devrinol	H	15299-99-7	.007	–	–
Parathion	several	I	56-38-2	.010	–	.013
Pebulate	Tillam	H	1114-71-2	.004	–	–
Pendimethalin	Prowl, Stomp	H	40487-42-1	.022	–	–
cis-Permethrin	ambush, Pounce	I	54774-45-7	.006	–	–
Phorate	Thimet, Rampart	I	298-02-2	.011	–	–
Prometon	Pramitol	H	1610-18-0	.015	[4]100	–
Propyzamide	Kerb	H	23950-58-5	.004	–	–
Propachlor[4]	Ramrod	H	1918-16-7	.010	[4]90	–
Propanil	Stampede	H	709-98-8	.011	–	–
Propargite	Comite, Omite	I	2312-35-8	.023	–	–

Table 4. Pesticide target analytes, laboratory reporting levels, drinking water standards or guidelines, and aquatic-life benchmarks—Continued

[If laboratory reporting level changed during the study, the most frequently used level is indicated. **Pesticide target analyte:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-triazine; GC/MS, gas chromatography/mass spectrometry; HPLC/MS, high-performance liquid chromatography/mass spectrometry. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Drinking-water standards and guidelines:** Maximum contaminant levels for drinking water from U.S. Environmental Protection Agency (2004a). **Freshwater aquatic-life benchmark:** From U.S. Environmental Protection Agency (2004b), unless otherwise footnoted. **Abbreviations:** CAS, Chemical Abstracts Service; µg/L, microgram per liter; –, no data or not available; *, interim values (Canadian Council of Resource and Environment Ministers, 1997)]

Pesticide target analyte	Trade or common name(s)	Type of pesticide	CAS registry No.	Laboratory reporting level (µg/L)	Drinking-water standard or guideline (µg/L)	Freshwater aquatic-life benchmark (µg/L)
Gas Chromatography/Mass Spectrometry analytical data—Continued						
Simazine	Aquazine, Princep	H	122-34-9	0.005	4	–
Tebuthiuron[1]	Spike	H	34014-18-1	.016	3,500	–
Terbacil[1,2]	Sinbar	H	5902-51-2	.034	390	–
Terbufos	Counter	I	13071-79-9	.017	30.9	–
Thiobencarb	Bolero	H	28249-77-6	.010	–	–
Triallate[5]	Far-Go	H	2303-17-5	.002	–	–
Trifluralin	Treflan, Trilin	H	1582-09-8	.009	35	–
High-Performance Liquid Chromatography/Mass Spectrometry analytical data						
2,4-D	Weedon-2,4,-DP	H	94-75-7	0.038	70	[3]4.0
2,4-D methyl ester	many	H	1928-38-7	.016	–	[3]4.0
2,4-DB[2]	none	H	94-82-6	.020	–	[3]4.0
OIET[2]	none	T	2163-68-0	.032	–	–
3(4-Chlorophenyl)-1-methyl urea	none	T	5352-88-5	.036	–	–
3-Ketocarbofuran[2]	none	T	16709-30-1	.02	–	–
Acifluorfen	Blazer, Tackle	H	50594-66-6	.028	[6]10	–
Aldicarb[2]	Temik	I	116-06-3	.04	3	[3]1
Aldicarb sulfone[2]	none	T	1646-88-4	.018	2	[3]1
Aldicarb sulfoxide[2]	none	T	1646-87-3	.022	4	[3]1
Atrazine[1]	Aatrexx, Atratol	H	1912-24-9	.008	3	1.8
Bendiocarb	Ficam	I	22781-23-3	.020	–	–
Benomyl[2]	Benlate	F	17804-35-2	.022	–	–
Bensulfuron-methyl[2]	Londax	H	83055-99-6	.018	–	–
Bentazon[2]	Adagio, Galaxy, Storm	H	25057-89-0	.012	3,200	–
Bromacil[2]	Hyvar, Uragon	H	314-40-9	.018	90	[3]5.0
Bromoxynil	Buctril, Bromanil, Torch	H	1689-84-5	.028	–	[3]5.0
Caffeine	None	S	58-08-2	.018		–
Carbaryl[1]	Sevin	H	63-25-2	.018	[4]700	[3].20
Carbofuran[1]	Furadan, Crisfuran	H	1563-66-2	.016	40	21.8
3-Hydroxycarbofuran	None	T	16655-82-6	.008	–	–
Chloramben, methyl ester[2]	Amiben	H	7286-84-2	.024	–	–
Chlorimuron-ethyl[2]	Classic	H	90982-32-4	.032	–	–
Chlorothalonil[2]	Bravo, Forturf	F	1897-45-6	.035	55	[3].18
Clopyralid	Stinger, Lontrel	H	1702-17-6	.024	–	–
Cycloate[2]	Ro-Neet, Marathon	H	1134-23-2	.014	–	–
Dacthal monoacid	None	T	887-54-7	.028	–	–
CIAT[1,2]	None	T	6190-65-4	.028	–	–
CAAT[2,6]	None	T	3397-62-4	.022	–	–
CEAT[2]	None	T	1007-28-9	.08	–	–
Dicamba	Banvel, Marksman, Clarity	H	1918-00-9	.036	[4]200	[3]10*
Dichlorprop	2,4-DP, Weedon DP	H	120-36-5	.028	–	–
Dinoseb[2]	DNBP, Caldon, Dynamite	H	88-85-7	.038	7	[3].05*
Diphenamid	Rideon, Dymid, Enide	H	957-51-7	.010	[4]200	–
Diuron	DCMU, Direx, Aguron	H	330-54-1	.015	[4]10	–

Table 4. Pesticide target analytes, laboratory reporting levels, drinking water standards or guidelines, and aquatic-life benchmarks—Continued

[If laboratory reporting level changed during the study, the most frequently used level is indicated. **Pesticide target analyte:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-triazine; GC/MS, gas chromatography/mass spectrometry; HPLC/MS, high-performance liquid chromatography/mass spectrometry. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Drinking-water standards and guidelines:** Maximum contaminant levels for drinking water from U.S. Environmental Protection Agency (2004a). **Freshwater aquatic-life benchmark:** From U.S. Environmental Protection Agency (2004b), unless otherwise footnoted. **Abbreviations:** CAS, Chemical Abstracts Service; µg/L, microgram per liter; –, no data or not available; *, interim values (Canadian Council of Resource and Environment Ministers, 1997)]

Pesticide target analyte	Trade or common name(s)	Type of pesticide	CAS registry No.	Laboratory reporting level (µg/L)	Drinking-water standard or guideline (µg/L)	Freshwater aquatic-life benchmark (µg/L)
High-Performance Liquid Chromatography/Mass Spectrometry analytical data—Continued						
Fenuron[2]	Beet-Kleen	H	101-42-8	0.032	–	–
Flumetsulam[2]	DE498, XRD 498	H	98967-40-9	.040	–	–
Fluometuron	Cotoran, Lanex, Cottonex	H	2164-17-2	.016	[4]90	–
Imazaquin[2]	Skepter 1.5L, Image 1.5LC	H	81335-37-7	.036	–	–
Imazethapyr[2]	Pursuit, Pursuit DG	H	81335-77-5	.038	–	–
Imidacloprid	Admire, Gaucho, Merit	I	138261-41-3	.020	–	–
Linuron[1]	Lorox, Linex, Afalon	H	330-55-2	.014	–	–
MCPA	Metaxon, Border Master	H	94-74-6	.030	34	[3]2.6*
MCPB[2]	Troptox, Can-Trol	H	94-81-5	.010	–	–
Metalaxyl	Apron, Subdue, Ridomil	F	57837-19-1	.012	–	–
Methiocarb	Draza, Mesurol	I	2032-65-7	.010	–	–
Methomyl[2]	Lannate,Nudrin, Lanox	I	16752-77-5	.020	[4]200	–
Metsulfuron methyl[2]	Escort, Gropper, Ally	H	74223-64-6	.025	–	–
Neburon	Granurex, Herbalt, Kloben	H	555-37-3	.012	–	–
Nicosulfuron[2]	Accent, Accent DF	H	111991-09-4	.04	–	–
Norflurazon[2]	Zorial, Evital, Solicam	H	27314-13-2	.020	–	–
Oryzalin[2]	Ryzelan, Surflan, Dirimal	H	19044-88-3	.012	–	–
Oxamyl[2]	Vydate: Thioxamyl	I	23135-22-0	.030	200	–
Picloram[7]	Tordon, Amdon, Grazon	H	1918-02-1	.020	500	[3]29*
Propham	Chem-Hoe, IPC, Premalox	H	122-42-9	.030	[4]100	–
Propiconazole	Tilt, Orbit, Wocosin	F	60207-90-1	.010	–	–
Propoxur	Baygon, PHC, Suncide	I	114-26-1	.008	[4]3	–
Siduron	Tupersan, Trey	H	1982-49-6	.020	–	–
Sulfometuron-methyl	Oust, DPX-T5648	H	74222-97-2	.038	–	–
Tebuthiuron[1]	Graslan, Spike, Perflan	H	34014-18-1	.032	[4]500	–
Terbacil[1,2]	Sinbar, DPX-D732, Geonter	H	5902-51-2	.016	[4]90	–
Tribenuron methyl[2,8]	Express, DPX-L5300	H	101200-48-0	.0088	–	–
Triclopyr	Garlon, Curtail, Redeem	H	55335-06-3	.026	–	–

[1]Analyzed by GC/MS and HPLC/MS.

[2]Because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated).

[3]Canadian water-quality guidelines for the protection of freshwater aquatic life (Canadian Council of Ministers of the Environment, 2003).

[4]U.S. Environmental Protection Agency lifetime-health advisory for a 70-kilogram adult (U.S. Environmental Protection Agency, 2004a).

[5]Great Lakes water-quality objective for protection of aquatic life, from the International Joint Commission (IJC) Canada and United States, 1978.

[6]U.S. Environmental Protection Agency risk-specific dose health advisory associated with a cancer risk of 10-5 (1 in 100,000) was calculated from risk-specific dose of 10-4 (RSD4) (U.S. Environmental Protection Agency, 2004a).

[7]U.S. Environmental Protection Agency risk-specific dose health advisory associated with a cancer risk of 10-5 (1 in 100,000), from USEPA Integrated Risk Information System (IRIS) data base (U.S. Environmental Protection Agency, 2005b).

[8]Tibenuron methyl was routinely reported by the laboratory as a null result because of problems with stability of calibration standards. The analyte was removed from the analytical method September 30, 2004.

Quality Assurance/Quality Control

About 15 percent of all samples submitted to the laboratories were quality-control samples, which included field blanks and equipment blanks to measure possible contamination and bias; replicate samples to measure variability; and field-matrix spike samples to measure recovery of analytes. All samples for pesticide analysis were spiked with surrogate analytes prior to extraction, to monitor accuracy and precision of the analytical procedures. Wilde and others (1999b) define these quality-control samples. Additionally, laboratory quality-control samples were routinely analyzed as part of the laboratory quality-assurance plan described by Maloney (2005).

Field- and equipment-blank samples for pesticide analysis were free of contamination, except for detection of EPTC in one field blank at a concentration of 0.043 µg/L and detection of caffeine in one field blank at an estimated concentration of 0.00043 µg/L. No adjustments were made in the data set or data analysis on the basis of these results.

Precision data were obtained for two sets of replicate pesticide samples (table 16, at back of report). Differences in concentration between replicates ranged from 0 to 71 percent, as measured by relative percentage of difference (94 percent of the differences were ≤5 percent). Percentage of relative differences for atrazine ranged from 5.1 to 71 percent. The relative percentage of difference was 5.1 for one set of replicates using the GS/MS techniques; the relative percentage of difference was 62 and 71 for two other sets of replicates analyzed using the HPLC/MS method. The GC/MS technique is the preferred method of analysis and is the value used for all data analysis. No modifications were made to the data set based on these results. Mean recovery percentages of GC/MS target analytes in field-matrix spike samples ranged from 33 to 213 percent, with a median recovery of 97.5 percent (table 17, at back of report). Mean recovery percentages of HPLC/MS target analytes in field-matrix spike samples ranged from 34 to 150 percent (table 17), with a median recovery of 86.5 percent. Although recoveries of HPLC/MS target analytes generally were lower than recoveries of GC/MS target analytes, recoveries generally are large enough and consistent enough that the data are acceptable and useful for analysis. However, because of lower recoveries and greater variability, the probability of false negatives is greater for HPLC/MS target analytes than for GC/MS and the effective detection level generally is larger. No modifications were made to the environmental data set, but recovery percentages for these analytes need to be considered when interpreting the data.

Seven pesticides were analyzed by GC/MS and HPLC/MS methods. Three pesticides (atrazine, CIAT, and tebuthiuron) were reported only by the "preferred" method (GC/MS). The remaining four pesticides (carbaryl, carbofuran, linuron, and terbacil) were reported with both methods. The NWQL uses a hierarchical procedure in selecting the "preferred" method for these compounds (Mark Sandstrom, USGS National Water Quality Laboratory, written commun., 2004). For the current study, all pesticides were included in the analysis of quality-control samples to determine intra-laboratory method precision and accuracy. Precision between analytical methods is summarized in table 18 (at back of report). Generally, precision between the two analytical methods is good. Comparison between the two methods can be summarized into four categories: (1) both methods reported no detections, (2) both methods reported a detection, (3) one method reported no detection and the other method reported a detection that was either near or less than the reporting level of the other method, and (4) one method reported no detection and the other method reported a detection that was larger than the reporting level of the other method. For example, case 3 is illustrated by a detection of CIAT ^{E}0.008 by GC/MS and the HPLC/MS method reporting of CIAT as less than 0.028. Case 4 only occurred with analysis of terbacil, and an example is the detection by GC/MS of ^{E}0.026 and the HPLC/MS method reporting of less than 0.010. One method reported a detection and the other did not a total of 13 percent of the time, 11 percent of the time as a case 3 difference and 2 percent of the time as a case 4 difference. This likely indicates the preference for the GC/MS method for the analysis of terbacil.

Occurrence, Distribution, and Transport of Pesticides

All samples were analyzed for concentrations of pesticides, major ions, iron, manganese, and nutrients. Summaries of results for inorganic constituents and pesticides are presented. Estimates of pesticide use are discussed and compared in relation to detected and non-detected pesticides, and a comparison is made between pesticides detected in this study and pesticides detected in earlier studies.

Field Measurements and Inorganic Constituents

Water temperature, pH, DO concentrations, specific conductance and concentrations of major ions, trace elements, and nutrients data were measured at all sampling sites where pesticide data were collected (table 5). Water-temperature measurements are subject to the water-temperature criteria for core and non-core designated use by fish in the Washington 2003 water-quality standards (State of Washington, 2003). (The term "non-core" to refers to "salmon and trout spawning, non-core rearing, and migration" designated use and "core" refers to the "salmon and trout spawning, core rearing, and migration" designated use.) The criteria specify that water temperature be measured by the 7-day average of daily maximum temperatures (7DADMax; State of Washington, 2003), but extended deployment of temperature sensors and calculation of a 7-day average of maximum temperatures were beyond the scope of this study. Water temperatures measured during this study are only an indication of instantaneous temperatures at time of sampling and indicate that the temperature criterion may have been exceeded.

Measured water temperature was greater than the State of Washington criterion of 16ºC for core rearing, salmon and trout spawning, and migration in 18 instances. These exceedances occurred 7 times at Red Rock Coulee, 5 times at Crab Creek, 4 times at Lind Coulee, and 2 times at Sand Hollow. In 11 of these 18 instances, measured temperature also was greater than the criterion of 17.5ºC for non-core rearing, salmon and trout spawning, migration, and salmon and trout rearing and migration only.

The State of Washington aquatic-life criteria for DO are listed as 1-day minimum. The criterion of 9.5 mg/L for salmon and trout spawning, core rearing, and migration was exceeded eight times at three sites during this study from June to early October: two times at Sand Hollow, three times at Red Rock Coulee, and three times at Crab Creek. State of Washington aquatic-life criterion for pH of 8.5 for fresh water was exceeded 12 times: 6 times at Red Rock Coulee, 3 times at Sand Hollow, 2 times at Lind Coulee, and 1 time at Crab Creek.

Table 5. Summary of field measurements and concentrations of inorganic constituents in surface-water samples collected from the four irrigation return-flow drainage basins, Columbia Basin Project, July 2002 through October 2004.

[Dissolved solids, residue on evaporation, dried at 180 degrees Celsius. **Abbreviations:** ft^3/s, cubic foot per second; ºC; degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; [E], estimated (below laboratory reporting level); <, less than]

Constituent or property	Number of samples	Value		
		Minimum	Maximum	Median
Crab Creek				
Field measurements				
Streamflow (ft^3/s)	12	129	331	214.5
Temperature (ºC)	12	4.9	22.4	15.05
pH (standard units)	12	8.1	8.6	8.4
Specific conductance (µS/cm)	12	492	885	540
Dissolved oxygen (mg/L)	12	8.6	12.6	10.45
Major ions				
Calcium (mg/L)	12	33.1	52.6	37.95
Magnesium (mg/L)	12	20.4	32.6	21.45
Sodium, (mg/L)	12	38.2	84.9	46.4
Potassium, (mg/L)	12	5.97	12.1	7.22
Chloride (mg/L)	12	12.8	29.6	14.9
Sulfate (mg/L)	12	46.8	100	51.95
Fluoride (mg/L)	12	.48	.83	.50
Silica (mg/L)	12	15.6	35.0	22.55
Alkalinity (mg/L as $CaCO_3$)	8	182	307	209
Dissolved solids (mg/L)	12	305	560	333.5

Table 5. Summary of field measurements and concentrations of inorganic constituents in surface-water samples collected from the four irrigation return-flow drainage basins, Columbia Basin Project, July 2002 through October 2004.—Continued

[Dissolved solids, residue on evaporation, dried at 180 degrees Celsius. **Abbreviations:** ft^3/s, cubic foot per second; ºC; degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; [E], estimated (below laboratory reporting level); <, less than]

Constituent or property	Number of samples	Value		
		Minimum	Maximum	Median
Crab Creek—Continued				
Trace elements				
Iron (µg/L)	12	5.0	27	8.5
Manganese (µg/L)	12	2.3	8.3	3.6
Nutrients				
Ammonia (mg/L as N)	12	<.010	.03	.010
Ammonia plus organic nitrogen (mg/L as N)	12	.04	.88	.355
Nitrite plus nitrate (mg/L as N)	12	1.05	2.5	1.56
Phosphorus (mg/L as P)	12	.024	.099	.034
Orthophosphate (mg/L as P)	12	<.003	.071	.016
Lind Coulee				
Field measurements				
Streamflow (ft^3/s)	12	58	355	255
Temperature (ºC)	12	8.1	19.8	14.85
pH (standard units)	12	8.1	8.8	8.4
Specific conductance (µS/cm)	12	203	573	292
Dissolved oxygen (mg/L)	11	10.6	14.5	11.4
Major ions				
Calcium (mg/L)	12	22.5	46.9	28.45
Magnesium (mg/L)	12	6.56	19.6	9.69
Sodium, (mg/L)	12	9.36	51.8	16.4
Potassium, (mg/L)	12	1.62	6.18	2.575
Chloride (mg/L)	12	2.95	15.7	5.4
Sulfate (mg/L)	12	15.0	65.9	22.25
Fluoride (mg/L)	12	<.2	.7	.29
Silica (mg/L)	12	9.49	42.6	13.4
Alkalinity (mg/L as $CaCO_3$)	8	81	204	105.5
Dissolved solids (mg/L)	12	124	391	186
Trace elements				
Iron (µg/L)	12	<10	16	9.0
Manganese (µg/L)	12	5.90	21.5	14.2
Nutrients				
Ammonia (mg/L as N)	12	<.01	.02	.02
Ammonia plus organic (mg/L as N)	12	.15	.28	.205
Nitrite plus nitrate (mg/L as N)	12	.56	5.02	1.735
Phosphorus (mg/L as P)	12	.027	.079	.050
Orthophosphate (mg/L as P)	12	.017	.057	.030
Red Rock Coulee				
Field measurements				
Streamflow (ft^3/s)	12	43	114	71.5
Temperature (ºC)	12	4.6	23.1	16.55
pH (standard units)	12	8.2	8.9	8.55
Specific conductance (µS/cm)	12	374	660	420
Dissolved oxygen (mg/L)	12	8.3	12.7	9.85

Table 5. Summary of field measurements and concentrations of inorganic constituents in surface-water samples collected from the four irrigation return-flow drainage basins, Columbia Basin Project, July 2002 through October 2004.—Continued

[Dissolved solids, residue on evaporation, dried at 180 degrees Celsius. **Abbreviations:** ft^3/s, cubic foot per second; ºC; degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; [E], estimated (below laboratory reporting level); <, less than]

Constituent or property	Number of samples	Value		
		Minimum	Maximum	Median
Red Rock Coulee—Continued				
Major ions				
Calcium (mg/L)	12	21.3	53.8	37.05
Magnesium (mg/L)	12	16.6	29.8	18.45
Sodium, (mg/L)	12	17.8	38.6	22.1
Potassium, (mg/L)	12	2.02	3.55	2.705
Chloride (mg/L)	12	9.03	19.3	11.0
Sulfate (mg/L)	12	31.5	63.9	36.4
Fluoride (mg/L)	12	.3	.6	.4
Silica (mg/L)	12	19.3	40.8	23.5
Alkalinity (mg/L as $CaCO_3$)	8	137	224	155.5
Dissolved solids (mg/L)	12	230	411	266
Trace elements				
Iron (µg/L)	12	<6.0	6.0	5.0
Manganese (µg/L)	12	<2.0	3.4	1.8
Nutrients				
Ammonia (mg/L as N)	12	<.01	.05	.02
Ammonia plus organic (mg/L as N)	12	.20	.36	.285
Nitrite plus nitrate (mg/L as N)	12	1.72	5.5	2.195
Phosphorus (mg/L as P)	12	.019	.036	.023
Orthophosphate (mg/L as P)	12	<.003	.016	.006
Sand Hollow				
Field measurements				
Streamflow (ft^3/s)	12	23	141	92
Temperature (ºC)	12	8.1	22.0	13.7
pH (standard units)	12	8.1	8.6	8.45
Specific conductance (µS/cm)	12	141	719	336.5
Dissolved oxygen (mg/L)	12	8.4	12.0	10.55
Major ions				
Calcium (mg/L)	12	27.6	76.3	35.8
Magnesium (mg/L)	12	9.79	36.1	14.1
Sodium, (mg/L)	12	9.0	29.1	12.65
Potassium, (mg/L)	12	1.18	2.51	1.57
Chloride (mg/L)	12	5.04	27.9	9.32
Sulfate (mg/L)	12	16.9	66.1	25.05
Fluoride (mg/L)	12	.17	.50	.23
Silica (mg/L)	12	9.8	43.9	17.35
Alkalinity (mg/L as $CaCO_3$)	8	89	106	124.5
Dissolved solids (mg/L)	12	167	491	213.5
Trace elements				
Iron (µg/L)	12	[E]4	<10	<6
Manganese (µg/L)	12	[E].70	[E]2.5	1.15
Nutrients				
Ammonia (mg/L as N)	12	<.01	.07	.02
Ammonia plus organic (mg/L as N)	12	.06	.45	.235
Nitrite plus nitrate (mg/L as N)	12	2.46	17.9	4.515
Phosphorus (mg/L as P)	12	<.010	.052	.023
Orthophosphate (mg/L as P)	12	<.003	.027	.006

Dissolved-solids concentrations varied spatially and seasonally. Dissolved-solids concentrations increased during the non-irrigation season and concentrations between sites generally increased as water moved through the CBP, from Lind Coulee down to Crab Creek (fig. 2). Average concentration of dissolved solids at Lind Coulee during this study was 211 mg/L, increasing to an average of 379 mg/L in samples from Crab Creek. Average concentrations from intermediate sites at Sand Hollow and Red Rock Coulee were 250 and 296 mg/L, respectively. Dissolved-solids concentrations increased during the non-irrigation season, reflecting a larger ground-water contribution to base flow. Average dissolved-solids concentration at all sites was 249 mg/L during irrigation season and 454 mg/L during non-irrigation season.

