U.S. Department of the Interior
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Pesticides in the Lower Clackamas River Basin, Oregon, 2000-01

Water-Resources Investigations Report 03-4145

Prepared in cooperation with the
Clackamas River Water Providers and
Clackamas County Department of Water Environment Services

Cover photograph:

The lower Clackamas River winds westward through agricultural, urban, and industrial land before flowing into the Willamette River downstream of Oregon City (*photograph by Dennis Lynch, U.S. Geological Survey*).

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By KURT D. CARPENTER

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Pesticides in the Lower Clackamas River Basin, Oregon, 2000–01

By Kurt D. Carpenter

SUMMARY

In 2000–01, the U.S. Geological Survey sampled the Clackamas River and its major lower-basin tributaries for 86 dissolved pesticides and selected breakdown products during storm runoff conditions. In all, 27 compounds, including 18 herbicides, 7 insecticides, and 2 pesticide breakdown products, were detected in 18 stream samples. The most commonly detected pesticides, in decreasing frequency, included atrazine, simazine, diazinon, metolachlor, and diuron, which occurred in 46–92% of samples collected from the tributaries. Of these, atrazine, simazine, and metolachlor, plus six other compounds, also were detected in the main-stem Clackamas River.

Pesticides were consistently detected with greater frequency and at higher concentrations in the four lowermost tributaries (Deep, Richardson, Rock, and Sieben Creeks). In these streams, a total of 12 to 18 pesticides were detected per stream in samples collected during spring and fall. Pesticides always occurred with at least one other pesticide, and about half of the samples, including one sample from the Clackamas River in October 2000, contained six or more pesticides.

Nine pesticides—the insecticide diazinon and the herbicides 2,4-D, atrazine, dichlobenil, diuron, imazaquin, metolachlor, simazine, and trifluralin—were detected at relatively low concentrations in five samples of Clackamas River water. Despite these detections, no pesticides were detected in three samples of treated Clackamas River water used for drinking.

Concentrations of six compounds—carbaryl, chlorpyrifos, diazinon, dieldrin, malathion, and the breakdown product of DDT (*p,p'*-DDE)—exceeded established or recommended criteria for the protection of aquatic life in some of the tributaries, sometimes for multiple pesticides in one sample. The greatest number of aquatic-life criterion exceedances occurred in Rock and Sieben Creeks, which drain both agricultural land and urban developments. Concentrations of three pesticides exceeded aquatic-life criteria in each of these streams, and concentrations of the organophosphate insecticides diazinon and chlorpyrifos exceeded their respective criteria by several-fold in both streams. Diazinon was detected in all of the four lowermost tributaries, at concentrations that exceeded the U.S. Environmental Protection Agency aquatic-life criterion (0.1 μg/L) in all five samples collected from Sieben and Rock Creeks. The highest diazinon concentration (0.160 μg/L measured in Sieben Creek in May 2000) exceeded the maximum concentration recommended by the National Academy of Sciences/National Academy of Engineering by a factor of 18.

Such aquatic-life criteria consider only one pesticide at a time, and therefore do not evaluate the effects of multiple pesticides detected at once in a sample. To do this, a composite pesticide toxicity index (PTI) was used. The highest PTI values were found in samples collected from Rock and Sieben Creeks, where relatively fewer sensitive invertebrates were observed in other studies conducted in 1997–99. These two streams, with

the highest pesticide concentrations and greatest number of pesticide detections, supported fewer high-quality invertebrates (1–10 taxa) compared with other streams sampled (15–31 taxa).