The predominant major ions from all sites generally were from calcium, magnesium, and bicarbonate (fig. 3). Although some overlap was present between the major-ion characteristics of the four sites, each site generally was grouped differently on a major-ion diagram and all were uniquely different from the irrigation source water, represented by the Columbia River. Additionally, samples from Sand Hollow and Lind Coulee during the non-irrigation season were clearly differentiated from samples

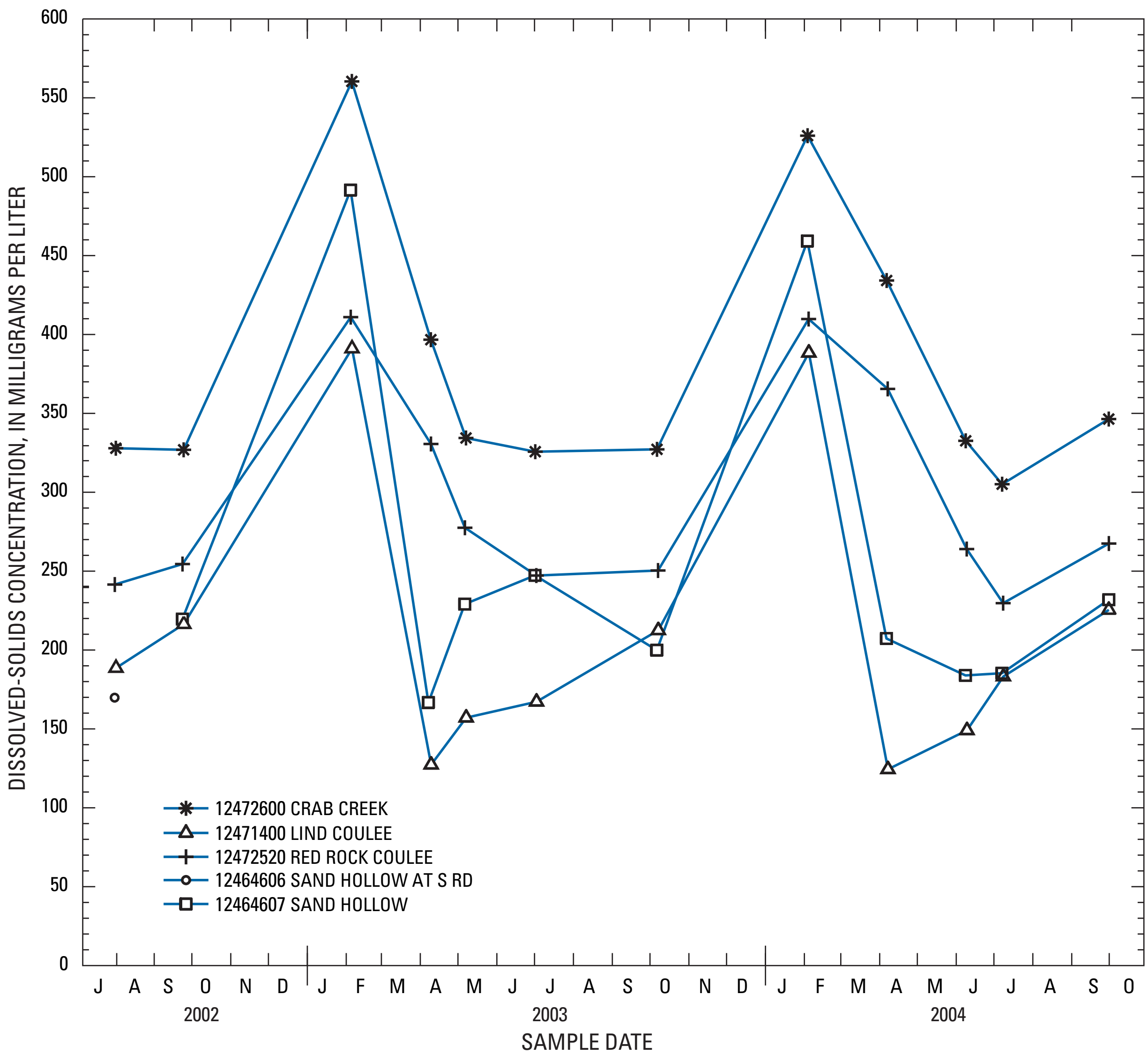


Figure 2. Concentrations of dissolved solids in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.
Site 12464606 was sampled only once in July 2002, and all other samples for Sand Hollow drainage basin were from site 12464607.

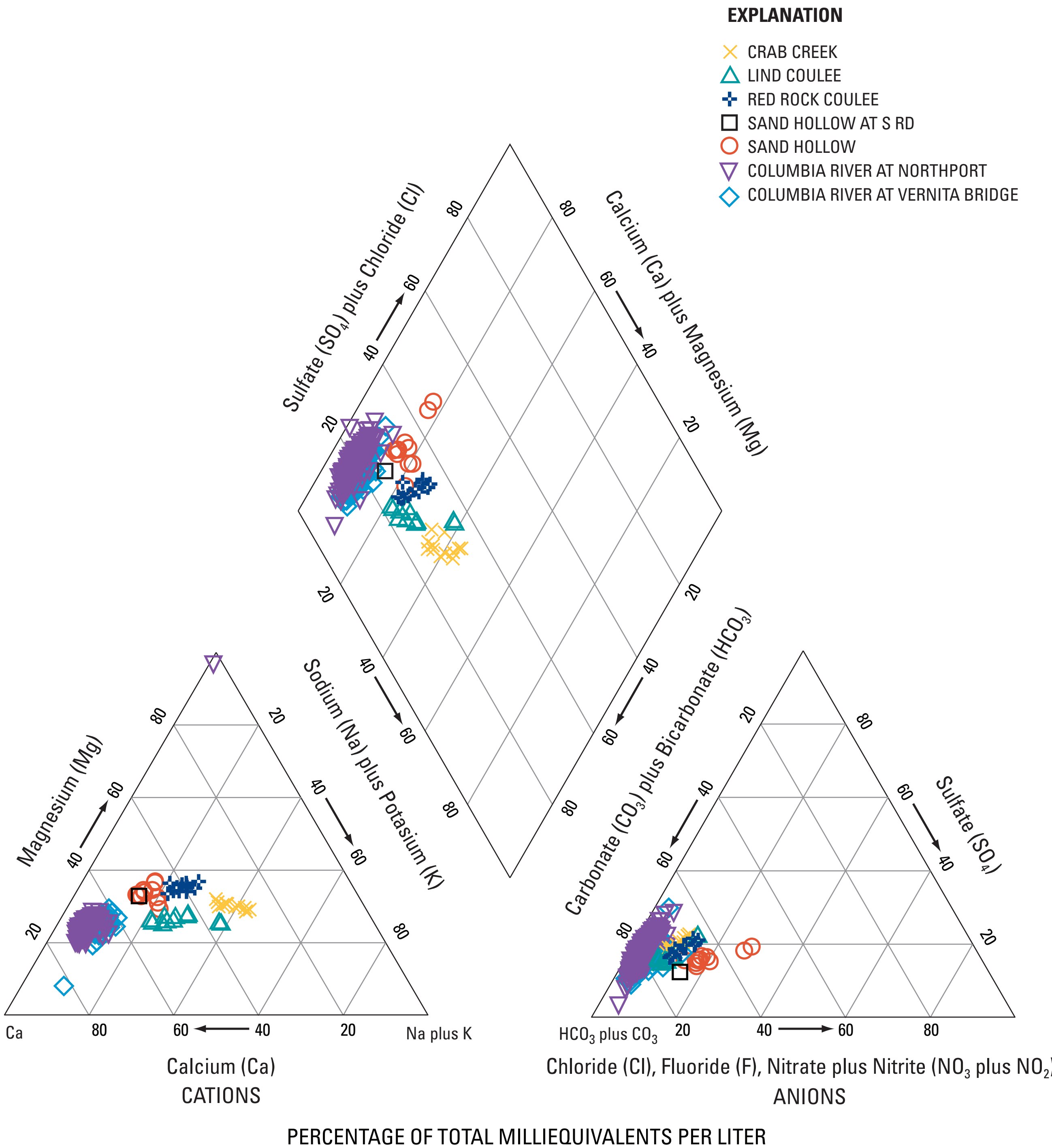


Figure 3. Percentage of major ions in surface water from the Columbia River and from the four irrigation return-flow drainage basins, Columbia Basin Project, Washington.

collected during the irrigation season. Anions for all samples were predominantly from bicarbonate and cations were predominantly from calcium. During the irrigation season, calcium was the predominant cation for both sites. However, during the non-irrigation, concentrations of chloride and nitrate increased in samples from Sand Hollow and reflect a shift in the percentage of chloride, fluoride, and nitrite plus nitrate. Similarly, the percentage of sulfate plus chloride for Sand Hollow also increased during the non-irrigation season. Samples from Lind Coulee during the non-irrigation season also are readily differentiated from irrigation season samples because of an increase in sodium plus potassium during the non-irrigation season. However, the percentage of nitrite plus nitrate for samples from Sand Hollow nearly doubled during the non-irrigation season and the percentages of sulfate and chloride increased. Similarly, samples from Lind Coulee during the non-irrigation season were clearly differentiated from samples collected during the irrigation season because of a shift in the cation percentages, with less calcium and more sodium.

Generally, the ratio of dissolved solids divided by specific conductance is a well-defined relation (Hem, 1985) for many rivers and streams. Because no long-term data for irrigation source water (from Lake Roosevelt or Banks Lake) are publicly available, historical information for the Columbia River above Lake Roosevelt (at Northport, Wash.) and downstream of Lake Roosevelt (near Priest Rapids Dam) can be used to approximate the quality of irrigation source water. The median ratio of dissolved solids to specific conductance ranges from 0.58 to 0.64 for the sites in the four irrigation return-flow basins and the Columbia River sites (table 6). However, the relation between silica and calcium provides an even better "signature" of major ions in the irrigation return flow (table 17). The long-term median silica-calcium ratios for the sites at Columbia River at Northport and Priest Rapids Dam are 0.23 and 0.26, respectively. As the irrigation water flows through the CBP, the ratio in samples increases, reflected by the higher ratios. Although ranges of the ratio overlap, each individual sample ratio was uniquely different from the others during that sampling period. Major-ion, trace-element, and nutrient concentrations generally were within State and Federal criteria. Concentrations of nitrite plus nitrate in two samples collected from Sand Hollow during the non-irrigation season exceeded the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) for drinking water of 10 mg/L.

Table 6. Summary of calculated major ion ratios in surface-water samples collected from the four irrigation return-flow drainage basins, Columbia Basin Project, and the Columbia River, Washington, July 2002 to October 2004.

[Columbia River data are from 1960–2000. The Sand Hollow sites were combined for analysis. **Abbreviations:** SiO_2/Ca: ratio of silica and calcium; Dissolved solids/SC, ratio of dissolved solids and specific conductance in microsiemens per centimeter at 25 degrees Celsius]

Sampling site	SiO_2/Ca			Dissolved solids/SC		
	Minimum	Maximum	Median	Minimum	Maximum	Median
Crab Creek	0.44	0.69	0.59	0.60	0.66	0.62
Lind Coulee	.40	.91	.70	.59	.77	.64
Red Rock Coulee	.53	.76	.64	.57	.68	.62
Sand Hollow	.36	.58	.49	.57	.70	.62
Columbia River at Northport	.15	.67	.23	.33	.89	.58
Columbia River at Vernita Bridge, near Priest Rapids Dam	.19	.57	.26	.46	.80	.58

Occurrence and Distribution of Pesticides

Forty-two pesticides and five metabolites were detected in samples from the four irrigation return-flow drainage basins in the CBP from July 2002 to October 2004 (table 7). The greatest number of compounds, 37, was detected at Sand Hollow, followed by 33 at Lind Coulee, 30 at Red Rock Coulee, and 28 at Crab Creek. Herbicides were the most frequently detected pesticides, followed by insecticides, metabolites, and fungicides. Atrazine, bentazon, diuron, and 2,4-D were the most frequently detected herbicides, and chlorpyrifos and azinphos-methyl were the most frequently detected insecticides. Of the five metabolites detected, four were degradation products of triazine herbicides and one was the degradation product of DCPA (dacthal monoacid). CIAT (commonly referred to as deethylatrazine), CEAT, CAAT, and OIET were the most frequently detected metabolites.

Pesticide concentrations in samples from the CBP did not exceed any drinking-water standards or guidelines, but concentrations of three insecticides and one herbicide did exceed USEPA or Canadian freshwater aquatic-life benchmarks (table 8). Concentrations of the insecticide azinphos-methyl exceeded USEPA recommended chronic water-quality criterion for the protection of freshwater aquatic life of 0.01 µg/L at least once at each of the four sites. Concentrations in samples from Sand Hollow also exceeded USEPA recommended freshwater chronic criterion for the protection of freshwater aquatic life for chlorpyrifos (0.041), and Canadian guidelines for the protection of freshwater aquatic life for lindane and dinoseb (0.01, and 0.05 µg/L, respectively). Water-quality aquatic-life benchmarks generally were exceeded in June and July, during the middle of the irrigation season, except the criterion for dinoseb, which was exceeded in one sample during non-irrigation season in February 2003, at a concentration of 0.14 µg/L.

Pesticides can be toxic to aquatic life in streams, and the ECOTOX (ECOTOXicology) database (U.S. Environmental Protection Agency, 2005a) provides single-chemical toxicity information for aquatic freshwater life (table 9). Data retrieved from ECOTOX contained a substantial number of apparent duplicate entries (Munn and Gilliom, 2001, and Patrick Moran, U.S. Geological Survey, oral commun., November 2005), and these were removed. Because of the complex mixtures and seasonal patterns of pesticides, it is difficult to link chemical conditions in streams to effects on aquatic biota (Munn and Gilliom, 2001). The endpoint concentration for comparison of aquatic toxicity to fish used in this study is median lethal concentrations (LC_{50}), which is a statistically estimated concentration that is expected to be lethal to 50 percent of a group of organisms tested. LC_{50} for all pesticides analyzed during this study are far greater than concentrations detected in samples collected from irrigation-return flows during this study. However, data are not available for all pesticides, and additive or possible synergistic effects of multiple chemicals are not accounted for by this measure of aquatic toxicity. The most toxic insecticides analyzed during this study are azinphos-methyl, chlorpyrifos, lindane, and malathion, with LC_{50} values that range from 1.3 to 2.4 µg/L. Concentrations of pesticides analyzed during this study are far less than these LC_{50} concentrations. The most toxic herbicides were trifluralin, pendimethalin, ethalfluvalin, and diacamba, with LC_{50} values that range from 8.4 to 138 µg/L. LC_{50} values for specific pesticides are a factor of 110 greater than maximum concentrations of pesticides detected in samples from the four drainage basins during this study. Munn and Gilliom (2001) suggest use of a pesticide toxicity index (PTI), which is the sum of toxicity quotients for each compound measured in a stream. This approach may be useful in relating pesticide toxicity between drainage basins and over time, but it is beyond the scope of this study.

Total number of pesticide detections and total concentrations of those detections show a distinct seasonal pattern at the four sites, with the highest number of detections and total concentrations during the middle of the irrigation season, April to October (fig. 4). Samples from Sand Hollow basin generally had the greatest number of pesticides per sample, ranging from about 8 pesticides detected in a sample during the end of irrigation season to more than 20 pesticides detected in samples collected during the middle of irrigation season. Samples from Lind Coulee basin had the fewest number of pesticides per sample, ranging from 4 to 18 pesticides with the highest number also occurring during the middle of irrigation season.

The pattern for total pesticides concentrations for Sand Hollow basin was slightly different than those for the other three basins, with a substantially higher total concentration in the sample collected during the 2003 non-irrigation season. This may be an aberration that occurred only in 2003, but it likely is due to the increase in concentrations of atrazine, CIAT, bentazon, and bromacil during base-flow conditions in the non-irrigation season. Total pesticide concentrations in the sample collected during the 2004 non-irrigation season were higher than those in late-irrigation season samples, but it is not clear why the 2003 non-irrigation sample was substantially higher. The increase in concentration of these compounds during base flow indicates that ground water contributes a substantial part of the pesticide load for these compounds. Further study of pesticides in the irrigation return-flow drainage basins during the non-irrigation season would be helpful.

Table 7. Maximum concentrations and number of pesticide detections in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.

[All concentrations are in micrograms per liter. Concentrations in **bold** represent values that exceed freshwater aquatic-life benchmarks (see table 4). **Pesticide:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-tirazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isopropylamino-t-ethylamino-*s*-triazine. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Number of detections:** All, sum of all detections at all surface-water sites. **Abbreviations**: LRL, laboratory reporting level; SH, Sand Hollow; LCWA, Lind Coulee; CRCR, Crab Creek; RRCU, Red Rock Coulee; M, presence of material verified but not quantified; [E], because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; –, not detected]

Pesticide	Type of pesticide	LRL	Maximum concentration				Number of detections				All
			SH	LCWA	CRCR	RRCU	SH	LCWA	CRCR	RRCU	
Atrazine[1]	H	0.007	0.029	0.012	0.026	0.032	11	10	12	12	45
CIAT[1]	T	.006	[E].036	[E].009	[E].019	[E].015	11	9	12	12	44
Bentazon	H	.012	[E].25	[E].01	[E].04	[E].07	12	6	12	11	41
Diuron	H	.014	[E].22	.26	.10	.11	10	10	10	10	40
2,4-D	H	.038	.23	.44	.36	.77	10	8	11	10	39
Simazine	H	.005	.213	.024	.017	.022	7	1	9	10	27
Terbacil[1]	H	.034	[E]1.01	–	[E].061	[E].075	12	0	6	7	25
DCPA	H	.003	.011	.044	.05	.169	4	7	6	7	24
EPTC	H	.004	.085	.12	.075	.1	4	4	7	8	23
Bromacil	H	.018	[E].12	[E].13	[E].01	[E].03	8	5	2	5	20
Metolachlor	H	.006	[E].008	.134	[E].010	[E].011	4	7	4	5	20
Terbacil[2]	H	.016	[E]1.35	–	[E].031	[E].090	10	0	3	5	18
Metribuzin	H	.006	.052	.016	[E].005	.008	7	4	1	4	16
Alachlor	H	.005	.012	–	.017	.013	6	0	3	4	13
2,4-D methyl ester	H	.016	.013	.017	.041	[E].080	2	1	4	4	13
Chlorpyrifos	I	.005	**.053**	.006	.011	.027	5	2	3	3	13
Pendimethalin	H	.022	.388	.033	–	–	7	5	0	0	12
Azinphos-methyl	I	.05	[E]**.034**	[E]**.026**	[E]**.019**	[E]**.018**	4	3	2	2	11
Dicamba	H	.036	[E].03	[E].19	[E].06	[E].13	2	3	3	3	11
Dinoseb	H	.038	**.14**	–	–	–	10	0	0	0	10
CEAT	T	.08	M	–	[E].01	[E].01	1	0	2	4	7
CAAT	T	.040	[E].01	[E].01	[E].01	[E].01	3	2	1	1	7
OIET	T	.032	[E].007	[E].006	[E].007	[E].006	2	2	2	1	7
Carbaryl[1]	I	.041	[E].070	–	[E].009	–	4	0	2	0	6
Linuron[1]	H	.035	[E].007	[E].013	[E].013	[E].014	1	2	1	1	5
Benomyl	F	.022	–	.082	[E].006	[E].017	0	1	1	2	4
Caffeine	S	.018	.0331	[E].0052	–	[E].0089	2	1	0	1	4
Diazinon	I	.005	.007	–	.008	.03	1	0	1	2	4
Diphenamid	H	.010	[E].02	–	[E].01	[E].03	1	0	1	2	4
Carbaryl[2]	I	.018	[E].01	–	–	–	3	0	0	0	3
Bromoxynil	H	.028	[E].01	M	–	–	2	1	0	0	3
Malathion	I	.027	[E].015	[E].017	–	.03	1	1	0	1	3
Metalaxyl	F	.012	[E].01	.04	–	–	1	2	0	0	3
Methomyl	I	.020	[E].016	[E].011	–	–	1	2	0	0	3
Norflurazon	H	.020	[E].01	–	–	M	1	0	0	2	3
Trifluralin	H	.009	–	[E].004	–	–	0	2	0	0	3
Linuron[2]	H	.014	[E].01	–	–	[E].01	1	0	0	1	2
2,4-DB	H	.020	–	[E].06	–	–	0	2	0	0	2
Dacthal monoacid	T	.028	–	–	.02	.02	0	0	1	1	2
Ethalfluralin	H	.009	–	[E].009	–	–	0	2	0	0	2
Ethoprophos	I	.005	.016	–	–	.009	1	0	0	1	2
MCPA	H	.030	[E].03	M	–	–	1	1	0	0	2
Prometon	H	.010	M	–	–	[E].01	1	0	0	1	2
Chlorothalonil	F	0.035	–	[E]0.06	–	–	0	1	0	0	1

Table 7. Maximum concentrations and number of pesticide detections in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.—Continued

[All concentrations are in micrograms per liter. Concentrations in **bold** represent values that exceed freshwater aquatic-life benchmarks (see table 4). **Pesticide:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-tirazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isopropylamino-t-ethylamino-*s*-triazine. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Number of detections:** All, sum of all detections at all surface-water sites. **Abbreviations**: LRL, laboratory reporting level; SH, Sand Hollow; LCWA, Lind Coulee; CRCR, Crab Creek; RRCU, Red Rock Coulee; M, presence of material verified but not quantified; E, because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; –, not detected]

Pesticide	Type of pesticide	LRL	Maximum concentration				Number of detections				All
			SH	LCWA	CRCR	RRCU	SH	LCWA	CRCR	RRCU	
Clopyralid	H	.024	–	–	E0.01	–	0	0	1	0	1
Lindane	I	.004	**0.018**	–	–	–	1	0	0	0	1
Nicosulfuron	H	.04	–	–	E.01	–	0	0	1	0	1
Oxamyl	I	.030	–	.03	–	–	0	1	0	0	1
Propiconazole	F	.010	–	E.01	–	–	0	1	0	0	1
Triallate	H	.006	–	.004	–	–	0	1	0	0	1
Triclopyr	I	.026	E.01	–	–	–	1	0	0	0	1
			Number of samples analyzed				**12**	**12**	**12**	**12**	**48**

[1]Analysis by gas chromatography/mass spectrometry (GC/MS).
[2]Analysis by high-performance liquid chromatography/mass spectrometry (HPLC/MS).