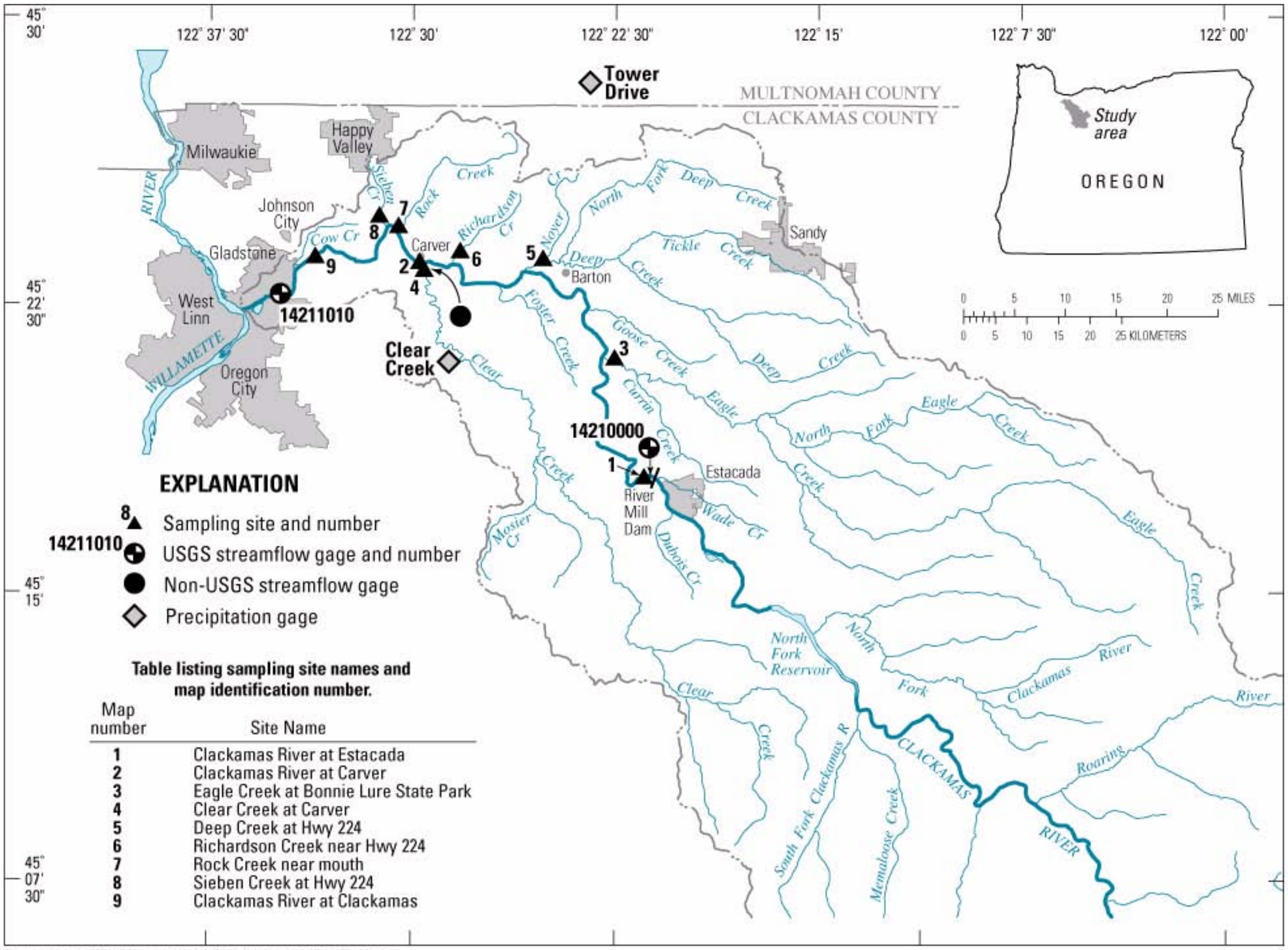
During the May 2000 storm, two tributaries—Deep and Rock Creeks—contributed most (65% and 15%, respectively) of the total measured pesticide load from the 6 tributaries sampled. Most (90%) of the total measured pesticide load during the October 2000 storm could be accounted for by inputs from Sieben Creek alone. Note, however, that because of the dynamic nature of precipitation, rainfall runoff, and streamflow during storms, instantaneous pesticide loads constitute best estimates, not precise calculations.

Identification of pesticide sources in the Clackamas River Basin is difficult because of the diverse land uses in the basin and the multiple-use nature of many of the pesticides detected. Of the 25 parent compounds detected, 22 have agricultural uses, 24 have urban uses, 16 are applied to golf courses, 11 are applied along roads and other right-of-ways, and 5 have or had forestry applications. Based on current available crop acreages for Clackamas County and best estimates of chemical application rates in the Pacific Northwest, most (49%) of the pesticide estimated to be applied to agricultural lands in Clackamas County (for those detected) is used for nursery and greenhouse crops. Lesser amounts, ranging from 4 to 15%, are applied to pastureland, Christmas trees, alfalfa and hay fields, hazelnuts, and grass seed fields. Such estimates could be improved with more detailed pesticide use information. Although pesticide use data are available at the county level, such data are too coarse to identify particular areas with subbasins where pesticide contamination is occurring. Also, because only a small fraction of the thousands of pesticide products registered for use in Oregon were tested for during this study, pesticide use information would help ensure that high-use pesticides are included in future studies.

INTRODUCTION

Approximately 9,500 pesticide products are registered for use in Oregon to control brush, weeds, insects, fungi, rodents, nematodes, and other pests on agricultural crops, lawns, and landscaping in urban and industrial areas, home gardens, golf courses, forestland, and vegetation along right-of-ways such as roads, railways, and utility lines. Despite educational programs and regulations geared toward preventing pesticide contamination, studies have shown that a wide variety of these compounds are making their way into streams and ground water. A U.S. Geological Survey (USGS) study on pesticide occurrence in streams found 1 or more pesticides in 95% of 8,000 streams across the country, and 50% of streams contained 5 or more pesticides (U.S. Geological Survey, 1999; Gilliom and others, 1999). Studies in Oregon have found numerous pesticides in streams (Anderson and others, 1997; Wentz and others, 1998; Rinella and Janet, 1998; Sandahl and Jenkins, 2002; Grange, 2002) and ground water (Hinkle, 1997), particularly in agricultural and urban areas, where most pesticide applications occur. The great diversity of crops grown in Oregon, particularly in the northern Willamette Valley, results in a wide variety of pesticides being applied and later detected in streams (Anderson and others, 1997).