Table 8. Summary of pesticide concentrations in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.

[All concentrations are in micrograms per liter. Concentrations of pesticides in **bold** represent values that exceed freshwater aquatic-life benchmarks (see table 4). **Pesticide:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isoprobylamino-6-ethylamino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-triazine. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Drinking-water standards:** Maximum contaminant levels for drinking water from U.S. Environmental Protection Agency (2004a). **Freshwater aquatic-life benchmarks:** Standards from U.S. Environmental Protection Agency (2004b), unless otherwise footnoted. **Abbreviations:** LRL, laboratory reporting limit; M, presence of material verified, but not quantified; n, number of samples; E, because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; <, less than; –, no data or not available; *, interim values (Canadian Council of Resources and Environment Ministers, 1997)]

Pesticide	Type of pesticide	LRL	Median	Maximum	Percentage of detections (n=12)	Number of detections that exceed aquatic-life benchmarks	Number of detections that exceed drinking water standards
Crab Creek							
CIAT	T	0.006	E0.011	E0.019	100	–	–
Atrazine	H	.007	.018	.026	100	0	0
Bentazon	H	.012	E.02	E.04	100	–	–
2,4-D	H	.038	.06	.36	92	0	–
Diuron	H	.014	.02	.1	83	–	–
Simazine	H	.005	.007	.017	75	–	0
EPTC	H	.004	E.002	.075	58	–	–
DCPA	H	.003	<.003	.05	50	–	0
Terbacil[1]	H	.034	<.025	E.061	50	–	0
2,4-D methyl ester	H	.016	<.009	.041	50	0	–
Metolachlor	H	.006	<.013	E.010	50	0	0
Alachlor	H	.006	<.004	.017	25	–	0
Chlorpyrifos	I	.005	<.005	.011	25	0	0
Dicamba	H	.036	<.01	E.06	25	0	0
Terbacil[2]	H	.016	<.010	E.031	25	–	0

Table 8. Summary of pesticide concentrations in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.—Continued

[All concentrations are in micrograms per liter. Concentrations of pesticides in **bold** represent values that exceed freshwater aquatic-life benchmarks (see table 4). **Pesticide:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isoprobylamino-6-ethylamino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-triazine. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Drinking-water standards:** Maximum contaminant levels for drinking water from U.S. Environmental Protection Agency (2004a). **Freshwater aquatic-life benchmarks:** Standards from U.S. Environmental Protection Agency (2004b), unless otherwise footnoted. **Abbreviations:** LRL, laboratory reporting limit; M, presence of material verified, but not quantified; n, number of samples; [E], because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; <, less than; –, no data or not available; *, interim values (Canadian Council of Resources and Environment Ministers, 1997)]

Pesticide	Type of pesticide	LRL	Median	Maximum	Percentage of detections (n=12)	Number of detections that exceed aquatic-life benchmarks	Number of detections that exceed drinking water standards
Crab Creek—Continued							
CEAT[1]	T	0.08	<0.04	[E]0.01	17	–	–
OIET	T	.032	<.008	[E].007	17	–	–
Azinphos-methyl	I	.05	<.050	[E]**.019**	17	**1**	–
Bromacil	H	.018	<.03	[E].01	17	0	–
Carbaryl[1]	I	.041	<.041	[E].009	17	0	–
Benomyl	H	.022	<.004	[E].006	8	–	–
Chlorodiamino-s-triazine	T	.040	<.01	[E].01	8	–	–
Clopyralid	H	.024	<.01	[E].01	8	–	–
Dacthal monoacid	T	.028	<.01	.02	8	–	–
Diazinon	I	.005	<.005	.008	8	0	0
Diphenamid	H	.010	<.03	[E].01	8	–	–
Linuron[1]	H	.035	<.035	[E].013	8	–	–
Metribuzin	H	.006	<.006	[E].005	8	0	0
Nicosulfuron	H	.04	<.01	[E].01	8	–	–
Lind Coulee							
Atrazine	H	0.007	0.010	0.012	83	0	0
Diuron	H	.014	.02	.26	83	–	0
CIAT	T	.006	[E].004	[E].009	75	–	–
2,4-D	H	.038	[E].02	.44	67	0	0
DCPA	H	.003	.004	.044	58	–	0
Metolachlor	H	.006	[E].005	.134	58	0	0
Bentazon	H	.012	<.01	[E].01	50	–	0
Bromacil	H	.018	<.03	[E].13	42	0	0
Pendimethalin	H	.022	<.022	.033	42	–	–
EPTC	H	.004	<.004	.12	33	–	–
Metribuzin	H	.006	<.006	.016	33	0	0
Azinphos-methyl	I	.05	<.050	[E]**.026**	25	**2**	–
Dicamba	H	.036	<.01	[E].19	25	0	0
2,4-DB	H	.020	<.02	[E].06	17	0	–
OIET	T	.032	<.008	[E].006	17	–	–
Chlorodiamino-s-triazine	T	.040	<.01	[E].01	17	–	–
Chlorpyrifos	I	.005	<.005	.006	17	0	0
Ethalfluralin	H	.009	<.009	[E].009	17	–	–
Linuron[1]	H	.035	<.035	[E].013	17	0	–
Metalaxyl	F	.012	<.02	.04	17	–	–
Methomyl	I	.020	<.004	[E].011	17	–	0
Trifluralin	H	.009	<.009	[E].004	17	–	0
2,4-D methyl ester	H	.016	<.009	.017	8	0	–
Benomyl	H	.022	<.004	.082	8	–	–
Bromoxynil	H		<.02	M	8	0	–
Caffeine	S	.018	<.0096	[E].0052	8	–	–

Table 8. Summary of pesticide concentrations in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.—Continued

[All concentrations are in micrograms per liter. Concentrations of pesticides in **bold** represent values that exceed freshwater aquatic-life benchmarks (see table 4). **Pesticide:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isoprobylamino-6-ethylamino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-triazine. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Drinking-water standards:** Maximum contaminant levels for drinking water from U.S. Environmental Protection Agency (2004a). **Freshwater aquatic-life benchmarks:** Standards from U.S. Environmental Protection Agency (2004b), unless otherwise footnoted. **Abbreviations:** LRL, laboratory reporting limit; M, presence of material verified, but not quantified; n, number of samples; E, because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; <, less than; –, no data or not available; *, interim values (Canadian Council of Resources and Environment Ministers, 1997)]

Pesticide	Type of pesticide	LRL	Median	Maximum	Percentage of detections (n=12)	Number of detections that exceed aquatic-life benchmarks	Number of detections that exceed drinking water standards
Lind Coulee—Continued							
Chlorothalonil	F	0.035	<0.04	E0.06	8	0	0
Malathion	I	.027	<.027	E.017	8	0	0
MCPA	H	.030	<.02	M	8	0	0
Oxamyl	I	.030	<.01	.03	8	–	–
Propiconazole	F	.010	<.02	E.01	8	–	–
Simazine	H	.005	<.005	.024	8	–	0
Triallate	H	.002	<.002	.004	8	–	–
Red Rock Coulee							
CIAT	T	0.006	E0.011	E0.015	100	–	–
Atrazine	H	.007	.019	.032	100	0	0
Bentazon	H	.012	E.04	E.07	92	–	0
2,4-D	H	.038	.09	.77	83	0	0
Diuron	H	.014	.02	.11	83	–	0
Simazine	H	.005	.011	.022	83	–	0
EPTC	H	.004	E.003	.1	67	–	–
DCPA	H	.003	E.003	.169	58	–	–
Terbacil1	H	.034	E.012	E.075	58	–	0
2,4-D methyl ester	H	.016	.014	E.080	50	0	–
Bromacil	H	.018	<.03	E.03	42	0	–
Metolachlor	H	.006	<.013	E.011	42	0	0
Terbacil[2]	H	.016	<.027	E.090	42	–	0
CEAT	T	.08	<.04	E.01	33	–	–
Alachlor	H	.006	<.005	.013	33	–	–
Metribuzin	H	.006	<.006	.008	33	0	0
Chlorpyrifos	I	.005	<.005	.027	25	0	0
Dicamba	H	.036	<.01	E.13	25	0	0
Azinphos-methyl	I	.05	<.050	**E.018**	17	**1**	–
Benomyl	H	.022	<.004	E.017	17	–	–
Diazinon	I	.005	<.005	.03	17	0	0
Diphenamid	H	.010	<.03	E.03	17	–	0
Norflurazon	H	.020	<.02	M	17	–	–
OIET	T	.032	<.008	E.006	8	–	–
Caffeine	S	.018	<.0096	E.0089	8	–	–
Chlorodiamino-s-triazine	T	.040	<.01	E.01	8	–	–
Dacthal monoacid	T	0.028	<0.01	0.02	8	–	–
Ethoprophos	I	.005	<.005	.009	8	–	–
Linuron[2]	H	.014	<.01	E.01	8	0	–
Linuron[1]	H	.035	<.035	E.014	8	0	–
Malathion	I	.027	<.027	.03	8	0	0
Prometon	H	.010	<.01	E.01	8	–	0

Table 8. Summary of pesticide concentrations in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.—Continued

[All concentrations are in micrograms per liter. Concentrations of pesticides in **bold** represent values that exceed freshwater aquatic-life benchmarks (see table 4). **Pesticide:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; CAAT, chlorodiamino-*s*-triazine; OIET, 2-hydroxy-4-isoprobylamino-6-ethylamino-*s*-triazine; CEAT, 2-chloro-6-ethylamino-4-amino-*s*-triazine. **Type of pesticide:** F, fungicide; H, herbicide; I, insecticide; S, stimulant; T, transformation product. **Drinking-water standards:** Maximum contaminant levels for drinking water from U.S. Environmental Protection Agency (2004a). **Freshwater aquatic-life benchmarks:** Standards from U.S. Environmental Protection Agency (2004b), unless otherwise footnoted. **Abbreviations:** LRL, laboratory reporting limit; M, presence of material verified, but not quantified; n, number of samples; E, because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; <, less than; –, no data or not available; *, interim values (Canadian Council of Resources and Environment Ministers, 1997)]

Pesticide	Type of pesticide	LRL	Median	Maximum	Percentage of detections (n=12)	Number of detections that exceed aquatic-life benchmarks	Number of detections that exceed drinking water standards
Sand Hollow							
Bentazon	H	0.012	E0.10	E0.25	100	–	–
Terbacil[1]	H	.034	E.082	E1.01	100	–	0
CIAT	T	.006	E.008	E.036	92	–	–
Atrazine[1]	H	.007	.012	.029	92	0	0
2,4-D	H	.038	.04	.23	83	0	0
Dinoseb	H	.038	E.01	**.14**	83	[3]**1**	0
Diuron	H	.014	.02	E.22	83	–	0
Terbacil[2]	H	.016	E.056	E1.35	83	–	0
Bromacil	H	.018	E.01	E.12	67	0	0
Metribuzin	H	.006	E.0055	.052	58	0	0
Pendimethalin	H	.022	E.006	.388	58	–	–
Simazine	H	.005	E.004	.213	58	–	0
Alachlor	H	.005	<.005	.012	50	–	0
Chloropyrifos	I	.005	<.005	**.053**	42	**1**	0
Azinphos-methyl	I	.05	<.050	E**.034**	33	**4**	–
Carbaryl[1]	I	.041	<.041	E.070	33	0	0
DCPA	H	.003	<.003	.011	33	–	0
EPTC	H	.004	<.004	.085	33	–	–
Metolachlor	H	.006	<.013	E.008	33	0	0
Carbaryl[2]	I	.018	<.03	E.01	25	0	0
CAAT	T	.040	<.03	E.01	25	–	–
2,4-D methyl ester	H	.016	<.009	.013	17	0	–
OIET	T	.032	<.0018	E.007	17	–	–
Bromoxynil	H	.028	<.02	E.01	17	0	–
Caffeine	S	.018	<.0096	.0331	17	–	–
Dicamba	H	.036	<.01	E.03	17	0	0
CEAT	T	.08	<.04	M	8	–	–
Diazinon	I	.005	<.005	.007	8	–	0
Diphenamid	H	.010	<.03	E.02	8	–	0
Ethoprophos	I	.005	<.005	.016	8	–	–
Lindane	I	.004	<.004	**.018**	8	[3]**1**	0
Linuron[2]	H	.014	<.01	E.01	8	0	–
Linuron[1]	H	.035	<.035	E.007	8	0	–
Malathion	I	.027	<.027	E.015	8	0	0
MCPA	H	.030	<.02	E.03	8	0	0
Metalaxyl	F	.012	<.02	E.01	8	–	–
Methomyl	I	.020	<.004	E.016	8	–	0
Norflurazon	H	.020	<.02	E.01	8	–	–
Prometon	H	.010	<.01	M	8	–	0
Triclopyr	I	.026	<.02	E.01	8	–	–

[1]Analysis by gas chromatography/mass spectrometry (GC/MS).
[2]Analysis by high-performance liquid chromatography/mass spectrometry (HPLC/MS).
[3]Canadian water-quality guidelines for the protection of freshwater aquatic life (Canadian Council of Ministers of the Environment, 2003).

Table 9. Summary of pesticide toxicity values for freshwater fish in the Columbia Basin Project, Washington.

[All concentrations are lethal concentrations for 50 percent of the target species (LC_{50}) at 96 hours, in micrograms per liter. All data are compiled from the U.S. Environmental Protection Agency ECOTOX database (U.S. Environmental Protection Agency, 2005a). **Abbreviations:** N, number of references for specific studies; CAS, Chemical Abstract Services; –. not available]

Compound	CAS registry No.	Name	Species	N	Minimum	Median	Maximum
2,4-D	94-75-7	Carp	*Cyprinus carpio*	9	5,100	21,450	270,000
		Pumpkinseed	*Lepomis gibbosus*	1	–	94,600	–
		Bluegill	*Lepomis macrochirus*	4	7,400	221,500	263,000
		Smallmouth bass	*Micropterus dolomieui*	1	–	3,100	–
		Cutthroat trout	*Oncorhynchus clarki*	2	24,500	44,250	64,000
		Rainbow trout	*Oncorhynchus mykiss*	8	1,400	27,300	358,000
		Chinook salmon	*Oncorhynchus tshawytscha*	1	–	4800	–
		Lake trout	*Salvelinus namaycush*	2	44,500	44,750	45,000
2,4-DB	94-82-6	Bluegill	*Lepomis macrochirus*	3	7,500	7,500	16,800
		Rainbow trout	*Oncorhynchus mykiss*	4	2,000	3,700	14,300
Acrolein	107-02-8	Bluegill	*Lepomis macrochirus*	5	22	70	100
		Largemouth bass	*Micropterus salmoides*	1	–	160	–
		Coho salmon, silver salmon	*Oncorhynchus kisutch*	1	–	68	–
		Rainbow trout, Donaldson trout	*Oncorhynchus mykiss*	7	16	74	187
Alachlor	15972-60-8	Carp	*Cyprinus carpio*	1	–	4,600	–
		Channel catfish	*Ictalurus punctatus*	1	–	6,500	–
		Bluegill	*Lepomis macrochirus*	10	2,800	4,950	12,400
		Rainbow trout	*Oncorhynchus mykiss*	10	240	2,100	4,200
Atrazine	1912-24-9	Black bullhead	*Ameiurus melas*	1	–	35,000	–
		Whitefish	*Coregonus lavaretus*	2	11,200	18,750	26,300
		Carp	*Cyprinus carpio*	1	–	18,800	–
		Bluegill	*Lepomis macrochirus*	7	6,700	42,000	69,000
		Rainbow trout	*Oncorhynchus mykiss*	6	4,500	11,750	24,000
		Yellow perch	*Perca flavescens*	1	–	50,000	–
		Brook trout	*Salvelinus fontinalis*	3	4,900	4,900	6,300
Azinphos-methyl	86-50-0	Black bullhead	*Ameiurus melas*	3	3,500	3,500	3,500
		Carp	*Cyprinus carpio*	3	695	695	695
		Threespine stickleback	*Gasterosteus aculeatus*	2	4.8	8.45	12.1
		Channel catfish	*Ictalurus punctatus*	4	3,220	3,290	3,290
		Bluegill	*Lepomis macrochirus*	17	4.1	7.4	120
		Largemouth bass	*Micropterus salmoides*	3	4.8	4.8	5
		Coho salmon	*Oncorhynchus kisutch*	4	4.2	6.1	17
		Rainbow trout	*Oncorhynchus mykiss*	10	3.2	6.95	28
		Chinook salmon	*Oncorhynchus tshawytscha*	1	–	4.3	–
		Yellow perch	*Perca flavescens*	5	2.4	13	40
		Black crappie	*Pomoxis nigromaculatus*	2	3	3	3
		Brown trout	*Salmo trutta*	3	3.5	4	4.6
		Brook trout	*Salvelinus fontinalis*	1	–	1.2	–
Bentazon	25057-89-0	Carp	*Cyprinus carpio*	1	–	978,000	–
Bromacil	314-40-9	Bluegill	*Lepomis macrochirus*	1	–	127,000	–
		Rainbow trout	*Oncorhynchus mykiss*	2	36,000	50,500	65,000
Bromoxynil	1689-84-5	Bluegill	*Lepomis macrochirus*	2	4,000	13,500	23,000
		Rainbow trout	*Oncorhynchus mykiss*	2	2,090	10,045	18,000
Carbaryl	63-25-2	Black bullhead	*Ameiurus melas*	3	20,000	20,000	20,000
		Red shiner	*Cyprinella lutrensis*	1	–	9,200	–
		Carp	*Cyprinus carpio*	11	1,190	3,300	5,280
		Threespine stickleback	*Gasterosteus aculeatus*	2	399	2,194.5	3,990
		Channel catfish	*Ictalurus punctatus*	8	140	10,095	15,800
		Bluegill	*Lepomis macrochirus*	26	760	6,760	290,000
		Largemouth bass	*Micropterus salmoides*	3	6,400	6,400	6,400
		Cutthroat trout	*Oncorhynchus clarki*	9	970	3,950	7,100
		Coho salmon	*Oncorhynchus kisutch*	5	764	1,300	4,340
		Rainbow trout	*Oncorhynchus mykiss*	25	800	1,470	5,400
		Chinook salmon	*Oncorhynchus tshawytscha*	2	2,400	2,400	2,400

Table 9. Summary of pesticide toxicity values for freshwater fish in the Columbia Basin Project, Washington.—Continued

[All concentrations are lethal concentrations for 50 percent of the target species (LC_{50}) at 96 hours, in micrograms per liter. All data are compiled from the U.S. Environmental Protection Agency ECOTOX database (U.S. Environmental Protection Agency, 2005a). **Abbreviations:** N, number of references for specific studies; CAS, Chemical Abstract Services]

Compound	CAS registry No.	Name	Species	N	Minimum	Median	Maximum
Carbaryl–Continued	63-25-2	Yellow perch	*Perca flavescens*	3	350	745	5,100
		Black crappie	*Pomoxis nigromaculatus*	2	2,600	2,600	2,600
		Brown trout	*Salmo trutta*	4	700	4,125	6,300
		Brook trout	*Salvelinus fontinalis*	13	900	2,500	5,400
		Lake trout	*Salvelinus namaycush*	2	690	690	690
Chlorothalonil	1897-45-6	Threespine stickleback	*Gasterosteus aculeatus*	1	–	69	–
		Channel catfish	*Ictalurus punctatus*	3	43	52	430
		Bluegill	*Lepomis macrochirus*	5	26.3	62	386
		Rainbow trout	*Oncorhynchus mykiss*	14	7.6	17.55	250
Chlorpyrifos	2921-88-2	Threespine stickleback	*Gasterosteus aculeatus*	1	–	8.54	–
		Channel catfish	*Ictalurus punctatus*	3	280	280	806
		Bluegill	*Lepomis macrochirus*	10	1.3	6.52	108
		Cutthroat trout	*Oncorhynchus clarki*	2	5.4	11.7	18
		Rainbow trout	*Oncorhynchus mykiss*	9	7.1	8	51
		Lake trout	*Salvelinus namaycush*	2	73	85.5	98
DCPA (Dacthal)	1861-32-1	Rainbow trout	*Oncorhynchus mykiss*	2	6,600	18,300	30,000
Diazinon	333-41-5	Black bullhead	*Ameiurus melas*	1	–	8,000	–
		Carp	*Cyprinus carpio*	2	3,430	4,200	4,970
		Bluegill	*Lepomis macrochirus*	21	22	170	530
		Cutthroat trout	*Oncorhynchus clarki*	4	1,700	2,230	3,850
		Rainbow trout	*Oncorhynchus mykiss*	11	90	400	3,200
		Brown trout	*Salmo trutta*	1	–	602	–
		Trout family	*Salmonidae*	1	–	8,000	–
		Brook trout	*Salvelinus fontinalis*	4	450	785	1,050
		Lake trout	*Salvelinus namaycush*	2	600	601	602
Dicamba	1918-00-9	Bluegill	*Lepomis macrochirus*	2	135,300	157,650	180,000
		Rainbow trout	*Oncorhynchus mykiss*	5	28,000	130,000	153,000
		Channel catfish	*Ictalurus punctatus*	6	28	53.5	118
		Cutthroat trout	*Oncorhynchus clarki*	13	41	87	1,350
		Fathead minnow	*Pimephales promelas*	12	88	155	700
		Lake trout	*Salvelinus namaycush*	11	32	79	1,400
Diphenamid	957-51-7	Bluegill	*Lepomis macrochirus*	3	32,000	65,000	75,000
		Rainbow trout, Donaldson trout	*Oncorhynchus mykiss*	2	97,000	97,000	97,000
Diuron	330-54-1	Carp	*Cyprinus carpio*	1	–	2,900	–
		Bluegill	*Lepomis macrochirus*	8	2,800	6,750	84,000
		Cutthroat trout	*Oncorhynchus clarki*	3	710	1,400	1,400
		Rainbow trout	*Oncorhynchus mykiss*	6	1,950	16,000	23,800
		Trout family	*Salmonidae*	1	–	1,100	–
		Lake trout	*Salvelinus namaycush*	3	1,200	2,700	2,700
		Tench	*Tinca tinca*	1	–	15,500	–
EPTC	759-94-4	Bluegill	*Lepomis macrochirus*	3	22,400	24,800	–
		Cutthroat trout	*Oncorhynchus clarki*	3	12,500	17,000	–
		Rainbow trout	*Oncorhynchus mykiss*	3	19,960	20,720	26,700
		Lake trout	*Salvelinus namaycush*	2	11,500	13,850	23,300
Ethalfluralin	55283-68-6	Bluegill	*Lepomis macrochirus*	2	32	67	102
		Rainbow trout	*Oncorhynchus mykiss*	2	37	86.5	136
Ethoprophos	13194-48-4	Carp	*Cyprinus carpio*	1	–	640	–
		Bluegill	*Lepomis macrochirus*	3	300	2,070	8,900
		Rainbow trout	*Oncorhynchus mykiss*	5	1,100	7,800	13,800
Glyphosate	1071-83-6	Carp	*Cyprinus carpio*	2	11,000	315,500	620,000
		Channel catfish	*Ictalurus punctatus*	6	3,300	8,700	130,000
		Bluegill	*Lepomis macrochirus*	17	1,800	5,600	220,000
		Chum salmon	*Oncorhynchus keta*	4	10,000	60,500	148,000
		Coho salmon, silver salmon	*Oncorhynchus kisutch*	5	27,000	111,000	174,000

Table 9. Summary of pesticide toxicity values for freshwater fish in the Columbia Basin Project, Washington.—Continued

[All concentrations are lethal concentrations for 50 percent of the target species (LC_{50}) at 96 hours, in micrograms per liter. All data are compiled from the U.S. Environmental Protection Agency ECOTOX database (U.S. Environmental Protection Agency, 2005a). **Abbreviations:** N, number of references for specific studies; CAS, Chemical Abstract Services]

Compound	CAS registry No.	Name	Species	N	Minimum	Median	Maximum
Glyphosate–Continued	1071-83-6	Rainbow trout, Donaldson trout	*Oncorhynchus mykiss*	26	1,300	8,650	7,815,670
		Sockeye salmon	*Oncorhynchus nerka*	1	–	26,700	–
		Chinook salmon	*Oncorhynchus tshawytscha*	5	19,000	102,000	211,000
		Brown trout	*Salmo trutta*	1	–	5,400	–
Imazypyr	81334-34-1	Channel catfish	*Ictalurus punctatus*	1	–	100,000	–
		Bluegill	*Lepomis macrochirus*	1	–	100,000	–
		Rainbow trout, Donaldson trout	*Oncorhynchus mykiss*	1	–	100,000	–
Lindane (gamma-HCH)	58-89-9	Black bullhead	*Ameiurus melas*	3	64	64	64
		Carp	*Cyprinus carpio*	6	90	145	13,000
		Threespine stickleback	*Gasterosteus aculeatus*	2	44	47	50
		Channel catfish	*Ictalurus punctatus*	4	44	44	450
		Bluegill	*Lepomis macrochirus*	22	25	66.5	810
		Largemouth bass	*Micropterus salmoides*	3	32	32	32
		Coho salmon	*Oncorhynchus kisutch*	4	23	32	50
		Rainbow trout	*Oncorhynchus mykiss*	11	18	30	120
		Chinook salmon	*Oncorhynchus tshawytscha*	1	–	42	–
		Yellow perch	*Perca flavescens*	4	23	68	68
		Brown trout	*Salmo trutta*	4	1.7	1.85	22
		Brook trout	*Salvelinus fontinalis*	1	–	44.3	–
		Lake trout	*Salvelinus namaycush*	3	24	32	32
Linuron	330-55-2	Channel catfish	*Ictalurus punctatus*	2	1,800	2,350	2,900
		Bluegill	*Lepomis macrochirus*	3	9,200	9,600	16,200
		Rainbow trout	*Oncorhynchus mykiss*	2	3,000	9,700	16,400
Malathion	121-75-5	Black bullhead	*Ameiurus melas*	3	11,700	12,900	12,900
		Red shiner	*Cyprinella lutrensis*	1	–	25	–
		Carp	*Cyprinus carpio*	14	2	6,590	13,800
		Threespine stickleback	*Gasterosteus aculeatus*	2	76.9	85.45	94
		Channel catfish	*Ictalurus punctatus*	5	7,620	8,970	52,200
		Pumpkinseed	*Lepomis gibbosus*	1	–	480	–
		Bluegill	*Lepomis macrochirus*	13	20	103	1,200
		Largemouth bass	*Micropterus salmoides*	4	250	267.5	285
		Cutthroat trout	*Oncorhynchus clarki*	4	150	240.5	1,740
		Coho salmon	*Oncorhynchus kisutch*	4	101	170	265
		Rainbow trout	*Oncorhynchus mykiss*	17	2.8	122	234
		Chinook salmon	*Oncorhynchus tshawytscha*	2	23	71.5	120
		Yellow perch	*Perca flavescens*	3	263	263	263
		Brown trout	*Salmo trutta*	3	101	101	200
		Brook trout	*Salvelinus fontinalis*	2	120	125	130
		Lake trout	*Salvelinus namaycush*	2	76	76	76
		Walleye	*Stizostedion vitreum v.*	2	64	64	64
MCPA	94-74-6	Carp	*Cyprinus carpio*	1	–	59,000	–
		Bluegill	*Lepomis macrochirus*	1	–	97,000	–
		Rainbow trout	*Oncorhynchus mykiss*	2	91,000	91,000	91,000
		Trout family	*Salmonidae*	1	–	25,000	–
		Tench	*Tinca tinca*	1	–	45,000	–
Metalaxyl	57837-19-1	Black bullhead	*Ameiurus melas*	1	–	100,000	–
		Carp	*Cyprinus carpio*	1	–	100,000	–
		Bluegill	*Lepomis macrochirus*	3	27,000	139,000	150,000
		Rainbow trout, Donaldson trout	*Oncorhynchus mykiss*	3	18,400	130,000	132,000
		Channel catfish	*Ictalurus punctatus*	9	300	320	1,800
		Bluegill	*Lepomis macrochirus*	18	370	850	7,700
		Largemouth bass	*Micropterus salmoides*	4	760	1,005	1,250
		Cutthroat trout	*Oncorhynchus clarki*	2	4,050	5,425	6,800
		Rainbow trout	*Oncorhynchus mykiss*	19	860	1,600	32,000
		Brook trout	*Salvelinus fontinalis*	5	1,200	1,500	2,200

Table 9. Summary of pesticide toxicity values for freshwater fish in the Columbia Basin Project, Washington.—Continued

[All concentrations are lethal concentrations for 50 percent of the target species (LC_{50}) at 96 hours, in micrograms per liter. All data are compiled from the U.S. Environmental Protection Agency ECOTOX database (U.S. Environmental Protection Agency, 2005a). **Abbreviations:** N, number of references for specific studies; CAS, Chemical Abstract Services]

Compound	CAS registry No.	Name	Species	N	Minimum	Median	Maximum
Metolachlor	51218-45-2	Channel catfish	*Ictalurus punctatus*	1	–	4,900	–
		Bluegill	*Lepomis macrochirus*	1	–	10,000	–
		Rainbow trout	*Oncorhynchus mykiss*	1	–	3,900	–
Metribuzin	21087-64-9	Channel catfish	*Ictalurus punctatus*	1	–	3,400	–
		Bluegill	*Lepomis macrochirus*	3	75,960	92,000	131,300
		Rainbow trout	*Oncorhynchus mykiss*	5	42,000	76,770	147,000
Metsulfuron methyl	74223-64-6	Bluegill	*Lepomis macrochirus*	1	–	150,000	–
		Rainbow trout, Donaldson trout	*Oncorhynchus mykiss*	1	–	150,000	–
Norflurazon	27314-13-2	Bluegill	*Lepomis macrochirus*	1	–	16,300	–
		Rainbow trout	*Oncorhynchus mykiss*	1	–	8,100	–
Oxamyl	23135-22-0	Channel catfish	*Ictalurus punctatus*	2	13,500	15,500	17,500
		Bluegill	*Lepomis macrochirus*	4	5,600	6,415	10,000
		Rainbow trout	*Oncorhynchus mykiss*	4	3,700	4,450	12,400
Pendimethalin	40487-42-1	Channel catfish	*Ictalurus punctatus*	2	418	1,159	1,900
		Bluegill	*Lepomis macrochirus*	4	199	980	90,400
		Rainbow trout	*Oncorhynchus mykiss*	4	138	760	86,600
Prometon	1610-18-0	Black bullhead	*Ameiurus melas*	1	–	20,000	–
		Bullhead catfish	*Ameiurus* sp.	1	–	20,000	–
		Bluegill	*Lepomis macrochirus*	3	15,500	40,000	41,500
		Rainbow trout	*Oncorhynchus mykiss*	5	12,000	16,000	20,000
Propiconazole	60207-90-1	Carp	*Cyprinus carpio*	5	5,700	21,000	46,000
		Channel catfish	*Ictalurus punctatus*	3	4,870	4,870	12,000
		Bluegill	*Lepomis macrochirus*	5	1,300	5,500	9,800
		Rainbow trout, Donaldson trout	*Oncorhynchus mykiss*	11	830	5,200	506,000
		Brown trout	*Salmo trutta*	3	1,200	3,390	3,390
Simazine	122-34-9	Black bullhead	*Ameiurus melas*	1	–	65,000	–
		Sunfish family	*Centrarchidae*	5	14,300	56,000	695,000
		Channel catfish	*Ictalurus punctatus*	1	–	85,000	–
		Pumpkinseed	*Lepomis gibbosus*	1	–	27,000	–
		Bluegill	*Lepomis macrochirus*	6	16,000	95,000	118,000
		Largemouth bass	*Micropterus salmoides*	1	–	46,000	–
		Rainbow trout	*Oncorhynchus mykiss*	5	40,500	56,000	70,500
		Yellow perch	*Perca flavescens*	1	–	90	–
Terbacil	5902-51-2	Bluegill	*Lepomis macrochirus*	2	102,900	107,450	112,000
		Rainbow trout	*Oncorhynchus mykiss*	3	46,200	54,000	79,000
Triallate	2303-17-5	Bluegill	*Lepomis macrochirus*	3	1,300	1,330	2,400
		Rainbow trout	*Oncorhynchus mykiss*	2	1,200	1,350	1,500
Triclopyr	55335-06-3	Chum salmon	*Oncorhynchus keta*	2	300	3,900	7,500
		Coho salmon	*Oncorhynchus kisutch*	6	260	1,150	9,600
		Rainbow trout	*Oncorhynchus mykiss*	3	1,100	2,200	7,500
		Sockeye salmon	*Oncorhynchus nerka*	4	400	1,300	7,500
		Chinook salmon	*Oncorhynchus tshawytscha*	2	1,100	5,400	9,700
Trifluralin	1582-09-8	Carp	*Cyprinus carpio*	1	–	660	–
		Channel catfish	*Ictalurus punctatus*	3	210	417	2,200
		Bluegill	*Lepomis macrochirus*	7	8.4	58	190
		Largemouth bass	*Micropterus salmoides*	2	75	75	75
		Rainbow trout	*Oncorhynchus mykiss*	8	10	41.5	210
Xylene	68920-06-9	Bluegill	*Lepomis macrochirus*	16	8,600	14,700	24,500
		Rainbow trout, Donaldson trout	*Oncorhynchus mykiss*	4	3,300	10,850	17,300

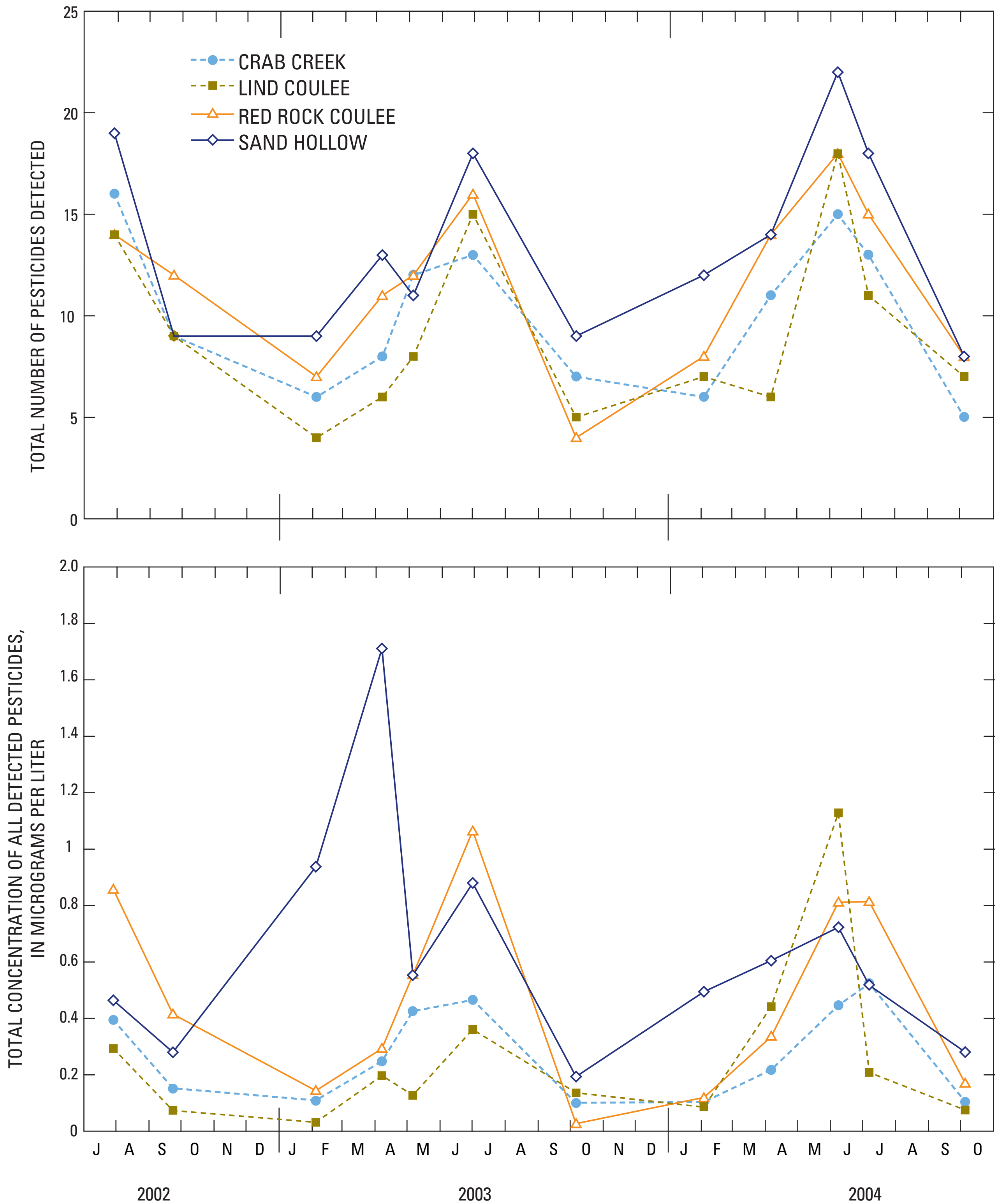


Figure 4. Pesticide concentrations in four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.

Relation of Pesticide Use and Pesticides Detected

The frequency of pesticide detections is related to chemical and physical properties of the specific pesticide, environmental conditions, and amount of pesticide used. Frequency of pesticide detection typically is low in areas of low use and high where pesticide use is high. Seventy to 80 percent of total annual pesticide use in the United States is in agriculture (Aspelin, 1997). Non-agricultural uses may be significant in some areas, however, and include residential pest control, aquatic pest control, rights-of-way applications for pest control, ornamental and turf pest control, and pest control in commercial, industrial, and institutional settings (Larson and others, 1997).

Pesticide-Use Data

For each pesticide detected in the drainage basins, the total quantity of each pesticide applied to agricultural fields in 2003 was estimated as the sum of annual pesticide applications to each crop type in the drainage basin. For each pesticide applied to a specific crop in a given drainage basin, the total quantity used annually was computed as the product of the rate of pesticide application to that crop in pounds of active ingredient per acre per year, the total acreage of the crop in the drainage basin, and the percentage of that total acreage estimated to be treated with the pesticide. Pesticide application rates and treatment percentages were obtained from the National Agriculture Statistics Service (NASS) where possible (U.S. Department of Agriculture, 2005) and from a 1995 survey conducted in the study area by the National Center for Food and Agricultural Policy (Anderson and Gianessi, 1995) for those crops that are not included in the NASS statistics. Data for total crop acreages were obtained from a geographic information system database of cultivated fields (Patricia Daly, Franklin County Conservation District, written commun., 2004). The crop-acreage database includes only acreages for alfalfa, corn, onions, potatoes, pasture, peas, mint, wheat, and orchards and does not include acreages for minor crops such as carrots; therefore, some pesticides that may be used in the basin were not included in the calculation if they are used specifically on only a few crops not in the database.

In addition to pesticides applied to agricultural lands for control of weeds and pests, herbicides are applied to roads and rights-of-way along irrigation canals, drains, and return flows by local irrigation districts to control terrestrial weed growth (table 10). Herbicide application for non-agricultural weed control ranged from 470 to 10,300 lb during 2003. Concentrations of only three of the eight herbicides (2,4-D, dicamba, and diuron were analyzed in samples of irrigation-return flow during this study. Diuron and 2,4-D were among the five most frequently detected pesticides and dicamba was detected in nearly 25 percent of samples collected during this study (table 7).

Pesticide-use data for residential and other non-agricultural uses are more limited than data for agricultural pesticide use (Barbash and Resek, 1996). No studies of non-agricultural pesticide use in the study area are known to exist. However, an estimate of residential use in the study area was computed on the basis of residential sales data collected in King County, Wash. (Phillip Dickey, Washington Toxics Coalition, written commun., 2004). A per-household sales rate was computed on the basis of total housing units in King County (U.S. Census Bureau, 2004), and this rate was multiplied by total housing units in each drainage basin. This method for computing the amount of residential pesticide use assumes that all pesticides purchased in a given year are used that year and that residential usage patterns in the study area are the same as those in King County. Pesticide registration data for the State of Washington are available from Washington State Pest Management (http://wsprs.wsu.edu/Pesticides.html), and the registration status of pesticides analyzed in this study is listed in table 19 (at back of report).

Table 10. Herbicides applied to irrigation canals, roads, and rights of way along irrigation canals, drains, and return flows in the four irrigation return-flow drainage basins, Columbia Basin Project, 2003.

[**Abbreviations:** CAS, Chemical Abstract Services; None, none applied in 2003; UH, used historically; –, not available]

Herbicide	Trade or common name	Amount applied (pounds)
2,4-D[1]	Weedestroy AM-40	10,300
Acrolein	Magnacide H	UH
Copper sulfate	–	UH
Dicamba	Banvel, Vanquish	510
Diuron	Diuron 4L1VM, Direx	8,560
Glyphosate[2]	AquaNeat	3,350
Imazypyr	Arsenal	UH
Metsulfuron methyl	Escort x P	470
Xylene	–	None

[1] Dimethylamine salt of 2,4-Dichlorophenoxyacetic acid was applied.
[2] Isopropylamine salt of glyphosate was applied.

Pesticides Applied and Detected in Surface-Water Samples

Of the 107 pesticides analyzed for in surface-water samples from the four drainage basins, 42 herbicides, insecticides, and fungicides were detected, and 31 of those detected were reported as being applied to the major agricultural crops in the basins (fig. 5). Pesticides that were analyzed for but not detected are listed in table 20 (at back of report).

The general pesticide-usage pattern in each basin varies depending on the acreage of crops grown in that basin. In drainage basins where orchards predominate, the largest applications are insecticides, whereas in basins with larger percentages of field crops the largest application is herbicides. Usage patterns in Crab Creek and Sand Hollow basins are similar: the largest total amounts applied are the insecticides azinphos-methyl, carbaryl, and chlorpyrifos and the herbicide EPTC (fig. 5). In Red Rock Coulee basin, DCPA was the most heavily applied pesticide, followed by the fungicide chlorothalonil, the herbicide EPTC, and the insecticides chlorpyrifos and azinphos-methyl. In Lind Coulee basin, which has a large percentage of dryland agricultural area, the herbicides 2,4-D and EPTC were applied in the largest amount, followed by the fungicide chlorothalonil.

The total amount of pesticides applied in a basin does not correspond directly with the percentage of samples with detections. Some pesticides, such as atrazine, bentazon, and diuron, are applied in small amounts but were detected in a large percentage of samples; others, such as chlorothalonil, are applied in large amounts but were not frequently detected. Other pesticides, such as carbofuran, methyl parathion, and oryzalin, are known to be used on agricultural crops in the study area but were not detected in any of the surface-water samples.

Eleven pesticides that were detected in the drainage basins are available for purchase and use for residential applications (table 11). A nationwide study in the early 1990s showed that total amounts of pesticides sold for agricultural use exceeded those used for non-agricultural use by a factor of three (Aspelin and others, 1992). However, in this study area, the total amount of non-agricultural pesticides applied in these basins was significantly less than amounts applied to major agricultural crops. For example, the highest total non-cropland usage of 2,4-D was 35 pounds applied in Crab Creek and Lind Coulee, whereas agricultural use amounted to greater than 29,000 lb in that basin. Prometon and triclopyr were the only residential or commercially applied pesticides not used on major agricultural crops; however, they have many commercial uses, such as on landscaping, highway, or power line rights-of-way, so detections can not be linked directly to residential use.