The Clackamas River in northwestern Oregon drains the western slope of the Cascade Range, descending from forested highlands into the Willamette Valley (fig. 1). Streamflows in the Clackamas River are typically sustained well into the dry season, making the river an important drinking-water supply for about 200,000 people in the Portland area. Other designated beneficial uses for the Clackamas River include water-contact recreation, fishing, boating, as well as passage, spawning, and rearing habitat for fish, including resident cutthroat and rainbow trout, spring and fall Chinook and coho salmon, and summer and winter steelhead trout. Today, fish populations in the Clackamas and other western rivers are declining (Nehlsen and others, 1991)—spring Chinook salmon and winter steelhead trout in the Clackamas Basin are listed as threatened on the Endangered Species List, and late-run Clackamas River coho salmon, the last remaining wild coho salmon stock in the Columbia River Basin, was listed as a candidate species in 1995 (Taylor, 1999).



Base map modified from various digital datasets from Portland, Oregon METRO and USGS; scales vary. Projection: State Plane, Zone 5076, North American Datum 1983.

Figure 1. Locations of sampling sites, rain gages, and streamflow measurement locations in the Clackamas River Basin, Oregon.

Streams in the lower Clackamas River Basin drain a diverse landscape of forest, agricultural areas, industrial land, and urban developments (see cover photograph). Based on the land use, the highest pesticide concentrations are likely to occur in the lower-basin tributaries, which drain areas where pesticide applications are most likely. Although specific information on pesticide use in the basin is limited, Hassanein and Peters (1998) reported use of at least 100 pesticides, mostly herbicides and insecticides, in the Clackamas River Basin. Anderson and others (1997) and Rinella and Janet (1998) found 36 and 50 pesticides, respectively, in Willamette River Basin streams draining lands with a similar mix of uses as those in the lower Clackamas River Basin.

The Clackamas River supports the last remaining wild coho salmon stock in the Columbia River Basin (photograph by Tim Shibahara, Portland General Electric).

As a drinking-water supply, the Clackamas River has been monitored for regulated pesticides since 1995, but none have been detected (Gordon McGhee, Clackamas River Water, written commun., 2000). This lack of detections is partly because of the relatively high laboratory detection limits for the pesticide analyses and because sampling has included only main-stem sites, where dilution reduces the chances of detecting pesticides. Previous pesticide sampling also has not targeted periods of storm runoff, when the highest pesticide concentrations typically occur (Anderson and others, 1997; Krastzer, 1998). To fill this data gap, the USGS began sampling for pesticides in the Clackamas River and its major lower-basin tributaries in 2000, using advanced laboratory methods that detect pesticides at parts-per-trillion concentrations.

This report describes the pesticide sampling program, presents the data from the study as it relates to pesticide use, compares pesticide concentrations in the main stem to those in the tributaries, evaluates potential risk to aquatic life by comparing pesticide concentrations to protective toxicity criteria, and examines the relationship between the relative pesticide toxicity and the benthic invertebrate community using data collected during 1997–99. Data used in this report can be obtained from the Clackamas Basin Water-Quality Assessment Web page at http://oregon.usgs.gov/clackamas.

STUDY DESIGN, METHODS, AND DATA QUALITY CONTROL

Water samples were collected from the Clackamas River and six of its lower-basin tributaries: Eagle, Clear, Deep, Richardson, Rock, and Sieben Creeks (fig. 1) in May and October 2000 during periods of storm runoff (fig. 2). Three small tributaries, Goose, Foster, and Cow Creeks, which drain areas of agricultural, urban, and industrial land, were not sampled. Samples were collected using standard USGS protocols (Shelton, 1994) and sampling occurred following periods when pesticides are typically applied in the basin. Two rain gages located in or near the study area (fig. 1) were used to determine the timing of sample collection. Following the detection of two pesticides in untreated drinking water from the lower Clackamas River in May, additional samples of untreated and treated drinking water were analyzed in October 2000 (high flow), January 2001 (moderate flow), and August 2001 (low flow).

Water samples were collected at equally spaced points along a transect across the stream channel using either a US DH-81 or US D-77 sampler (Edwards and Glysson, 1999) equipped with a 3-liter Teflon bottle-nozzle assembly. Individual samples were collected from the surface to the bottom at each point and composited into one bottle to form a representative sample. Samples of untreated and treated drinking water were obtained from taps at the treatment plants. Water samples were filtered through 0.7-micron glass-fiber filters and shipped to the USGS National Water-Quality Laboratory in Arvada, Colorado, where they were analyzed for 84 pesticides and 2 breakdown products using a C-18 solid phase extraction, gas chromatography/mass spectrometry (GC/MS) method (Crepeau and others, 1994; Zaugg and others, 1995). This sensitive method is compound-specific, meaning that when a pesticide is detected, there is a high degree of certainty (greater than 99% confidence) that the compound is present. Pesticides found at concentrations less than the detection limit, however, have a lower degree of statistical certainty regarding the actual concentration, and were therefore reported by the lab as estimates. Some of the pesticides that are widely used in the United States, but not tested for in this study, include the herbicides glyphosate (the active ingredient in Roundup™, Rodeo™, and other brands), MSMA, and propazine; the insecticides cryolite, acephate, dimethoate, methomyl, and thiodicarb; the inorganic pesticides copper and sulfur; and biological pesticides.

Streamflow was measured at sampling sites according to standard USGS guidelines (Rantz and others, 1982), and continuous streamflow data was obtained from the USGS gaging station in the Clackamas River at Estacada. In October, field parameters (water temperature, dissolved oxygen, pH, and specific conductance) were measured at each stream site using a Hydrolab Datasonde 3 multi-parameter probe, and the turbidity of each pesticide sample was measured at the USGS Oregon District laboratory using a Hach 2001AN turbidity analyzer.

Twenty-five percent of samples were submitted for quality control. Two equipment blanks and one laboratory blank sample were submitted to check clean techniques; two duplicate samples and one split sample

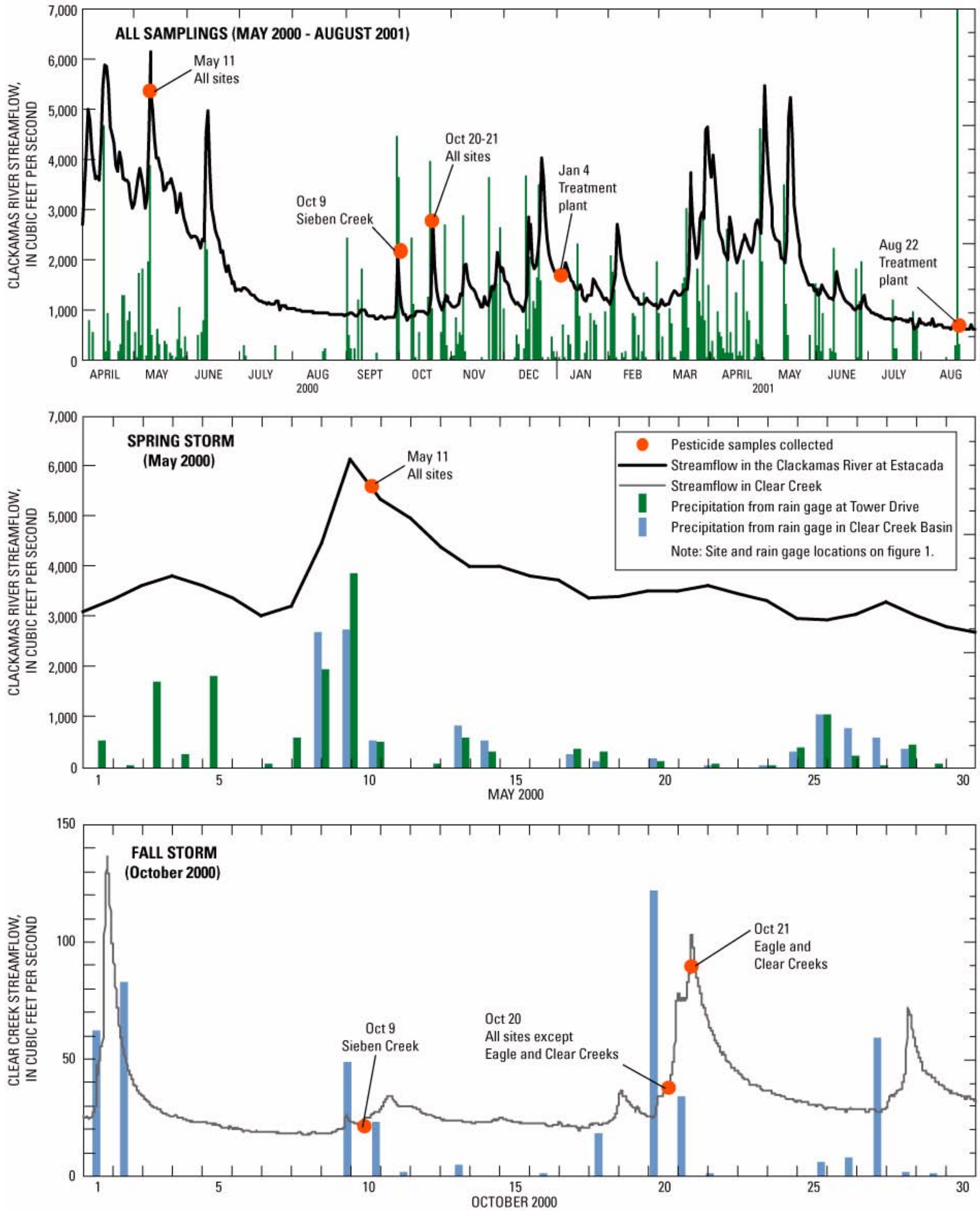


Figure 2. Precipitation and streamflow conditions during pesticide sampling in the Clackamas River Basin, 2000–01. (Clear Creek streamflow data provided by Kent Doughty, Duke Engineering; Data from Tower Drive rain gage, located just to the north of the Clackamas Basin, is shown because a longer period of record was available [data from the Clear Creek gage, in the Clackamas River Basin, was collected intermittently.])

were collected to check laboratory variability; and one sample was spiked to measure the recovery of each compound (see table A-2 and associated evaluation of quality-control results in the appendix).