Eight pesticides were detected in the drainage basins, but were not reported as having any major agricultural or residential use (table 12). Most of these were detected only once or twice, except for bromacil and dinoseb. Bromacil is an herbicide detected in samples from all drainage basins and is registered for use along highway right-of-ways, parking lots, and commercial landscaping. The USEPA banned dinoseb use in 1986. However, according to the Washington Agricultural Statistics Service (2005), dinoseb was reported as being used on apples as late as 2001. Possibly, the detection of dinoseb in the Sand Hollow basin indicates current use.

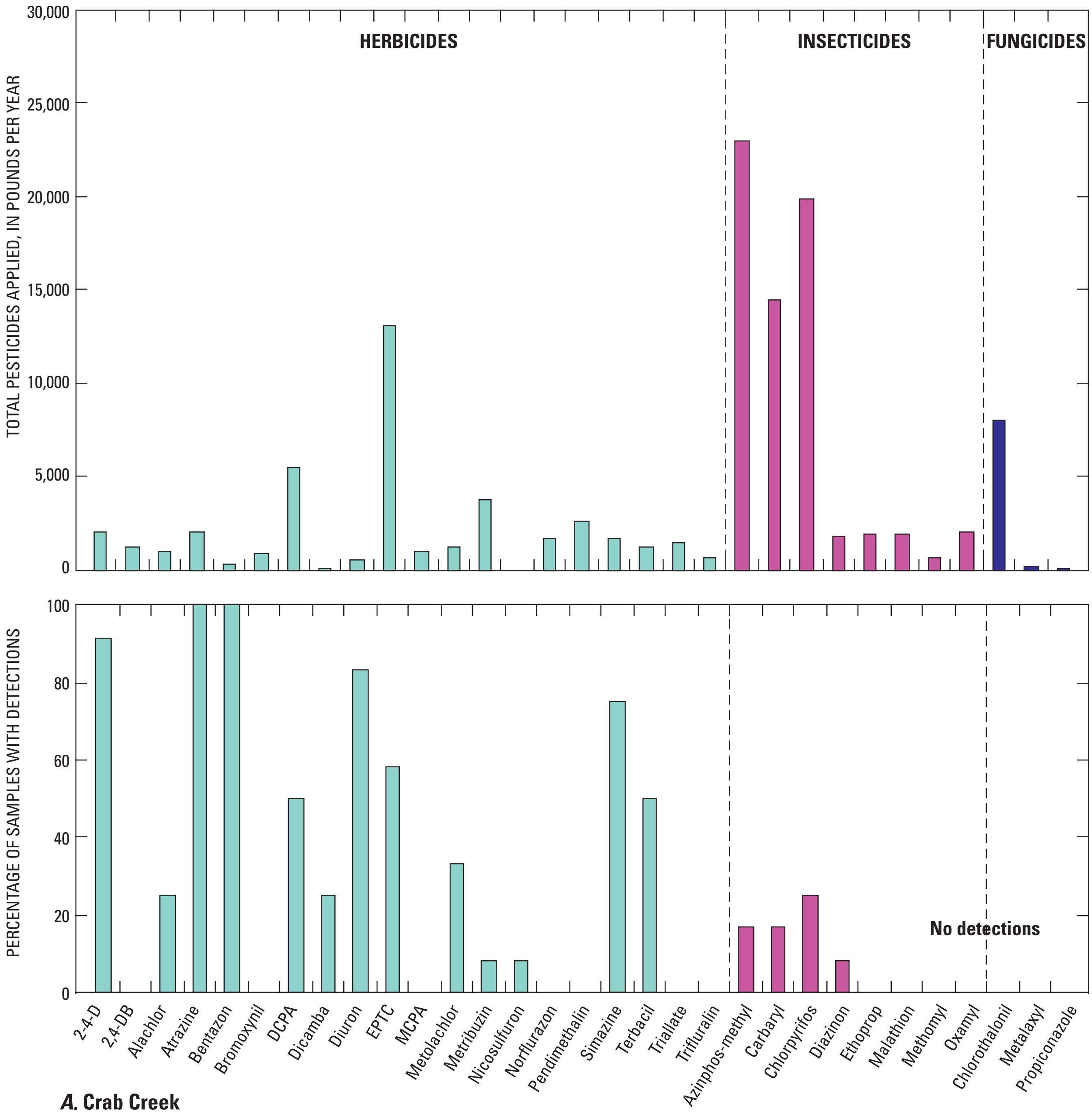
Table 11. Estimated application for residential use of non-agricultural pesticides detected in water samples from the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.

[All application values are in pounds per year. <, less than]

Pesticide	Estimated application of non-agricultural pesticides in irrigation-return flow drainages			
	Crab Creek	Lind Coulee	Red Rock Coulee	Sand Hollow
2,4-D	35	35	1.4	3.4
Carbaryl	14	14	.5	1.3
Chlorothalonil	1	1.0	.04	.1
Chlorpyrifos	.1	.1	<.01	.01
Diazinon	7.8	7.9	.3	.8
Dicamba	2.4	2.5	.1	.2
Malathion	5.5	5.6	.2	.5
Pendimethalin	1.7	1.7	.06	.2
Prometon	3.0	3.0	.1	.3
Triclopyr	2.1	2.1	.08	.2
Trifuluralin	4.1	4.1	.2	.4

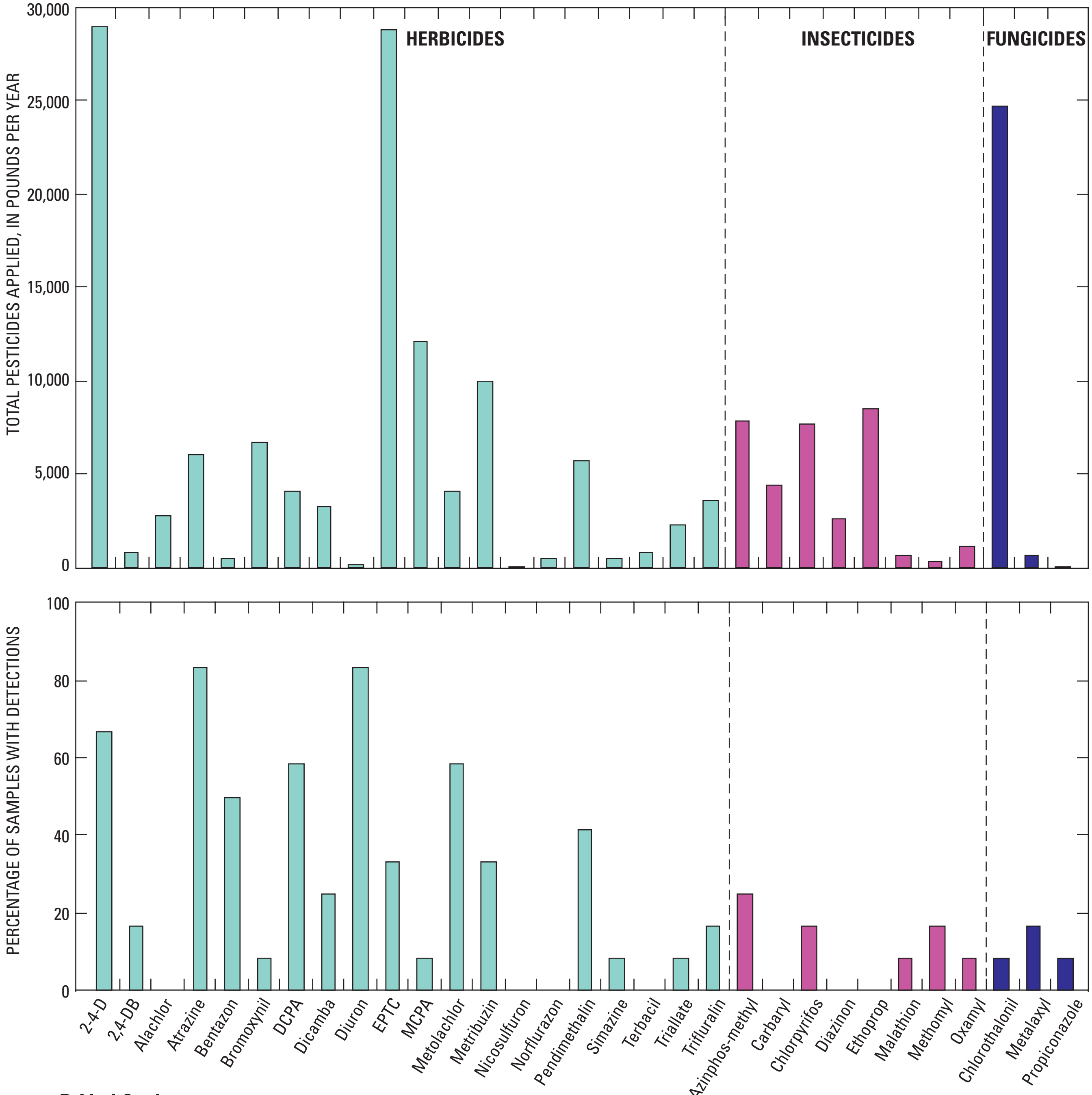
Table 12. Pesticides with no reported residential or major agricultural use detected in water samples from the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.

Pesticide	Possible sources
Benomyl	Minor agricultural use
Bromacil	Rights-of-way, parking lots, commercial landscaping
Clopyralid	Minor agricultural use
Dinoseb	Historical use, banned in 1986
Diphenamid	Unknown, not registered for use in Washington
Ethalfluralin	Minor agricultural use
gamma-HCH (Lindane)	Seed treatment, head-lice and animal shampoos
Linuron	Minor agricultural use



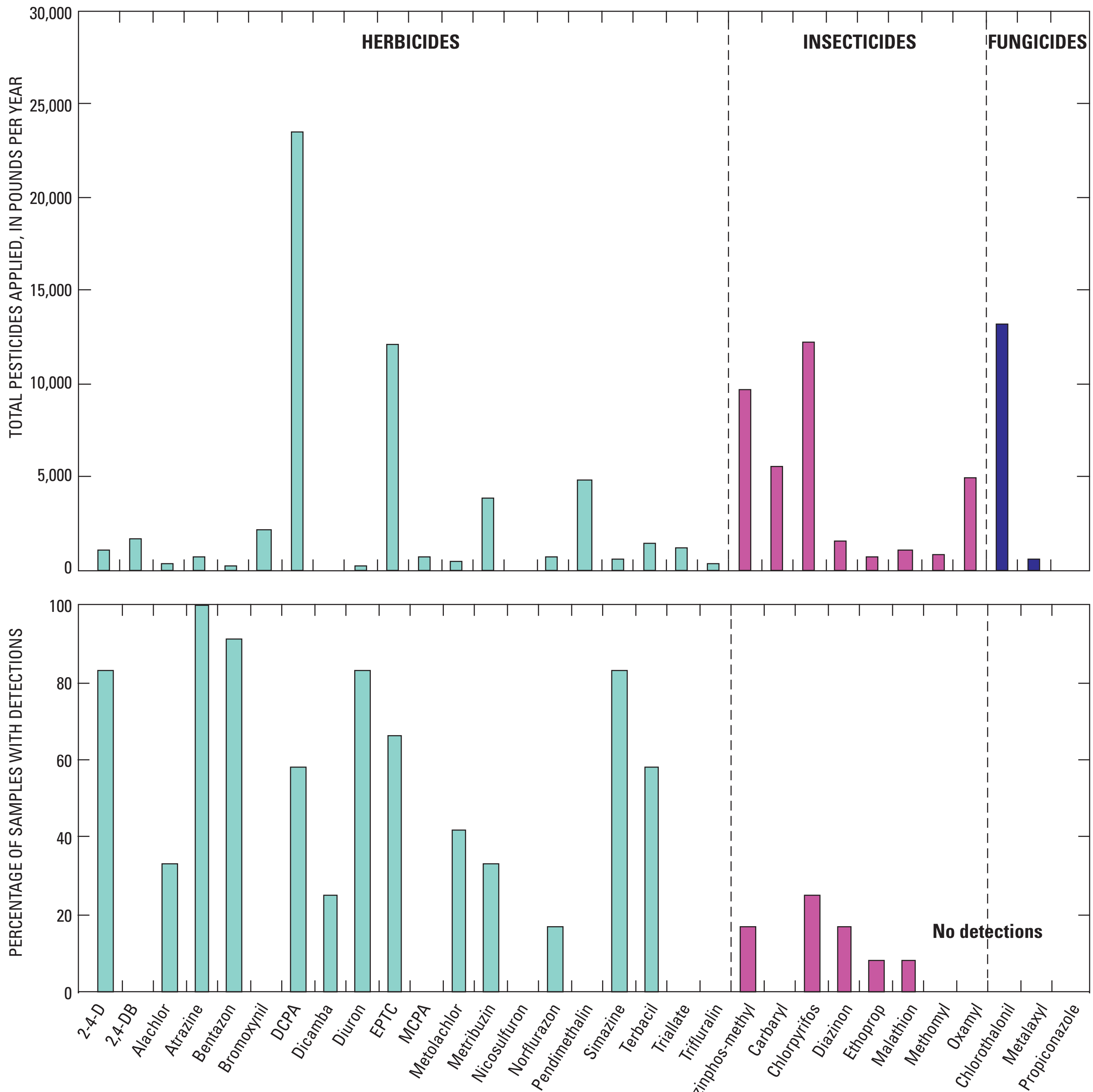
***A*. Crab Creek**

Figure 5. Pesticide-application rates and percentage of surface-water samples with pesticide detections in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.



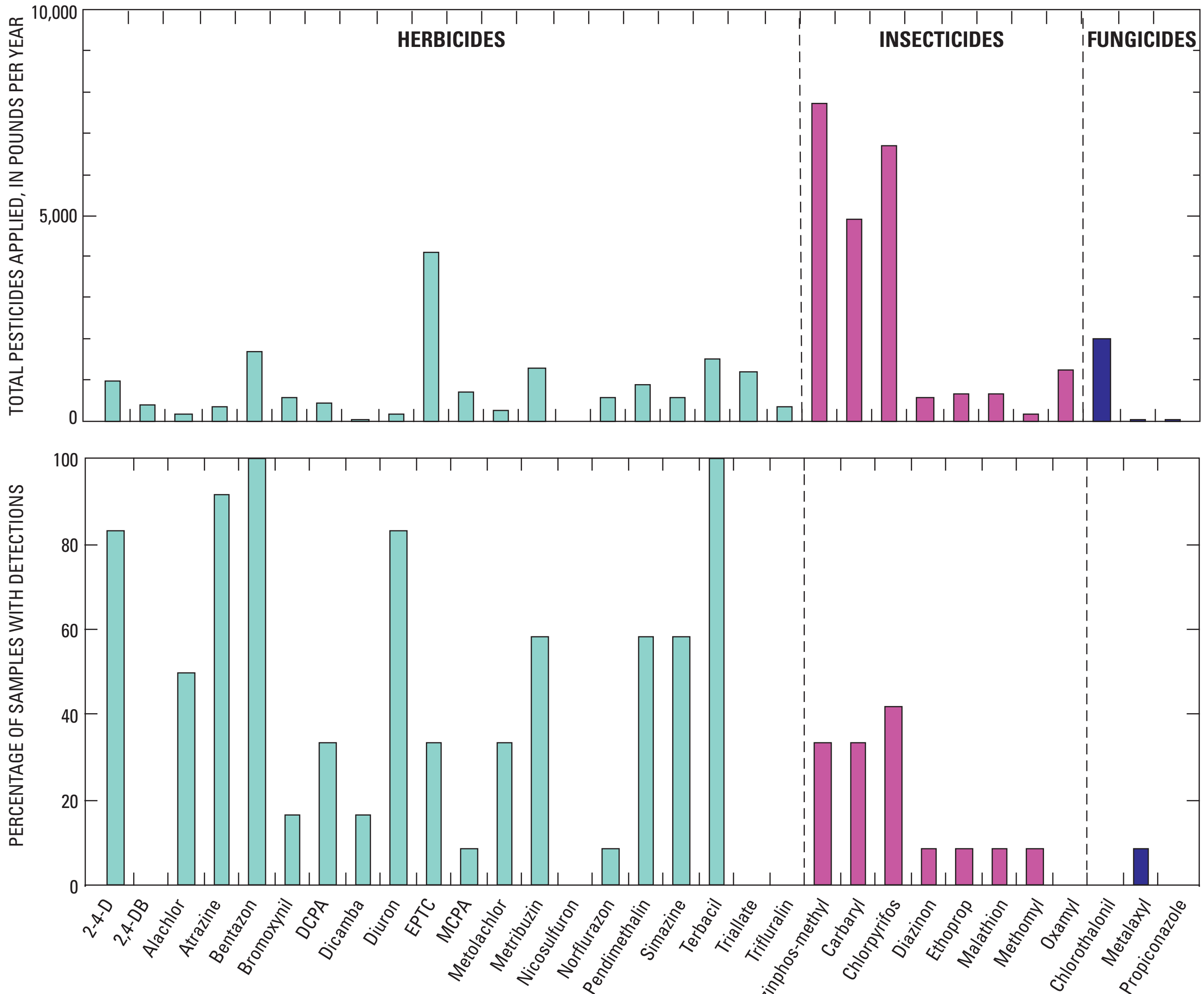
B. **Lind Coulee**

Figure 5. Continued.



C. **Red Rock Coulee**

Figure 5. Continued.



***D.* Sand Hollow**

Figure 5. Continued.

Transport of Pesticides

Comparison of Pesticide Detections with Historical Data

Most historical pesticide data for sites in this study were collected during the 1990s by the USGS NAWQA program. Samples also were collected in the mid-1970s in Crab Creek and Lind Coulee basins by the Bureau of Reclamation, and some samples were collected by the Washington State Department of Ecology. Only one previous sample exists for Red Rock Coulee basin, so no comparison was made for that basin.

Comparison with 1970s Data

Thirteen of the pesticides analyzed for in the 1970s in samples from Crab Creek and Lind Coulee basins also were analyzed for in this study (table 13). Of these pesticides, 4,4’-DDE, dieldrin, and lindane were detected in the 1970s (Greene and others, 1994) and diazinon, EPTC, malathion, and trifluralin were detected during this study. However, given the much lower reporting limits in the current study, the detections of diazinon, EPTC, malathion, and trifluralin do not necessarily represent an increase in detection rate for those compounds. If the detections in the current study were censored to the historical reporting limits, all of them would be reported as “less than” values. However, the lack of detections of 4,4’-DDE, dieldrin, and lindane in the current study represents a decrease in the detection rate of these compounds. Use of dieldrin and DDT (the parent compound of 4,4’-DDE) were banned in 1985 and 1972, respectively, which likely is a cause for the decrease in detection rates since the 1970s. Decreased detection rates can be a combination of a decrease in usage, the smaller number of samples collected during this study, and changes from furrow to sprinkler irrigation methods (Gruber and Munn, 1996; Ebbert and Kim, 1998). Crab Creek Lateral, a small drainage basin in the CBP north of Red Rock Coulee, was sampled 38 times from 1993 to 1997 during the NAWQA program; 8 of the 38 samples contained dieldrin and 5 of the 38 samples contained trace amounts of 4,4-DDE. Because dieldrin and DDT bind strongly to soil particles, the detection of these banned chemicals in water samples is attributed to erosion from agricultural fields (Gruber and Munn, 1996; Ebbert and Kim, 1998). Degradation of the original pesticides into metabolites that were not analyzed during the current study also may be a factor that makes comparison of older data difficult. Analysis of additional pesticide metabolites should be considered for future studies.

Table 13. Detection rates of pesticides analyzed during the 1970s and from July 2002 to October 2004 in Crab Creek and Lind Coulee irrigation return-flow drainage basins, Columbia Basin Project, Washington.

[Detection rates are number of detections/number of samples analyzed]

Pesticide	Detection rate			
	1970s		Current study (July 2002 to October 2004)	
	Crab Creek	Lind Coulee	Crab Creek	Lind Coulee
4,4’-DDE	2/37	2/38	0/12	0/12
Diazinon	0/37	0/38	1/12	0/12
Dieldrin	3/42	13/38	0/12	0/12
Disulfoton	0/37	0/38	0/12	0/12
EPTC	0/37	0/38	7/12	4/12
alpha-HCH	0/5	0/0	0/12	0/12
gamma-HCH (Lindane)	4/42	0/38	0/12	0/12
Malathion	0/37	0/38	0/12	1/12
Methyl parathion	0/37	0/38	0/12	0/12
Parathion	0/37	0/38	0/12	0/12
Trifluralin	0/37	0/38	0/12	2/12
Aldicarb	0/37	0/38	0/12	0/12
Cycloate	0/37	0/38	0/12	0/12

Comparison with 1990s Data

A better comparison than in the 1970s can be made between data collected during this study and data collected previously by the NAWQA program at Crab Creek, Lind Coulee, and Sand Hollow during the 1990s, because similar methods were used in both studies. All pesticides detected in the 1990s also were analyzed for in this study; however, some pesticides detected in the current study were not analyzed for in the 1990s, so those were excluded from further analysis.

Thirty-six of the pesticide compounds analyzed for in both studies were detected during the 1990s, and 36 were detected during the current study (table 14). Most compounds detected frequently in one study were detected frequently in

Table 14. Detection rates of pesticides analyzed for during the 1990s and from July 2002 to October 2004 in the Crab Creek, Lind Coulee, and Sand Hollow irrigation return-flow drainage basins, Columbia Basin Project, Washington.