RESULTS AND DISCUSSION

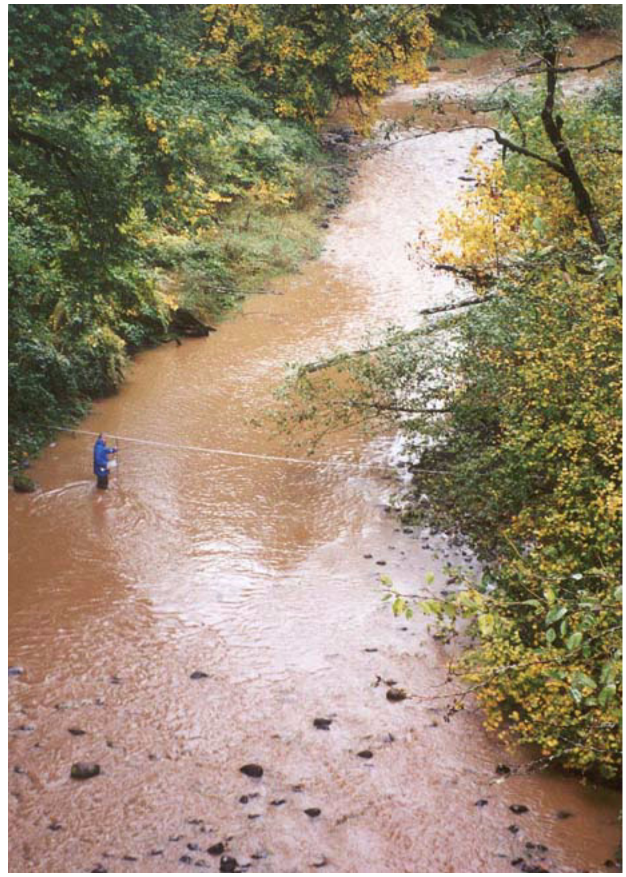
Stream Conditions During Sampling

The first samples of storm runoff were collected on May 11, 2000, following 3 consecutive days of about 0.5 inches of rain per day (total rainfall for this storm was about 1.75 inches) (fig. 2). Streamflow in the lower Clackamas River at Carver peaked at just over 7,000 cubic feet per second during the May sampling (fig. 3). This storm was preceded by another storm 1 month earlier that produced more than an inch of rain.

In the fall, the first runoff-producing storm occurred in mid-October, when about half an inch of rain produced observable turbidity in Sieben Creek. At this time, however, streamflows in the other tributaries did not increase significantly, and those streams were therefore not sampled. Most streams, including Sieben, Rock, Richardson, and Deep Creeks were sampled 10 days later, when a 1.2-inch storm produced observable runoff and high turbidity in Rock, Deep, and Sieben Creeks. Eagle and Clear Creeks, which continued to rise, were not as turbid, and were sampled the next day as their streamflows crested (see Clear Creek hydrograph, fig. 2). Streamflows during storm sampling were higher in May than in October at most of the tributary sites sampled, although a greater amount of runoff was observed in Sieben Creek in October (fig. 3). High levels of turbidity were observed during storms at most of the lower-basin tributary sites, particularly in October, when the turbidity in Rock Creek exceeded 1,000 NTU (nephelometric turbidity units), and Deep, Richardson, and Sieben Creeks ranged from 150 to 250 NTU.

Pesticide Detections

Twenty-seven compounds (18 herbicides, 7 insecticides, and 2 pesticide breakdown products) were detected in 18 samples collected from the Clackamas River and its tributaries (table 1, table 2, and table 3). Herbicides were detected more frequently and at higher concentrations than insecticides, making up about 80% of the pesticide detections. The most commonly detected pesticides, occurring in at least half of all samples collected from the tributaries, included the herbicides atrazine, simazine, diuron, metolachlor, and the insecticide diazinon (fig. 4). These results closely resemble those reported for other streams in the Willamette Basin (Anderson and others, 1997).



Stormwater runoff produces high turbidity in Deep Creek, October 2000.

Atrazine was detected at least once in each of the six lower-basin tributaries sampled, occurring in 92% of all samples collected from the tributaries, as well as in one of four samples collected from the main-stem Clackamas River. Atrazine concentrations were notably higher at all sites in May compared to October, probably indicating use during springtime. Atrazine and deethylatrazine (one of the atrazine breakdown products) were the only compounds detected in Eagle and Clear Creeks during May, suggesting that the primary land use/crops in these watersheds—forestry and Christmas trees—may be an important contributing source of atrazine in these streams.

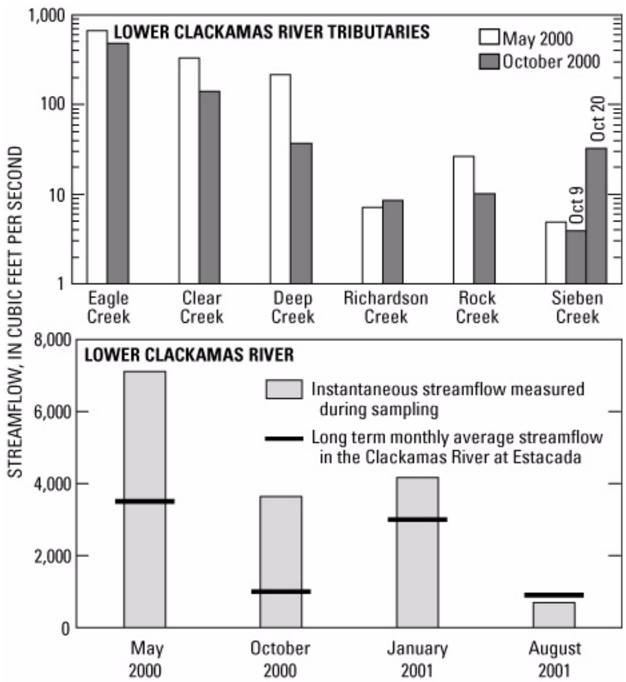


Figure 3. Streamflow conditions during pesticide sampling in the lower Clackamas River Basin, Oregon, 2000–01.

Certain pesticides showed seasonal patterns that may be related to the timing of their use or other factors, such as how quickly they break down in the environment. Detections of 2,4-D, an herbicide found in many weed and feed products that is applied in the spring to control broadleaf weeds on lawns, for example, occurred only in May and August. It was not, however, found in October (fig. 4), possibly because of the relatively short half-life of 2,4-D (10 days; appendix table A-1). Other pesticides, including the widely used herbicide metolachlor, and several insecticides, particularly chlorpyrifos, carbaryl, and dieldrin, were found more frequently in October (fig. 4), possibly from applications during summer.

Pesticide samples were collected during periods of storm runoff and likely represent conditions that occur at least twice annually if not more often. Several moderate rain storms occurred in the weeks prior to sampling, however, which may have produced even higher concentrations in the streams than those reported here. Further, because pesticide samples were filtered, and because some pesticides adhere strongly to sediment (those in appendix table A-1 with high organic carbon adsorption coefficient [Koc] values), some of the pesticide concentrations could have been higher than reported here.

While no pesticides were detected in the Clackamas River at Estacada (river mile 23.1), several compounds were found downstream in the lower main-stem Clackamas River. Nine pesticides, including the insecticide diazinon and the herbicides 2,4-D, atrazine, dichlobenil, diuron, imazaquin, metolachlor, simazine, and trifluralin were detected at relatively low concentrations in five water samples collected from the lower Clackamas River or water-treatment-plant intakes during high, moderate, and low-flow conditions (table 2 and table 3). Diazinon and diuron were each detected in the Clackamas River twice, whereas the other seven pesticides were detected once.

Despite these detections of pesticides in the Clackamas River and in untreated drinking water, no pesticides were detected in three samples of treated drinking water collected from a conventional-type treatment plant in October and January or from a sand filtration treatment plant in August (table 3). Although this is a positive finding, other studies are now showing that certain organophosphate insecticides, including some found in this study (malathion, diazinon, and chlorpyrifos), may produce toxic breakdown products called oxons during water treatment that were not tested for in this study. A national survey of pesticides in untreated and treated drinking water, for example, found malaoxon, the oxon of malathion, in treated water only (Blomquist and others, 2001). Of these parent compounds, only diazinon was found in the main-stem Clackamas River or in untreated drinking water, although all three were detected in the tributaries that discharge to the Clackamas River upstream from the drinking-water intakes.

Pesticides were detected with greater frequency (up to 15 pesticides in 1 sample) and at higher concentrations in the 4 lowermost tributaries (Deep, Richardson, Rock, and Sieben Creeks) compared with the main-stem Clackamas River, Eagle Creek, or Clear Creek. The 4 lowermost tributaries contained between 12 and 18 pesticides each (table 2). Much of the farmland and forestland in this part of the basin is being cleared and developed as Portland's urban growth boundary expands. Streams in this area are particularly susceptible to pesticide runoff, given the wide range of potential applications, moderate to steep drainages, and abundant rainfall.