[**Period of record for historical samples:** Crab Creek, 1994–95; Lind Coulee, 1994–2000; Sand Hollow, 1994–97. **Pesticide:** CIAT, 2-Chloro-4-isopropylamino-6-amino-s-triazine]

Pesticide	Percentage of samples with detections during the 1990s			Percentage of samples with detections during the current study (July 2002 to October 2004)		
	Crab Creek	Lind Coulee	Sand Hollow	Crab Creek	Lind Coulee	Sand Hollow
2,4-D	17	29	40	92	67	83
2,4-DB	0	0	0	0	17	0
2,6-Diethylaniline	0	0	43	0	0	0
Acetochlor	0	4	0	0	0	0
Alachlor	17	40	100	25	0	50
Atrazine	100	78	100	100	83	92
Azinphos-methyl	0	5	0	17	25	33
Benfluralin	0	2	0	0	0	0
Bentazon	50	0	80	100	50	100
Bromacil	0	0	0	17	42	67
Bromoxynil	0	0	0	0	8	17
Butylate	0	2	0	0	0	0
Carbaryl	0	24	14	17	0	33
Carbofuran	0	9	0	0	0	0
Chlorothalonil	0	0	0	0	8	0
Chlorpyrifos	17	29	29	25	17	42
CIAT	67	67	86	100	75	92
Clopyralid	0	0	0	8	0	0
Cyanazine	17	42	0	0	0	0
DCPA	67	65	86	50	58	33
Diazinon	0	16	0	8	0	8
Dicamba	0	0	0	25	25	17
Dieldrin	0	4	0	0	0	0
Dinoseb	0	0	20	0	0	83
Disulfoton	0	2	0	0	0	0
Diuron	17	43	0	83	83	83
EPTC	83	55	86	58	33	33
Ethalfluralin	0	16	0	0	17	0
Ethoprophos	50	13	29	0	0	8
Fonofos	0	2	0	0	0	0
Lindane	0	0	0	0	0	8
Linuron	0	5	0	8	17	8
Malathion	0	2	14	0	8	8
MCPA	0	0	0	0	8	8
Metolachlor	50	56	71	33	58	33
Metribuzin	17	22	71	8	33	58
Napropamide	0	2	0	0	0	0
Norflurazon	0	0	0	0	0	8
Oxamyl	0	0	0	0	8	0
4,4’-DDE	0	2	0	0	0	0
Pendimethalin	0	33	0	0	42	58
Prometon	0	0	0	0	0	8
Propyzamide	17	0	0	0	0	0
Simazine	83	20	71	75	8	58
Terbacil	83	22	86	50	0	100
Triallate	0	9	0	0	8	0
Triclopyr	0	0	0	0	0	8
Trifluralin	0	35	0	0	17	0
No. of samples collected	6	55	7	12	12	12

the other, with a few exceptions. For example, cyanazine was detected in more than 40 percent of samples collected from Lind Coulee in the 1990s, but was not detected at all in the current study, and bromacil was not detected at any of the sites in the 1990s but was detected in samples from all three sites in the current study. These differences in detections may be due to changes in land use, changes in crop rotations, or just a strategic change of pesticide applications.

Two methods were used to compare historical data with data from the current study to determine if any change in concentrations occurred over time: (1) the Wilcoxon rank-sum test for sites with a small number of samples and a large gap between sampling periods, and (2) the seasonal Kendall test for sites with a larger, more continuous sampling record (Helsel and Hirsch, 2002).

The Wilcoxon rank-sum test (Helsel and Hirsch, 2002) was used to compare historical and current pesticide concentrations at Crab Creek and Sand Hollow. A small number of samples (six to seven) were collected from Crab Creek and Sand Hollow during 1994–95 and 1994–97, respectively. One sample from Sand Hollow in 1992 was analyzed for a limited number of pesticides. This sample was not included in the historical comparison because it was unfiltered water rather than filtered water, as were the other samples.

The rank-sum test is a nonparametric test that uses relative ranks of data points to determine if one data set has higher values than another data set. For these tests, if the earlier data set included all lower ranks and the later data set included all higher ranks, the trend would be decreasing. If no trend was present, then the sums of the ranks would be about equal. A trend was considered to be statistically significant if the p-value from the rank-sum test was ≤ 0.05. Figure 6 shows statistically significant differences in pesticide concentrations between the two study periods.

Statistically significant increases in diuron concentrations (p-value = 0.048) were observed in samples from Crab Creek. Statistically significant decreases were observed in ethoprophos and atrazine concentrations (p-value = 0.012 and 0.038, respectively), and all other pesticides detected at Crab Creek showed no statistically significant trend. Statistically significant increases in bromacil, diuron, and pendimethalin concentrations were observed in samples from Sand Hollow (p-values of 0.026, 0.007, and 0.019, respectively) and statistically significant decreases in concentration of 2,6-diethylanaline, alachlor, atrazine, DCPA, and EPTC were observed (p-values of 0.02, 0.0005, 0.001, 0.023, and 0.023, respectively). Changes in concentration or detection frequency may be due to reductions in pesticide application, changes in agricultural land use, changes in pesticide use and application techniques, changes in managerial practices, environmental changes that may affect pesticide degradation, differences in times of sample collections, differences in sampling techniques, or any combination of these factors. Additional sampling would be needed to determine if these differences are an actual trend over time. Results from the mid-1990s focused mostly on the non-irrigation and early irrigation seasons, whereas the current study was weighted towards collecting samples throughout the irrigation season.

A larger data set exists for Lind Coulee, because samples were collected from 1994 to 2000 for the previous study and from 2002 to 2004 for the current study. Seasonal Kendall trend analysis was used to determine trends over time using the ESTREND program (Schertz and others, 1991). The seasonal Kendall test is a nonparametric test that compares relative ranks of data rather than actual concentration values. Because the data show changes depending on whether it is irrigation season or not, the seasons were defined to be November through March (non-irrigation season) and April through October (irrigation season) and irrigation season data are compared only with irrigation season data and similarly for non-irrigation season data.

No statistically significant trends were determined at Lind Coulee at p=0.05. However, simazine and terbacil showed marginally significant decreasing trends with p-values of 0.07 and 0.10, respectively. Almost all detections occurred prior to 1999 (fig. 7).

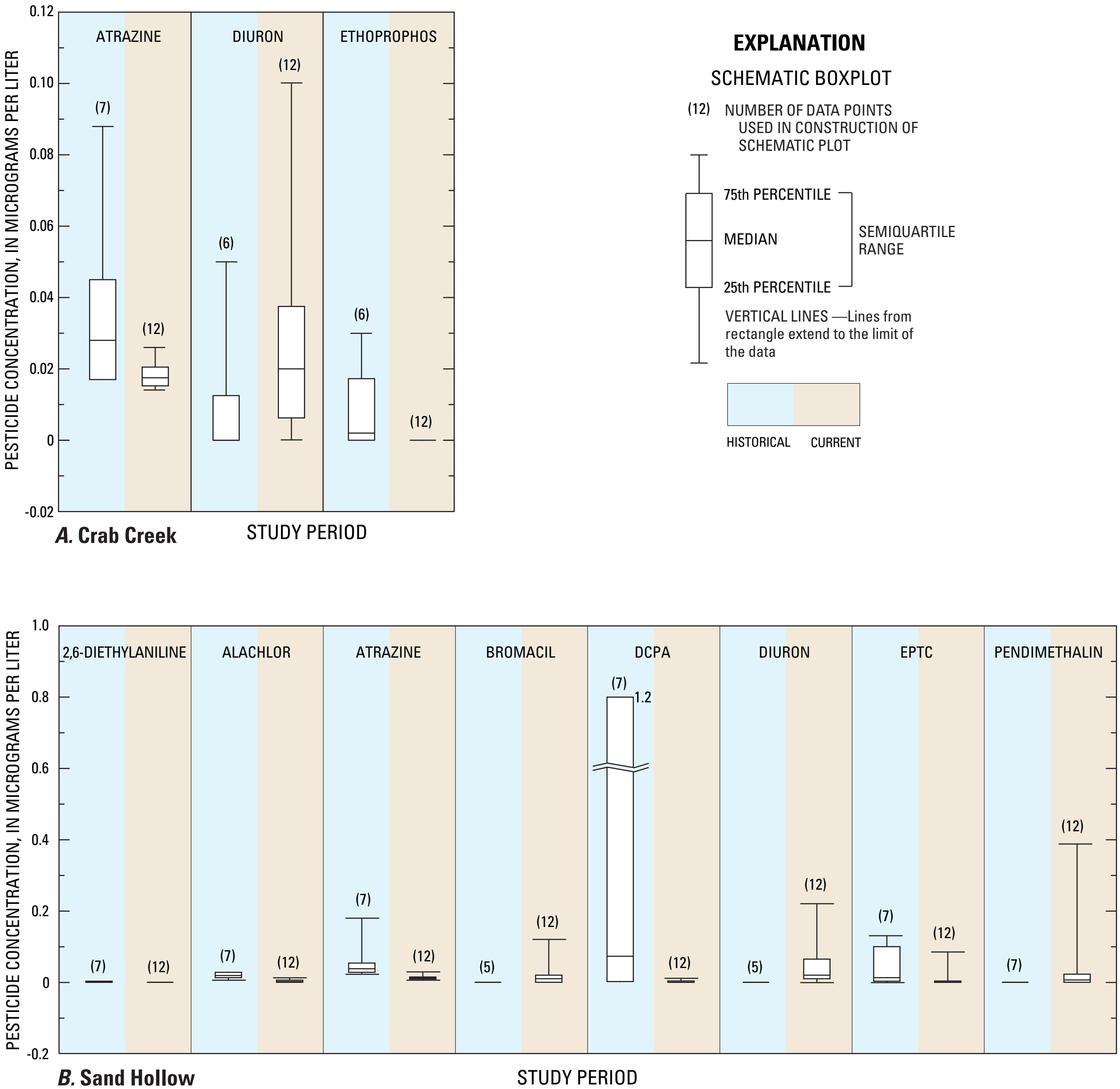


Figure 6 Comparison of historical and current pesticide concentrations in the Crab Creek and Sand Hollow irrigation return-flow drainage basins, Columbia Basin Project, Washington.

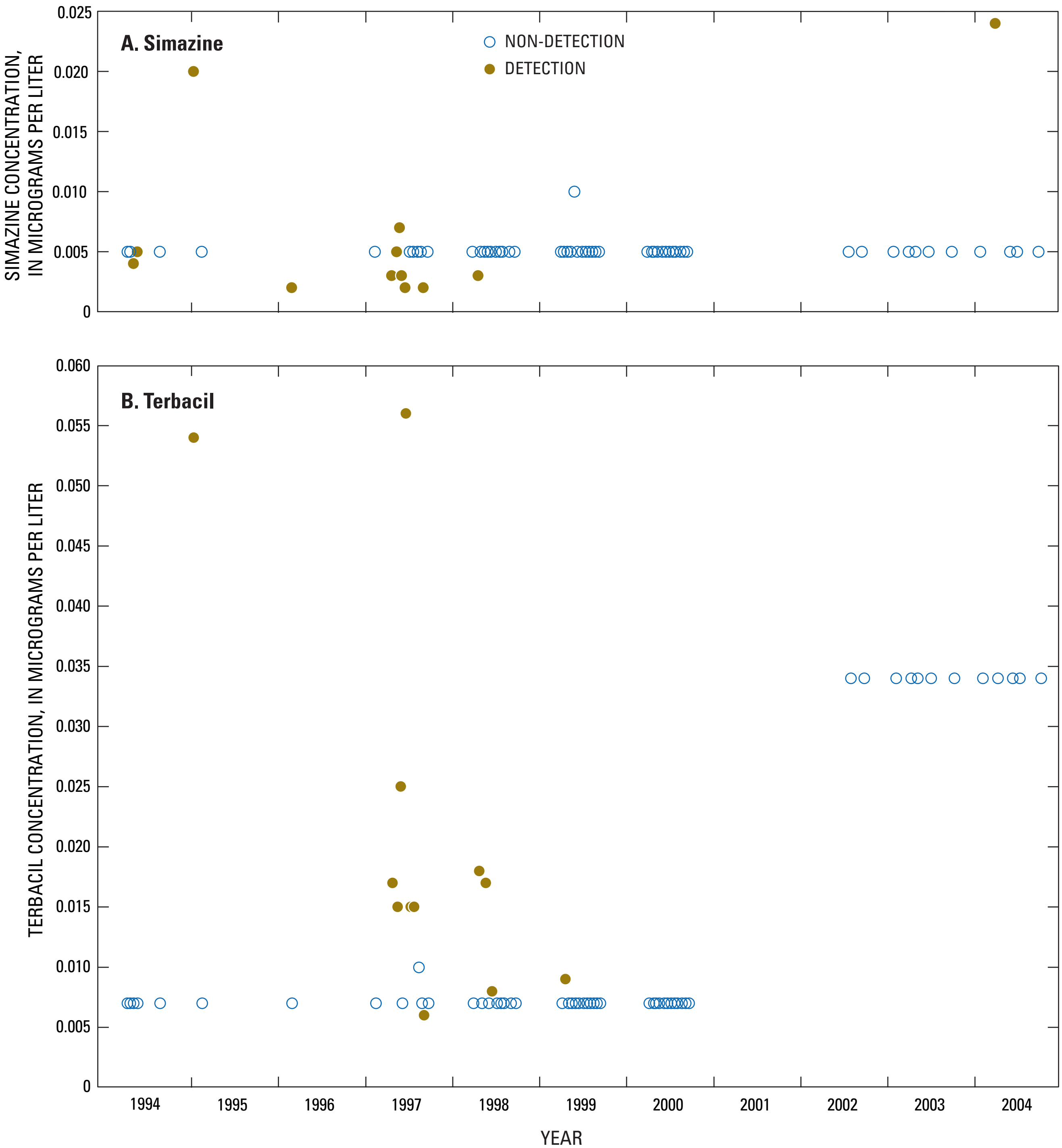


Figure 7. Concentrations of simazine and terbacil in the Lind Coulee irrigation return-flow drainage basin, Columbia Basin Project, Washington, 1994 to 2004.

Comparison of Pesticide Detections with National NAWQA Data

Pesticide concentrations detected in this study for the seven most frequently detected herbicides (table 8), as well as dinoseb and the three most frequently detected insecticides, were compared with pesticide concentrations in previous surface-water samples collected throughout the Central Columbia Plateau (Williamson and others, 1998), Yakima River basin (Fuhrer and others, 2004), and national NAWQA study units (fig. 8).

Overall, pesticide data in this study generally agree with those of the Central Columbia Plateau NAWQA study, which included some of the same sites. Pesticides detected during this study tend to decrease on the middle to lower end of the concentration range compared to all streams of the Central Columbia Plateau study area. This difference is partially explained by the NAWQA program goal to sample during all flow stages, including storm samples that likely transport a greater load of pesticides. Maximum concentrations detected in the Central Columbia Plateau study all were higher than those in this study except for terbacil and dinoseb. Although concentrations in this study tended to be lower, the detection rates were higher for all pesticides except simazine. Dinoseb was detected only twice in Central Columbia Plateau streams, one of which was Sand Hollow, where all 10 detections of dinoseb occurred during this study.

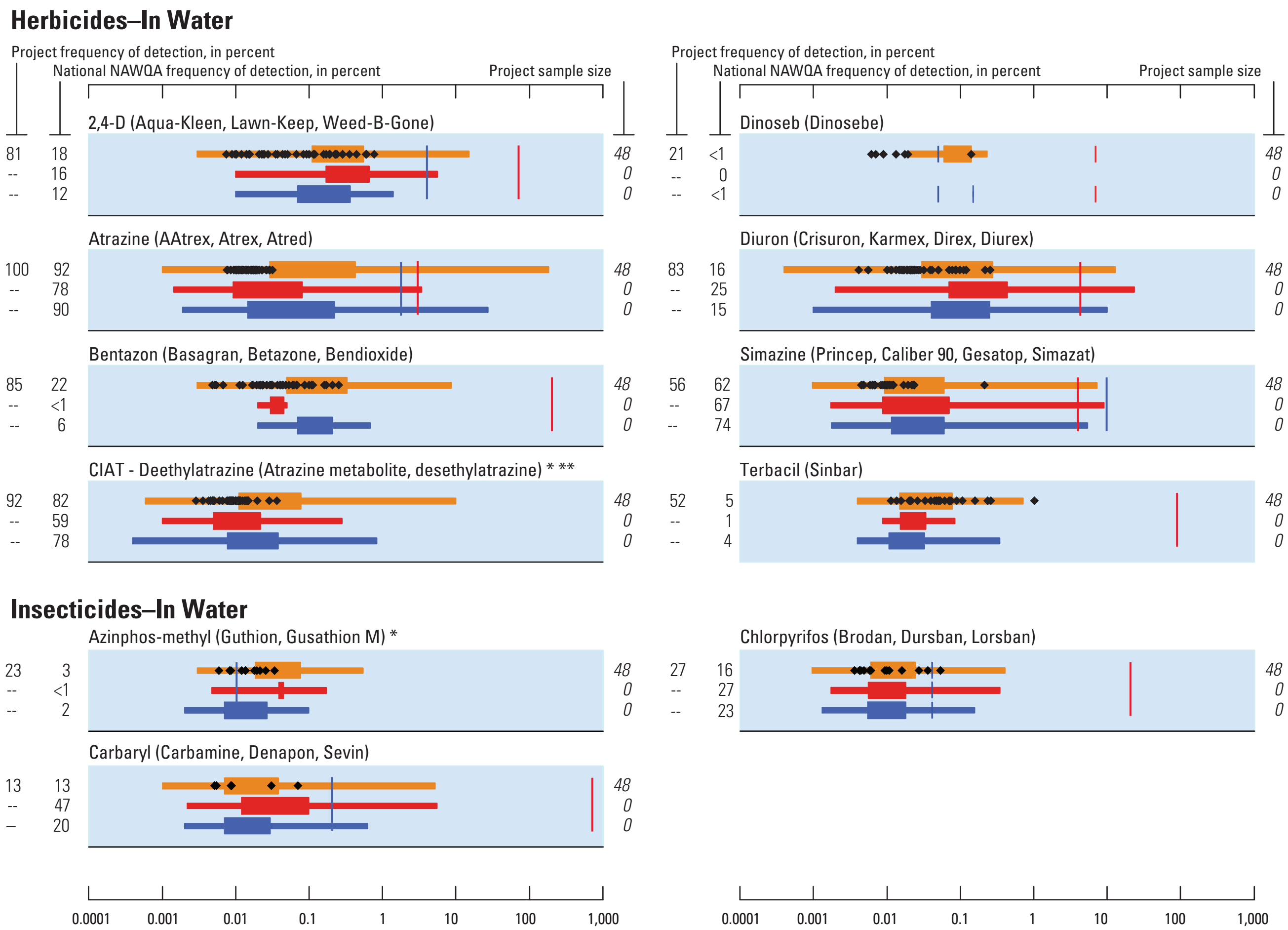
In the Yakima River basin, pesticide concentrations in agricultural streams also were similar to those detected in this study (Fuhrer and others, 2004). Pesticide concentration ranges generally overlapped in the mid to lower range for atrazine, simazine, azinphos-methyl, and carbaryl; terbacil and chlorpyrifos concentrations generally were higher in samples collected during this study. Detection rates also were slightly lower in this study than from streams in the Yakima River basin for all pesticides except chloropyrifos. 2,4-D, diuron, dinoseb, and bentazon were not analyzed for in the Yakima River basin, so no comparison was made for those compounds.

In comparing pesticide concentrations from this study with NAWQA data collected nationally, pesticide concentrations in this study generally were in the mid to lower one-half of the range of concentrations, except for terbacil detections during this study, which are in the upper end of the national range (fig. 8). The detection rate was similar for atrazine, CIAT, simazine, carbaryl, and chlorpyrifos, but was substantially higher in this study for terbacil, 2,4-D, bentazon, diuron, azinphos-methyl, and dinoseb. Dinoseb, in particular, stands out, because it was detected in less than 1 percent of all samples nationally but in 15 percent of samples in this study and about 60 percent of samples in the Sand Hollow drainage basin.

Pesticides are applied to agricultural crops and residential lawns and gardens for control of weeds, insects, fungus, and other undesirable factors. Once applied, pesticides are subject to three types of processes, as described by Larsen and others (1997), that control the behavior and fate of pesticides in the environment: (1) transformation processes that change the chemical structure, (2) phase-transfer processes that control pesticide movement between water, biota, sediment, and the atmosphere; and (3) transport processes that move pesticides from the initial point of application to the environment. Major pathways of pesticide transport in this study were irrigation-return flows, and major transport processes are by direct surface-water runoff from agricultural fields and by ground-water discharge that contains pesticides that have leached into ground water (Jones and Roberts, 1998). Pesticide runoff from right-of-way, commercial, and residential application also is a potential source of pesticide transport.

Streams interact with ground water in all landscapes (Winter and others, 1998). Streams lose water to ground water through the streambed and gain water from inflow of ground water through the streambed. Cessation of irrigation delivery water during non-irrigation seasons changes the relative difference between the altitude of the water table near the streams and the altitude of the surface-water surface, leading to ground-water flow to streams. Williamson and others (1998) showed that many irrigation wasteways and drains in the CBP receive large contributions of ground-water discharge. In the four drainage basins in this study, irrigation water is not delivered from November to March, and in the absence of natural runoff from rainfall, ground water is the predominant source of nitrate in surface-water irrigation-return flow (fig. 9). Fuhrer and others (2004) have shown that ground-water discharges are a major source of surface-water nitrate in irrigated areas of the western United States. Williamson and others (1998) note that, like nitrate, soluble pesticides such as atrazine can leach into ground water of the CBP and later be transported to agricultural irrigation-return flow drainages. Concentrations of atrazine in the study basins do not decrease during the non-irrigation season and actually increase in samples collected from Sand Hollow during the non-irrigation season (fig. 9).

Pesticides that are readily soluble in water, such as herbicides atrazine, bentazon, and diuron (table 15), also can be transported to irrigation-return flows by runoff from agricultural fields, highway or power line rights-of-way, and commercial or residential properties. Pesticide presence usually is related to the timing of pesticide application, pesticide properties, agricultural irrigation practices, and environmental conditions at the time of application (Wagner and others, 1996; Ebbert and Kim, 1998). Transport of pesticides also is dependent on the rate of application, the rate at which pesticides break down in soil and water, and the physical properties of the pesticide that allow it to dissolve and be transported by water (Williamson and others, 1998).



EXPLANATION

CHEMICALS IN WATER

Concentrations and detection frequencies, Columbia Basin Project 2002–04

◆ Detected concentrations in project

92 82 Frequencies of detection, in percent. Detection frequencies were not censored at any common reporting limit. The left-hand column is the study-unit frequency and the right-hand column is the national frequency.

< Less than

-- Not measured or sample size less than two

48 Project sample size

National ranges of detected concentrations, by land use, in 51 NAWQA Study Units, 1991–2001—Ranges include only samples in which a chemical was detected

Streams in agricultural areas

Streams in urban areas

Streams and rivers draining mixed land uses

Lowest 25 percent | Middle 50 percent | Highest 25 percent

National water-quality benchmarks

National benchmarks include standards and guidelines related to drinking-water quality, criteria for protecting the health of aquatic life. Sources include the U.S. Environmental Protection Agency and the Canadian Council of Ministers of the Environment

| Drinking-water quality (applies to ground water and surface water)

| Protection of aquatic life (applies to surface water only)

* No benchmark for drinking-water quality

** No benchmark for protection of aquatic life

Figure 8. Comparison of selected pesticide concentrations in the Columbia Basin Project, Washington, July 2002 to October 2004 with national NAWQA concentrations.