Table 1. Pesticides detected in the Clackamas River Basin, Oregon, 2000–01, and commercial products containing them

[µg/L, micrograms per liter, or parts per billion; 2,4-D, 2,4-dichlorophenoxyacetic acid; DCPA, dimethyl-2,3,5,6-tetrachloroterephthalate; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichoroethane; all product names are trademarked]

Pesticide or breakdown product	Commercial product	Chemical class	Use	Laboratory method detection limit (µg/L)
Atrazine	AAtrex, Atratol, Atred, Gesaprim	triazine	herbicide	0.004
Bromacil	Krovar, Bromax, Hyvar, Uragon	uracil	herbicide	.04
Carbaryl	Sevin, Savit, Carbamine, Denapon	carbamate	insecticide	.021
Chlorpyrifos	Dursban, Lorsban, Brodan	organophosphorus	insecticide	.003
2,4-D	Crossbow, Aqua-Kleen, Weed-B-Gone	chlorophenoxy acid	herbicide	.06
DCPA	Dacthal, DAC 893, Dachthalor	chlorobenzoic acid	herbicide	.0015
p,p'-DDE	*p,p'*-DDT breakdown product	organochlorine	none	.0013
Deethylatrazine	Atrazine breakdown product	triazine	none	.003
Diazinon	Gardentox, Knoxout, pest strips	organophosphorus	insecticide	.003
Dichlobenil	Casoron, Diclomec, Norosac	benzonitrile	herbicide	.025
Dieldrin	Dieldrex	organochlorine	insecticide	.0024
Diuron	Krovar, Diurex, Aguron, Karmex	urea	herbicide	.025
Ethoprop	Mocap	organophosphorus	nematcide	.002
Fonofos	Dyfonate	organophosphorus	insecticide	.0013
Imazaquin	Image, Scepter, Squadron, Tri-Scept	imidazolinone	herbicide	.008
Linuron	Afalon, Lorox, Dulain, Linex	urea	herbicide	.018
Malathion	Cythion, malathion	organophosphorus	insecticide	.014
Metolachlor	Dual, Pennant	acetanilide	herbicide	.006
Napropamide	Devrinol	amide	herbicide	.003
Pendimethalin	Prowl, Pendulum, Stomp	dinitroaniline	herbicide	.005
Prometon	Pramitol	triazine	herbicide	.007
Pronamide	Kerb	amide	herbicide	.0021
Simazine	Aquazine, Princep	triazine	herbicide	.006
Tebuthiuron	Graslan, Spike, Perflan	urea	herbicide	.008
Terbacil	Sinbar	uracil	herbicide	.017
Triclopyr	Garlon, Curtail, Crossbow, Remedy	organochlorine	herbicide	.04
Trifluralin	Treflan	dinitroaniline	herbicide	.005

Table 2. Summary of sampling regime and pesticide detections in the Clackamas River Basin, May 2000–August 2001

Sites		Number of samples	Number of pesticides detected				
				2000		2001	
			Total[a]	May	October	January	August
Main-stem	Clackamas River at Estacada	1	0	0	--	--	--
	Clackamas River at Carver or untreated water from drinking-water intakes	4	9	2	6	0	3
	Treated drinking water	3	0	--	0	0	0
Tributaries	Eagle Creek	2	2	2	0	--	--
	Clear Creek	2	4	2	4	--	--
	Deep Creek	2	14	12	11	--	--
	Richardson Creek	2	12	9	6	--	--
	Rock Creek	2	18	14	15	--	--
	Sieben Creek	3	16	12	13	--	--
	Total[a]	21	27	20	23	0	3

[a] Total number of individual pesticides detected.

Table 3. Pesticide concentrations in the main-stem Clackamas River, untreated, and treated drinking water, and tributaries of the Clackamas River, May 2000–August 2001

[All samples collected during storm runoff conditions; pesticide concentrations in micrograms per liter (µg/L), or parts per billion; e, estimated values; nd, not detected; H, herbicide; I, insecticide; IBP, insecticide breakdown product; HBP, herbicide breakdown product; N, nematocide; RM, Clackamas River mile; cfs, cubic feet per second; na, not applicable; 2,4-D, 2,4-Dichlorophenoxyacetic acid; DCPA, dimethyl-2,3,5,6-tetrachloroterephthalate; DDE, dichlorodiphenyldichloroethylene]