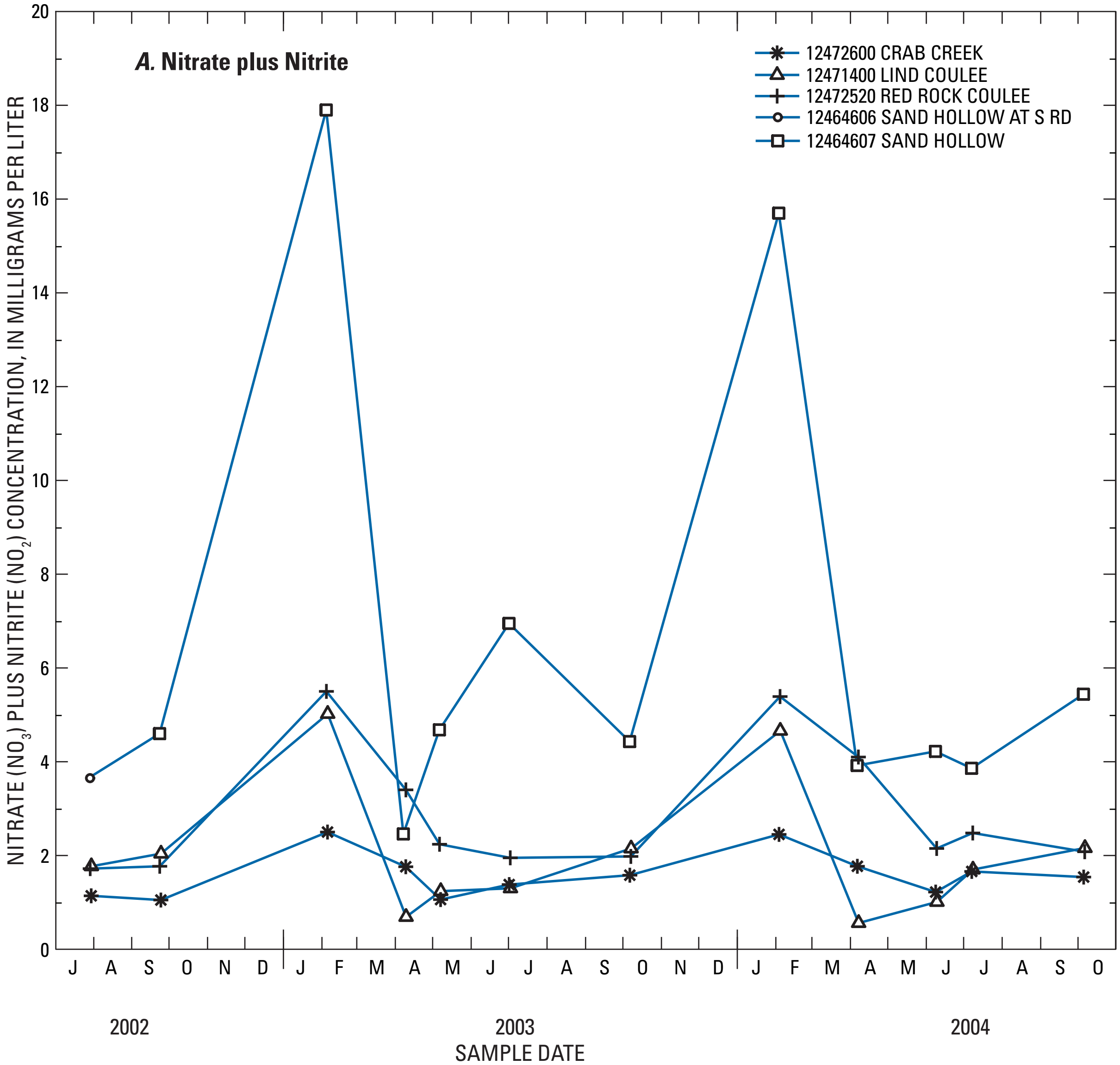


Figure 9. Concentrations of nitrate plus nitrite and atrazine in samples from streamflow-gaging stations in the four irrigation return-flow drainage basins, Columbia Basin Project, Washington, July 2002 to October 2004.
Site 12464606 was sampled only once, in July 2002, and all other samples for Sand Hollow basin were from site 12464607.

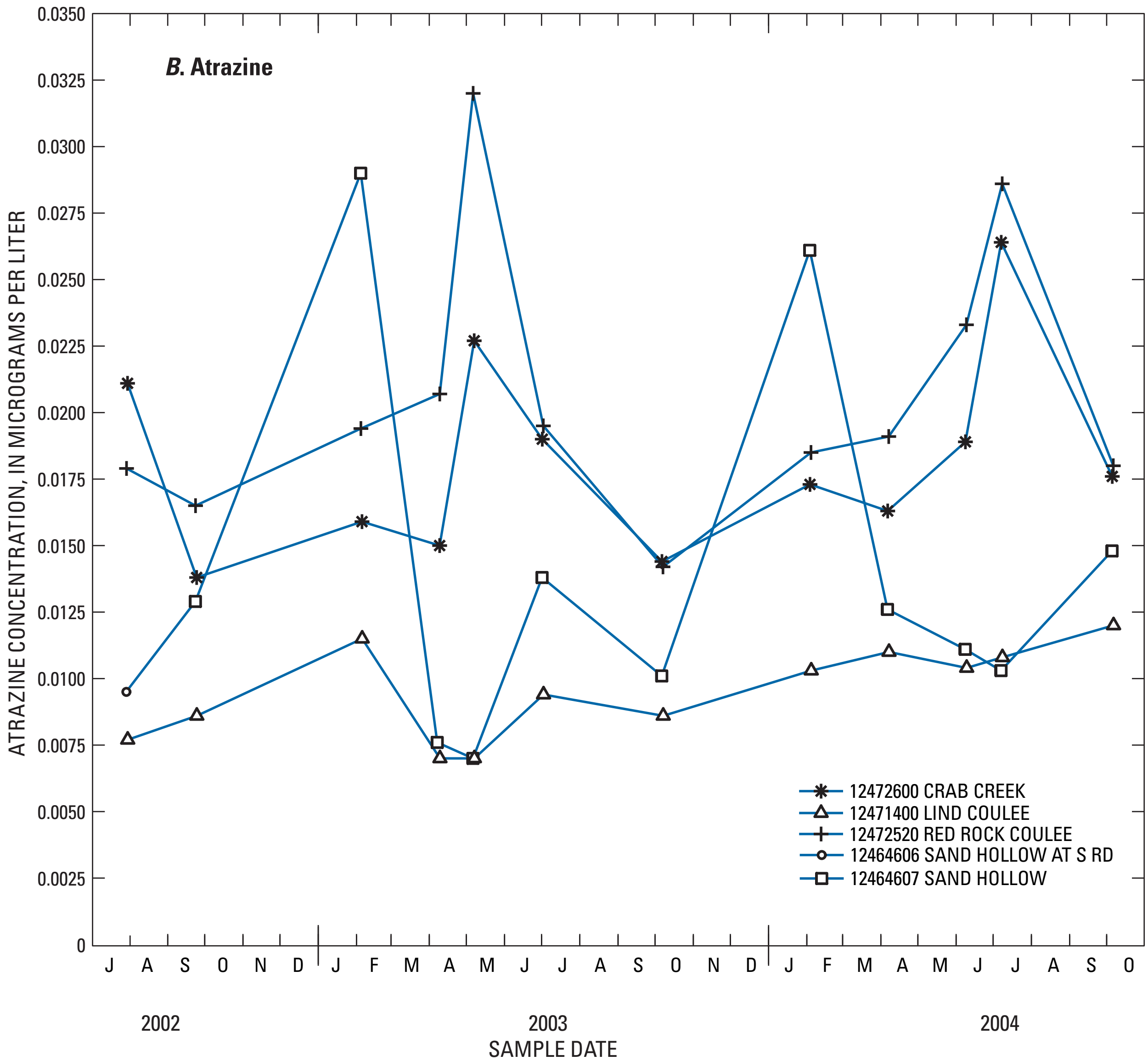


Figure 9. Continued.

Table 15. Physical and chemical properties of pesticides frequently detected in four irrigation-return flow drainage basins in the Columbia Basin Project, Washington, July 2002 to October 2004.

[Solubility and partition coefficient values are from Mackay and others (1997) unless otherwise indicated. **Solubility:** is at 25 degrees Celsius. **Partition coefficients:** K_{ow}, octanol-water partition coefficient; K_{oc}, adsorption partition coefficient. **Type of pesticide**: F, fungicide; H, herbicide; I, insecticide. **Abbreviations:** mg/L, milligram per liter, <, less than; –, no data]

Pesticide	Type of pesticide	Solubility (mg/L)	Partition coefficient		Pesticide	Type of pesticide	Solubility (mg/L)	Partition coefficient	
			log K_{ow}	log K_{oc}				log K_{ow}	log K_{oc}
Atrazine[1]	H	30	2.75	2.00	Diazinon	I	60	3.3	2.76
Bentazon[2]	H	500	–	–	Diphenamid	H	260	1.92	2.31
Diuron	H	40	2.78	2.6	Bromoxynil	H	130	<2.0	–
2,4-D	H	400	2.81	1.68-2.73	Malathion	I	145	2.8	3.26
2,4-D methyl ester	H	100	–	2.0	Metalaxyl	F	8,400	1.75	1.7
Simazine	H	5	2.8	2.11	Methomyl	I	58,000	.60	–
Terbacil[1]	H	710	1.89	1.74	Norflurazon[3]	H	34		2.79
DCPA[3]	H	.5	–	–	Trifluralin	H	[4].5	5.34	4.14
EPTC	H	370	3.2	2.3	2,4-DB	H	46	3.53	2.64
Bromacil	H	815	2.11	1.86	Ethalfluralin		–	–	[3]1.69
Metolachlor	H	430	3.13	2.26	Ethoprophos	I	750	3.59	1.85
Metribuzin[2]	H	1,050	1.60	1.79	MCPA	H	1,605	[4]2.69	2.03-2.07
Alachlor	H	240	2.8	2.23	Prometon	H	750	2.99	2.54
Chlorpyrifos	I	.73	4.92	3.78	Chlorothalonil	F	.6	2.64	3.2
Pendimethalin[2]	H	.3	5.18	3.70	Clopyralid	H	–	–	[3].67
Azinphos-methyl	I	30	2.7	2.61	Lindane	I	7.3	3.7	3.0
Dicamba	H	4,500	2.21	.34, -.4	Nicosulfuron[3]	H	18,486	1.56	–
Dinoseb	H	50	3.56	2.85	Oxamyl	H	282,000	-.47	1.4
Carbaryl[1]	I	120	2.36	2.36	Propiconazole	F	110	3.72	2.82
Linuron[1]	H	75	3.0	2.91	Triallate	H	4	4.29	3.38
Benomyl	F	[4]2.0	2.3	3.28	Triclopyr	H	440	.42	1.30-2.89

[1]Analyzed by gas chromatography/mass spectrometry (GC/MS) and by high-performance liquid chromatography/mass spectrometry (HPLC/MS).

[2]Solubility and partition coefficients are from the Extension Toxicology Network (EXTOXNET), accessed August 22, 2005, at http://extoxnet.orst.edu/.

[3]Solubility and partition coefficients are from the Pesticides Action Network (PAN) pesticides database, accessed August 22, 2005, at http://www.pesticideinfo.org/Index.html.

[4]Reported values vary considerably. Selected value represents best judgment by Mackay and others (1997) and may be subject to a large error.

The herbicides atrazine, bentazon, diuron, and 2,4-D were detected in more than one-half of samples collected at all four sites. Water solubility of these herbicides ranges from 30 to 500 mg/L, and the adsorption coefficients (log K_{oc}), which indicate a chemical's affinity to partition to soil particles, is relatively low. These physical and chemical characteristics lead to a low affinity for adhering to sediment and to a high potential for the compounds to dissolve and be transported in water.

The insecticides chlorpyrifos and azinphos-methyl each were detected in about one-fourth of samples collected during this study and were detected in all four irrigation return-flow basins, although most detections were in Sand Hollow drainage basin. The insecticide carbaryl was detected in 6 of 48 samples, primarily in samples from Sand Hollow drainage basin. Both azinphos-methyl and carbaryl are readily soluble in water, with 30 and 120 mg/L solubility, respectively. The relatively low adsorption coefficient means that these insecticides are likely to dissolve and be transported in water. Conversely, chlorpyrifos has a low solubility in water (0.73 mg/L) and a relatively large adsorption coefficient, so is more likely to bind to soil particles. Therefore, transport of chlorpyrifos is by means of soil erosion into the irrigation-return flows. Because chlorpyrifos recently was listed by USEPA as a Restricted Use Product (U.S. Environmental Protection Agency, 2003), expectations are that detections of this pesticide should decrease over time.

Summary

The U.S. Geological Survey, in cooperation with the Bureau of Reclamation, analyzed water-quality samples from sites in four irrigation-return flow drainage basins in the Columbia Basin Project (CBP) from July 2002 to October 2004 to determine the occurrence, distribution, and transport of pesticides, in response to a recommendation by the National Marine Fisheries Service to monitor water quality in surface-water return flows in the CBP. Ten samples were collected in the Crab Creek, Sand Hollow, Red Rock Coulee, and Lind Coulee drainage basins throughout the irrigation season (generally April through October) and two samples were collected during the non-irrigation season. Samples were analyzed for water temperature, pH, specific conductance, dissolved oxygen, trace elements, major ions, and nutrients, and a suite of 107 pesticides and pesticide metabolites (pesticide transformation products). Measured pesticide concentrations were compared with drinking-water standards and aquatic-life benchmarks, and the presence of pesticides in samples from the irrigation-return flows was compared with historical data and related to current pesticide use, land use, and other environmental factors.

The four drainage basins vary in size from 19 to 710 square miles and the percentage of agricultural cropland ranges from about 35 percent in Crab Creek basin to 75 percent in Lind Coulee basin. More than 95 percent of the cropland in Red Rock Coulee, Crab Creek, and Sand Hollow basins is irrigated, whereas only 30 percent of the cropland in Lind Coulee is irrigated. Estimates of agricultural crop acreage from 2003 were used to describe agricultural land use during the current study. The largest percentage of agricultural crop acreage in Red Rock Coulee, Sand Hollow, and Crab Creek basins was alfalfa. The second largest percentage of cropland in Crab Creek and Sand Hollow basins and third largest in Red Rock Coulee basin was orchards. During 2003, onions were the second largest percentage of crop acreage in Red Rock Coulee basin. Lind Coulee basin has the smallest percentage of irrigated cropland, and about one-third of the crop acreage in dryland wheat and another one-third in fallow cropland. Nearly one-third of the remaining acreage was planted in irrigated wheat, alfalfa, potatoes, corn, and peas.

Although State of Washington water-temperature standards specify that water-temperature criteria be measured by the 7-day average of daily maximum temperatures, this was beyond the scope of this study, so temperatures measured during this study are only an indication of instantaneous temperatures at the time of sampling. Water temperature in 18 samples was greater than the State of Washington criterion of 16 degrees Celsius for salmon and trout spawning, core rearing, and migration: 7 from Red Rock Coulee, 5 from Crab Creek, 4 from Lind Coulee, and 2 from Sand Hollow. In 11 of these 18 instances, temperature also was greater than the criterion of 17.5 degrees Celsius for salmon and trout spawning, non-core rearing, and migration. State of Washington aquatic-life dissolved-oxygen criteria are listed as 1-day minimum, and the criterion of 9.5 milligrams per liter for salmon and trout spawning, core rearing, and migration was exceeded eight times from June to early October during this study at three sites: two times at Sand Hollow, three times at Red Rock Coulee, and three times at Crab Creek. State of Washington aquatic-life criterion for pH of 8.5 for fresh water was exceeded 12 times: 6 at Red Rock Coulee, 3 at Sand Hollow, 2 at Lind Coulee and 1 at Crab Creek. Concentrations of nitrate plus nitrite in two samples collected from Sand Hollow during the non-irrigation season exceeded U.S. Environmental Protection Agency Maximum Contaminant Level for drinking water.

Forty-two pesticides and five metabolites were detected in samples from the four irrigation-return flow drainage basins: 37 in Sand Hollow, 33 in Lind Coulee, 30 in Red Rock Coulee, and 28 in Crab Creek. Herbicides were the most frequently detected pesticides, followed by insecticides, metabolites, and fungicides. Atrazine, bentazon, diuron, and 2,4-D were the most frequently detected herbicides and chlorpyrifos and azinphos-methyl were the most frequently detected insecticides.

Concentrations of three insecticides and one herbicide exceeded U.S. Environmental Protection Agency or Canadian freshwater aquatic-life benchmarks. Concentrations of the insecticide azinphos-methyl exceeded the aquatic-life benchmark at least once at each of the four sites. Concentrations in samples from Sand Hollow also exceeded the aquatic-life benchmark for chlorpyrifos, lindane, and dinoseb. Water-quality aquatic-life benchmarks generally were exceeded in June and July, during the middle of the irrigation season, except the criterion for dinoseb, which was exceeded in one sample during the non-irrigation season in February 2003.

Pesticide application rates and treatment percentages from the National Agriculture Statistics Service and from a 1995 survey conducted in the study unit by the National Center for Food and Agricultural Policy and total crop acreage in the drainage basins were used to estimate the total quantity of each pesticide applied to agricultural fields in 2003. Thirty-one of the 42 herbicides, insecticides, and fungicides detected in surface-water samples were applied to the major agricultural crops in the drainage basins, and 11 of the detected pesticides are sold for residential application. Eight pesticides that were not reported as used for agricultural or residential purposes were detected in the surface-water samples. The overall pattern of pesticide use depends on which crops are grown in each basin. In drainage basins with predominantly more orchards, greater amounts of insecticides are applied, whereas in basins with larger percentages of field crops, more herbicides are applied. Similar usage patterns were in Crab Creek and Sand Hollow basins: the most heavily applied insecticides were azinphos-methyl, carbaryl, and chlorpyrifos and the most heavily applied herbicide was EPTC. DCPA was the most heavily applied herbicide in Red Rock Coulee basin,

followed by the fungicide chlorothalonil, the herbicide EPTC, and the insecticides chlorpyrifos and azinphos-methyl. In Lind Coulee, which has a large percentage of dryland agricultural area, the most heavily applied pesticides were the herbicides 2,4-D and EPTC, followed by the fungicide chlorothalonil. The total amount of non-agricultural pesticides applied by residential homeowners and irrigation districts was negligible compared to total amounts applied to agricultural crops.

A statistical comparison of pesticide concentrations from this study with those in surface-water samples collected in the mid-1990s at Crab Creek and Sand Hollow showed a statistically significant increase in concentrations of diuron and a statistically significant decrease in concentrations of ethoprophos and atrazine in Crab Creek. At Sand Hollow, there were statistically significant increases in concentrations of bromacil, diuron, and pendimethalin and statistically significant decreases in concentrations of 2,6-diethylanaline, alachlor, atrazine, DCPA, and EPTC. A seasonal Kendall trend test on data from Lind Coulee showed no statistically significant trends for any pesticide for 1994 through 2004.

A comparison of pesticide concentrations detected in this study with those detected in previous U.S. Geological Survey National Water-Quality Assessment studies of the Central Columbia Plateau, the Yakima River basin, and national agricultural studies indicated that concentrations in this study generally were in the middle to lower end of the concentration spectrum for the most frequently detected herbicides and insecticides, but that the overall detection rate was at the high end.

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Table 16. Concentrations and precision data for pesticide replicate samples, Columbia Basin Project, Washington, July 2002 to October 2004.

[**Pesticide target analyte:** CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine; OIET, 2-hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine. **Abbreviations**: μg/L, microgram per liter; M, presence of material verified, but not quantified; ^{E}, because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; <, less than; –, no data]

Pesticide target analyte	Concentration in replicates (mg/L)	Percentage of relative difference
2,4-D methyl ester	0.017	19
	.014	
	.037	10
	.041	
2,4-D	.29	.0
	.29	
	.3	3.4
	.29	
CIAT	<.03	–
	^{E}.011	
	^{E}.01	.0
	^{E}.01	
	^{E}.01	9.5
	^{E}.011	
OIET	^{E}.009	25
	^{E}.007	
Alachlor	^{E}.004	–
	<.005	
Atrazine	.011	71
	.023	
	.02	5.1
	.019	
	.01	62
	.019	
Azinphos-methyl	^{E}.018	5.4
	^{E}.019	
Bentazon	^{E}.05	.0
	^{E}.05	
	^{E}.02	.0
	^{E}.02	
Chlorpyrifos	^{E}0.004	0.0
	^{E}.004	
DCPA	.008	.0
	.008	
Dicamba	^{E}.19	38
	^{E}.13	
	.02	67
	.01	
Diphenamid	M	.0
	M	
Diuron	.02	.0
	.02	
	^{E}.01	.0
	^{E}.01	
EPTC	.033	3.1
	.032	
Linuron	^{E}.014	7.4
	^{E}.013	
Metolachlor	^{E}.01	.0
	^{E}.01	
Metribuzin	^{E}.005	.0
	^{E}.005	
Nicosulfuron	^{E}.01	.0
	^{E}.01	
Simazine	.01	.0
	.01	
Terbacil	^{E}.022	4.7
	^{E}.021	

Table 17. Percentage of mean recoveries from field-matrix-pesticide analyses, Columbia Basin Project, Washington, July 2002 to October 2004.

[**Abbreviations**: M, presence of material verified, but not quantified; –, no data]

Pesticide target analyte	Percentage of mean recovery	Number of samples
Gas Chromatography/Mass Spectrometry analytical data		
Acetochlor	110	1
Alachlor	112	1
Atrazine	125	1
Azinphos-methyl	44	1
Benfluralin	105	1
Butylate	98	1
Carbyl	36	1
Carbofuran	145	1
Chlorpyrifos	99	1
Cyanazine	133	1
Gas Chromatography/Mass Spectrometry analytical data—Continued		
CIAT	33	1
DCPA	101	1
4,4'-DDE	53	1
Diazinon	92	1
Dieldrin	86	1
2,6-Diethylanaline	70	1
Disulfoton	53	1
EPTC	92	1
Ethalfluralin	121	1
Ethoprop	91	1

Table 17. Percentage of mean recoveries from field-matrix-pesticide analyses, Columbia Basin Project, Washington, July 2002 to October 2004—Continued.

[**Abbreviations**: M, presence of material verified, but not quantified; –, no data]

Pesticide target analyte	Percentage of mean recovery	Number of samples
Gas Chromatography/Mass Spectrometry analytical data—Continued		
Fipronil	166	1
Fipronil sulfide	121	1
Fipronil sulfone	108	1
Fonos	94	1
alpha-HCH	92	1
gamma-HCH	92	1
Linuron	97	1
Malathion	113	1
Methyl parathion	164	1
Metolachlor	114	1
Metribuzin	78	1
Molinate	88	1
Napropamide	90	1
Parathion	171	1
Pebulate	93	1
Pendimethalin	116	1
cis-Permethrin	55	1
Phorate	77	1
Prometon	116	1
Propyzamide	95	1
Propachlor	112	1
Propanil	121	1
Propargite	213	1
Simazine	99	1
Tebuthiuron	151	1
Terbacil	79	1
Terbufos	80	1
Thiobencarb	93	1
Triallate	92	1
Trifluralin	108	1
High-Performance Liquid Chromatography/Mass Spectrometry analytical data		
2,4-D	37	1
2,4-D methyl ester	50	1
2,4-DB	–	0
OIET	–	0
3(4-Chlorophenyl)-1-methyl urea	71	1
3-Ketocarbofuran	0/M	1
Acifluorfen	–	0
Aldicarb	60	1
Aldicarb sulfone	34	1
Aldicarb sulfoxide	62	1
Chloramben, methyl ester	45	1
Atrazine	78 (39,362)	1
Bendiocarb	60	1
Benomyl	85	1
Bensulfuron-methyl	150	1

Pesticide target analyte	Percentage of mean recovery	Number of samples
High-Performance Liquid Chromatography/Mass Spectrometry analytical data—Continued		
Bentazon	–	0
Bromacil	60	1
Bromoxynil	–	0
Caffeine	81	1
Carbaryl	82	1
Carbofuran	91	1
3-Hydroxycarbofuran	85	1
Chlorimuron-ethyl	96	1
Chlorothalonil	–	0
Clopyralid	–	0
Cycloate	86	1
Dacthal monoacid	–	0
CIAT	52	1
Chlordiamino-*s*-triazine	–	0
CEAT	124	1
Dicamba	–	0
Dichlorprop	–	0
Dinoseb	–	0
Diphenamid	97	1
Diuron	109	1
Fenuron	79	1
Flumetsulam	120	1
Fluometuron	97	1
Imazaquin	86	1
Imazethapyr	105	1
Imidacloprid	128	1
Linuron	97	1
MCPA	–	0
MCPB	–	0
Metalaxyl	101	1
Methiocarb	89	1
Methomyl	91	1
Metsulfuron methyl	79	1
Neburon	101	1
Nicosulfuron	127	1
Norflurazon	101	1
Oryzalin	86	1
Oxamyl	67	1
Picloram	–	0
Propham	74	1
Propiconazole	97	1
Propoxur	91	1
Siduron	105	1
Sulfometuron-methyl	121	1
Tebuthiuron	87	1
Terbacil	64	1
Tribenuron-methyl	87	1
Triclopyr	–	0

Table 18. Pesticide concentrations analyzed by gas chromatography/mass spectrometry and high-performance liquid chromatography/mass spectrometry, Columbia Basin Project, Washington, July 2002 to October 2004.

[GC/MS, analysis by gas chromatography/mass spectrometry; HPLC/MS, analysis by high-performance liquid chromatography/mass spectrometry. **Abbreviations:** ^{E}, because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; <, less than]

Sampling site	Date	Time	Atrazine		CIAT		Tebuthiuron	
			GC/MS	HPLC/MS	GC/MS	HPLC/MS	GC/MS	HPLC/MS
			39632	39632	4040	4040	82670	82670
Crab Creek								
12472600	07-30-02	1020	0.021	^{E}0.013	^{E}0.019	^{E}0.012	<0.02	<0.032
12472600	09-24-02	1100	.014	^{E}.008	^{E}.013	^{E}.009	<.02	<.032
12472600	02-05-03	1120	.016	.01	^{E}.014	^{E}.008	<.02	<.032
12472600	04-09-03	0930	.015	^{E}.006	^{E}.009	^{E}.007	<.02	<.032
12472600	05-07-03	0940	.023	.015	^{E}.007	^{E}.007	<.02	<.032
12472600	07-01-03	1400	.019	^{E}.009	^{E}.011	^{E}.006	<.02	<.032
12472600	10-06-03	1350	.014	^{E}.009	^{E}.004	^{E}.009	<.02	<.032
12472600	02-03-04	1330	.017	^{E}.005	^{E}.014	<.028	<.02	<.032
12472600	04-06-04	1310	.016	^{E}.008	^{E}.011	^{E}.007	<.02	<.032
12472600	06-08-04	1250	.019	.01	^{E}.010	<.028	<.02	<.032
12472600	07-07-04	1320	.026	.013	^{E}.012	^{E}.008	<.02	<.032
12472600	10-05-04	1310	.018	^{E}.006	^{E}.010	^{E}.005	<.02	^{E}.004
Lind Coulee								
12471400	07-30-02	1345	0.008	^{E}0.004	^{E}0.005	<0.028	<0.02	<0.032
12471400	09-24-02	1400	.009	^{E}.004	^{E}.006	^{E}.004	<.02	<.032
12471400	02-05-03	1440	.011	^{E}.006	^{E}.008	^{E}.005	<.02	<.032
12471400	04-09-03	1520	<.007	<.009	<.006	<.028	<.02	<.032
12471400	06-07-03	1320	<.007	<.009	<.006	<.028	<.02	<.032
12471400	07-02-03	1430	.009	^{E}.005	^{E}.004	<.028	<.02	<.032
12471400	10-07-03	1440	.009	^{E}.004	^{E}.003	^{E}.003	<.02	<.032
12471400	02-04-04	1350	.01	<.009	^{E}.009	<.028	<.02	<.032
12471400	04-07-04	1410	.011	^{E}.004	<.006	<.028	<.02	<.032
12471400	06-09-04	1310	.01	^{E}.003	^{E}.005	<.028	<.02	<.032
12471400	07-08-04	1240	.011	^{E}.004	^{E}.005	<.028	<.02	<.032
12471400	10-06-04	1410	.012	<.008	^{E}.004	<.028	<.02	<.032
Red Rock Coulee								
12472520	07-29-02	1450	0.018	^{E}0.011	^{E}0.011	^{E}0.008	<0.02	<0.032
12472520	09-23-02	1310	.017	^{E}.006	^{E}.011	^{E}.005	<.02	<.032
12472520	02-04-03	1350	.019	.012	^{E}.015	^{E}.009	<.02	<.032
12472520	04-09-03	1150	.021	^{E}.008	^{E}.015	^{E}.007	<.02	<.032
12472520	05-06-03	1310	.032	^{E}.030	^{E}.008	^{E}.012	<.02	<.032
12472520	07-02-03	1020	.019	.012	^{E}.009	^{E}.006	<.02	<.032
12472520	02-04-04	0910	.018	^{E}.006	^{E}.013	<.028	<.02	<.032
12472520	04-07-04	0910	.019	.011	^{E}.011	<.028	<.02	<.032
12472520	06-09-04	0810	.023	.011	^{E}.011	<.028	<.02	<.032
12472520	07-08-04	0830	.029	.017	^{E}.010	^{E}.007	<.02	<.032
12472520	10-06-04	0930	.018	^{E}.006	^{E}.009	^{E}.004	<.02	<.032
Sand Hollow								
12464606	07-29-02	1150	0.009	^{E}0.005	^{E}0.008	<0.005	<0.02	<0.032
12464607	09-23-02	1100	.013	^{E}.004	^{E}.013	^{E}.005	<.02	<.032
12464607	02-04-03	1050	.029	.021	^{E}.036	^{E}.021	<.02	<.032
12464607	04-07-03	1050	.008	<.009	^{E}.005	^{E}.004	<.02	<.032
12464607	05-06-03	1010	<.007	^{E}.005	<.006	^{E}.006	<.02	<.032
12464607	07-01-03	1020	.014	^{E}.007	^{E}.012	^{E}.007	<.02	<.032
12464607	10-06-03	1010	.01	^{E}.005	^{E}.005	^{E}.006	<.02	<.032
12464607	02-03-04	0920	.026	^{E}.007	^{E}.029	^{E}.005	<.02	<.032
12464607	04-06-04	0920	.013	^{E}.004	^{E}.009	^{E}.005	<.02	<.032
12464607	06-08-04	0840	.011	^{E}.005	^{E}.008	<.028	<.02	<.032
12464607	07-07-04	0930	.01	^{E}.005	^{E}.008	<.028	<.02	<.032
12464607	10-05-04	0930	.015	^{E}.004	^{E}.009	^{E}.004	<.02	<.032
Total sample			47		47		47	
Total <			2		3		46	
Total hits			41		29		0	
Negligent hit/miss			4		15		1	
Significant hits/miss			0		0		0	
Median percentage difference of hits			79		79			

Table 18. Pesticide concentrations analyzed by gas chromatography/mass spectrometry and high-performance liquid chromatography/mass spectrometry, Columbia Basin Project, Washington, July 2002 to October 2004.—Continued

[GC/MS, analysis by gas chromatography/mass spectrometry; HPLC/MS, analysis by high-performance liquid chromatography/mass spectrometry. **Abbreviations:** E, because recovery or variation in recovery was outside the acceptable range, compound is qualified with an E-code (estimated) or concentration reported is less than laboratory reporting level and is qualified as estimated; <, less than]

Sampling site	Date	Time	Carbaryl		Carbofuran		Linuron		Terbacil	
			GC/MS	HPLC/MS	GC/MS	HPLC/MS	GC/MS	HPLC/MS	GC/MS	HPLC/MS
			P82680	P49310	P82674	P49309	P82666	P38478	P82665	P04032
Crab Creek										
12472600	07-30-02	1020	E.005	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12472600	09-24-02	1100	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12472600	02-05-03	1120	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12472600	04-09-03	0930	<.041	<.03	<.020	<.006	<.035	<.01	E.061	E.031
12472600	05-07-03	0940	<.041	<.03	<.020	<.006	<.035	<.01	E.033	E.025
12472600	07-01-03	1400	<.041	<.03	<.020	<.006	<.035	<.01	E.026	<.010
12472600	10-06-03	1350	<.041	<.03	<.020	<.006	<.035	<.01	<.034	E.006
12472600	02-03-04	1330	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12472600	04-06-04	1310	<.041	<.03	<.020	<.006	<.035	<.01	E.016	<.010
12472600	06-08-04	1250	<.041	<.03	<.020	<.006	E.013	<.01	E.021	<.010
12472600	07-07-04	1320	E.009	<.03	<.020	<.006	<.035	<.01	E.021	<.010
12472600	10-05-04	1310	<.041	<.02	<.020	<.016	<.035	<.01	<.034	<.016
Lind Coulee										
12471400	07-30-02	1345	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	09-24-02	1400	<.041	<.03	<.020	<.006	E.006	<.01	<.034	<.010
12471400	02-05-03	1440	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	04-09-03	1520	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	06-07-03	1320	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	07-02-03	1430	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	10-07-03	1440	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	02-04-04	1350	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	04-07-04	1410	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	06-09-04	1310	<.041	<.03	<.020	<.006	E.013	<.01	<.034	<.010
12471400	07-08-04	1240	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12471400	10-06-04	1410	<.041	<.02	<.020	<.016	<.035	<.01	<.034	<.016
Red Rock Coulee										
12472520	07-29-02	1450	<.041	<.03	<.020	<.006	<.035	<.01	<.034	<.010
12472520	09-23-02	1310	<.041	<.03	<.020	<.006	<.035	<.01	E.014	<.010
12472520	02-04-03	1350	<.041	<.03	<.020	<.006	<.035	E.01	<.034	E.005
12472520	04-09-03	1150	<.041	<.03	<.020	<.006	<.035	<.01	E.044	E.020
12472520	05-06-03	1310	<.041	<.03	<.020	<.006	<.035	<.01	E.075	E.090
12472520	07-02-03	1020	<.041	<.03	<.020	<.006	<.035	<.01	E.020	E.010
12472520	02-04-04	0910	<.041	<.03	<.020	<.006	<.035	<.01	<.034	E.006
12472520	04-07-04	0910	<.041	<.03	<.020	<.006	<.035	<.01	E.040	<.027
12472520	06-09-04	0810	<.041	<.03	<.020	<.006	E.014	<.01	E.050	<.010
12472520	07-08-04	0830	<.041	<.03	<.020	<.006	<.035	<.01	E.011	<.010
12472520	10-06-04	0930	<.041	<.02	<.020	<.016	<.035	<.01	<.034	<.016
Sand Hollow										
12464606	07-29-02	1150	E0.005	<0.03	<0.020	<0.006	<0.035	<0.01	E0.071	E0.042
12464607	09-23-02	1100	<.041	<.03	<.020	<.006	<.035	<.01	E.106	.051
12464607	02-04-03	1050	<.041	<.03	<.020	<.006	<.035	<.01	E.157	E.085
12464607	04-07-03	1050	<.041	<.03	<.020	<.006	<.035	<.01	E1.01	E1.35
12464607	05-06-03	1010	E.009	E.01	<.020	<.006	<.035	<.01	E.070	E.069
12464607	07-01-03	1020	<.041	<.03	<.020	<.006	<.035	<.01	E.237	E.176
12464607	10-06-03	1010	<.041	<.03	<.020	<.006	<.035	E.01	E.047	E.044
12464607	02-03-04	0920	<.041	<.03	<.020	<.006	<.035	<.01	E.259	E.123
12464607	04-06-04	0920	<.041	<.03	<.020	<.006	<.035	<.01	E.053	<.019
12464607	06-08-04	0840	E.070	E.01	<.020	<.006	E.007	<.01	E.088	E.030
12464607	07-07-04	0930	E.031	E.01	<.020	<.006	<.035	<.01	E.075	<.032
12464607	10-05-04	0930	<.041	<.02	<.020	<.016	<.035	<.01	E.051	E.033
Total sample			47		47		47		47	
Total <			41		47		40		19	
Total hits			3		0		0		15	
Negligent hit/miss			3		0		7		5	
Significant hits/miss			0		0		0		8	
Median percentage difference of hits			56						39	

Table 19. Registration status of pesticides analyzed, Columbia Basin Project, Washington, July 2002 to October 2004.

[**Type of pesticide**: F, fungicide; H, herbicide; I, insecticide; S, stimulant. **Registered use:** Home and (or) commercial]

Pesticide target analyte	Trade or common name(s)	Type of pesticide	Registered use
2,4-D	Weedon-2,4,-DP	H	Both
2,4-D methyl ester	none	H	Both
2,4-DB	none	H	Commercial
Acetochlor	Acenit, Sacenid	H	Commercial
Acifluorfen	Blazer, Tackle	H	Home
Alachlor	Lasso	H	Commercial
Aldicarb	Temik	I	Commercial
alpha-HCH	none	I	Neither
Atrazine	Aatrexx, Atratol	H	Both
Azinphos-methyl	Guthion	I	Commercial
Bendiocarb	Ficam	I	Both
Benfluralin	Balan, Benefin	H	Both
Benomyl	Benlate	F	Both
Bensulfuron-methyl	Londax	H	Neither
Bentazon	Adagio, Galaxy, Storm	H	Both
Bromacil	Hyvar, Uragon	H	Both
Bromoxynil	Buctril, Bromanil, Torch	H	Commercial
Butylate	Sutran +, Genate Plus	H	Commercial
Caffeine	none	S	Neither
Carbaryl	Sevin, Savit	I	Both
Carbofuran	Furadan	I	Commercial
Chloramben, methyl ester	Amiben	H	Neither
Chlorimuron-ethyl	Classic	H	Neither
Chlorothalonil	Bravo, Forturf	F	Both
Chlorpyrifos	Lorsban	I	Both
cis-Permethrin	Ambush, Pounce	I	Both
Clopyralid	Stinger, Lontrel	H	Both
Cyanazine	Bladex	H	Commercial
Cycloate	Ro-Neet, Marathon	H	Commercial
DCPA	Dacthal	H	Commercial
Diazinon	several	I	Both
Dicamba	Banvel, Marksman, Clarity	H	Both
Dichlorprop	2,4-DP, Weedon DP	H	Both
Dieldrin	Panoram D-31	I	Neither
Dinoseb	DNBP, Caldon, Dynamite	H	Neither
Diphenamid	Rideon, Dymid, Enide	H	Neither
Disulfoton	Di-Syston	I	Both
Diuron	DCMU, Direx, Aguron	H	Both
EPTC	Eptam, Eradicane	H	Both
Ethalfluralin	Sonalan, Curbit EC	H	Commercial
Ethoprop	Mocap	I	Commercial
Fenuron	Beet-Kleen	H	Neither
Fipronil	Regent	I	Both
Flumetsulam	DE498, XRD 498	H	Commercial
Fluometuron	Cotoran, Lanex, Cottonex	H	Neither
Fonos	Dyfonate	I	Neither
gamma-HCH	Lindane	I	Both
Imazaquin	Skepter 1.5L, Image 1.5LC	H	Commercial
Imazethapyr	Pursuit, Pursuit DG	H	Commercial
Imidacloprid	Admire, Gaucho, Merit	I	Both
Linuron	Lorox, Linex, Afalon	H	Commercial
Malathion	several	I	Both
MCPA	Metaxon, Border Master	H	Both
MCPB	Troptox, Can-Trol	H	Commercial
Metalaxyl	Apron, Subdue, Ridomil	F	Both
Methiocarb	Draza, Mesurol	I	Commercial
Methomyl	Lannate, Nudrin, Lanox	I	Both
Methyl parathion	Penncap-M	I	Commercial
Metolachlor	Dual, Pennant	H	Commercial
Metribuzin	Lexone, Sencor	H	Commercial
Metsulfuron methyl	Escort, Gropper, Ally	H	Commercial
Molinate	Ordram	H	Neither
Napropamide	Devrinol	H	Both
Neburon	Granurex, Herbalt, Kloben	H	Neither
Nicosulfuron	Accent, Accent DF	H	Commercial
Norflurazon	Zorial, Evital, Solicam	H	Commercial
Oryzalin	Ryzelan, Surflan, Dirimal	H	Both
Oxamyl	Vydate: Thioxamyl	I	Commercial
Parathion	several	I	Commercial
Pebulate	Tillam	H	Commercial
Pendimethalin	Prowl, Stomp	H	Both
Phorate	Thimet, Rampart	I	Commercial
Picloram	Tordon, Amdon, Grazon	H	Commercial
Prometon	Pramitol	H	Both
Propachlor	Ramrod	H	Commercial
Propanil	Stampede	H	Neither
Propargite	Comite, Omite	I	Commercial
Propham	Chem-Hoe, IPC, Premalox	H	Neither
Propiconazole	Tilt, Orbit, Wocosin	F	Both
Propoxur	Baygon, PHC, Suncide	I	Both
Propyzamide	Kerb	H	Neither
Siduron	Tupersan, Trey	H	Both
Simazine	Aquazine, Princep	H	Both
Sulfometuron-methyl	Oust, DPX-T5648	H	Commercial
Tebuthiuron	Graslan, Spike, Perflan	H	Commercial
Terbacil	Sinbar, DPX-D732, Geonter	H	Commercial
Terbufos	Counter	I	Commercial
Thiobencarb	Bolero	H	Neither
Triallate	Far-Go	H	Commercial
Tribenuron-methyl	Express, DPX-L5300	H	Commercial
Triclopyr	Garlon, Curtail, Redeem	H	Both
Trifluralin	Treflan, Trilin	H	Both

Table 20. Summary of pesticides not detected, Columbia Basin Project, Washington, July 2002 to October 2004.

[Type of pesticide: H, herbicide; I, insecticide; T, transformation product]

Pesticide target analyte	Trade or common name(s)	Type of pesticide
2,6-Diethylanaline	none	T
3(4-Chlorophenyl)-1-methyl urea	none	T
3-Hydroxycarbofuran	none	T
3-Ketocarbofuran	none	T
4,4’-DDE	none	T
Acetochlor	Acenit, Sacenid	H
Acifluorfen	Blazer, Tackle	H
Aldicarb	Temik	I
Aldicarb sulfone	none	T
Aldicarb sulfoxide	none	T
alpha-HCH	none	I
Bendiocarb	Ficam	I
Benfluralin	Balan, Benefin	H
Bensulfuron-methyl	Londax	H
Butylate	Sutran +, Genate Plus	H
Carbofuran	Furadan	I
Chloramben, methyl ester	Amiben	H
Chlorimuron-ethyl	Classic	H
cis-Permethrin	Ambush, Pounce	I
Cyanazine	Bladex	H
Cycloate	Ro-Neet, Marathon	H
Desulfinylfipronil	none	T
Desulfinylfipronil amide	none	T
Dichlorprop	2,4-DP, Weedon DP	H
Dieldrin	Panoram D-31	I
Disulfoton	Di-Syston	I
Fenuron	Beet-Kleen	H
Fipronil	Regent	I
Fipronil sulfide	none	T
Fipronil sulfone	none	T
Flumetsulam	DE498, XRD 498	H
Fluometuron	Cotoran, Lanex, Cottonex	H
Fonos	Dyfonate	I
gamma-HCH	Lindane	I
Imazaquin	Skepter 1.5L, Image 1.5LC	H
Imazethapyr	Pursuit, Pursuit DG	H
Imidacloprid	Admire, Gaucho, Merit	I
MCPB	Troptox, Can-Trol	H
Methiocarb	Draza, Mesurol	I
Methyl parathion	Penncap-M	I
Metsulfuron methyl	Escort, Gropper, Ally	H
Molinate	Ordram	H
Napropamide	Devrinol	H
Neburon	Granurex, Herbalt, Kloben	H
Oryzalin	Ryzelan, Surflan, Dirimal	H
Parathion	several	I
Pebulate	Tillam	H
Phorate	Thimet, Rampart	I
Picloram	Tordon, Amdon, Grazon	H
Propachlor	Ramrod	H
Propanil	Stampede	H
Propargite	Comite, Omite	I
Propham	Chem-Hoe, IPC, Premalox	H
Propoxur	Baygon, PHC, Suncide	I
Propyzamide	Kerb	H
Siduron	Tupersan, Trey	H
Sulfometuron-methyl	Oust, DPX-T5648	H
Tebuthiuron	Spike	H
Terbacil	Sinbar	H
Terbufos	Counter	I
Thiobencarb	Bolero	H

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