		Clackamas River at Estacada RM 23.1	Clackamas River at Carver RM 7.9	Clackamas River—untreated water (lower river intake)			Clackamas River—treated drinking water[a]			Eagle Creek RM 16.6	
Pesticide or breakdown product	Type	May 2000	May 2000	October 2000	January 2001	August 2001	October, January, and August 2000-01			May 2000	October 2000
Atrazine	H	nd	0.011	nd	nd	nd	nd	nd	nd	0.013	nd
Bromacil	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Carbaryl	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlorpyrifos	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4-D	H	nd	nd	nd	nd	0.052	nd	nd	nd	nd	nd
DCPA	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
p,p'-DDE	IBP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Diazinon	I	nd	nd	e0.003	nd	e.003	nd	nd	nd	nd	nd
Deethylatrazine	HBP	nd	nd	nd	nd	nd	nd	nd	nd	e.005	nd
Dichlobenil	H	nd	nd	.24	nd	nd	nd	nd	nd	nd	nd
Dieldrin	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Diuron	H	nd	e.014	e.016	nd	nd	nd	nd	nd	nd	nd
Ethoprop	N	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fonofos	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Imazaquin	H	nd	nd	nd	nd	e.047	nd	nd	nd	nd	nd
Linuron	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Malathion	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metolachlor	H	nd	nd	e.004	nd	nd	nd	nd	nd	nd	nd
Napropamide	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Pendimethalin	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Prometon	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Pronamide	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Simazine	H	nd	nd	e.003	nd	nd	nd	nd	nd	nd	nd
Tebuthiuron	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Terbacil	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Triclopyr	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Trifluralin	H	nd	nd	e.002	nd	nd	nd	nd	nd	nd	nd
Streamflow (cfs)		5,390	7,110	3,640	4,170	690	na	na	na	670	482
Number of detections		0	2	6	0	3	0	0	0	2	0

Table 3. Pesticide concentrations in the main-stem Clackamas River, untreated, and treated drinking water, and tributaries of the Clackamas River, May 2000–August 2001—Continued

		Clear Creek RM 8.0		Deep Creek RM 12.1		Richardson Creek RM 9.1		Rock Creek RM 6.4		Sieben Creek RM 5.8		
Pesticide or breakdown product	**Type**	**May 2000**	**October 2000**	**May 2000**	**October 2000**	**May 2000**	**October 2000**	**May 2000**	**October 2000**	**May 2000**	**9-October 2000**	**20-October 2000**
Atrazine	H	0.017	e0.002	0.12	0.007	0.012	e0.004	0.30	e0.006	0.009	e0.005	e0.003
Bromacil	H	nd	nd	.27	nd	nd	nd	nd	nd	nd	nd	nd
Carbaryl	I	nd	nd	nd	nd	nd	nd	nd	nd	e.026	e.014	e.009
Chlorpyrifos	I	nd	nd	nd	nd	nd	nd	nd	.056	.025	e.014	.023
2,4-D	H	nd	nd	e.079	nd	e.057	nd	.24	nd	.30	nd	nd
DCPA	H	nd	nd	nd	nd	nd	nd	.020	.46	nd	nd	nd
p,p'-DDE	IBP	nd	nd	nd	e.002	nd	nd	nd	nd	nd	nd	nd
Diazinon	I	nd	nd	.004	e.004	.005	nd	.052	.009	.16	.064	.041
Deethylatrazine	HBP	e.007	nd	e.013	e.005	e.006	nd	e.021	nd	e.004	nd	nd
Dichlobenil	H	nd	nd	nd	nd	e.014	nd	e.031	nd	e.62	e16.8	e8.0
Dieldrin	I	nd	nd	nd	nd	nd	e.005	nd	e.008	nd	nd	nd
Diuron	H	nd	nd	.15	nd	e.016	nd	.071	.086	e.051	nd	.22
Ethoprop	N	nd	nd	.008	.010	nd	nd	nd	nd	nd	nd	nd
Fonofos	I	nd	nd	nd	nd	nd	.007	nd	nd	nd	nd	nd
Imazaquin	H	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Linuron	H	nd	nd	nd	nd	nd	nd	nd	.59	nd	nd	nd
Malathion	I	nd	nd	nd	nd	nd	nd	nd	nd	nd	.025	nd
Metolachlor	H	nd	e.004	.060	e.008	nd	e.006	nd	.017	nd	e.007	.015
Napropamide	H	nd	nd	.039	.110	nd	nd	.012	.008	1.30	.043	.043
Pendimethalin	H	nd	.008	nd	e.004	nd	nd	nd	.011	nd	nd	.030
Prometon	H	nd	nd	nd	e.002	e.010	e.006	e.011	e.012	e.007	nd	nd
Pronamide	H	nd	nd	nd	nd	nd	nd	.011	.17	nd	nd	nd
Simazine	H	nd	nd	.024	.017	.080	e.007	.19	.015	.011	nd	e.009
Tebuthiuron	H	nd	nd	nd	nd	nd	nd	.026	.034	nd	nd	nd
Terbacil	H	nd	nd	e.026	nd	nd	nd	nd	nd	nd	nd	nd
Triclopyr	H	nd	.045	nd	nd	e.084	nd	e.087	1.30	nd	nd	1.20
Trifluralin	H	nd	nd	.012	e.001	nd	nd	e.004	nd	e.005	e.001	.082
Streamflow (cfs)		330	141	217	36	7.2	8.6	26	10	4.9	3.9	32.5
Number of detections		2	4	12	11	9	6	14	15	12	9	12

[a] Collected from a conventional (settling basin plus filtration) drinking-water treatment plant in October and January, and from a slow-sand filtration drinking-water treatment plant in August.

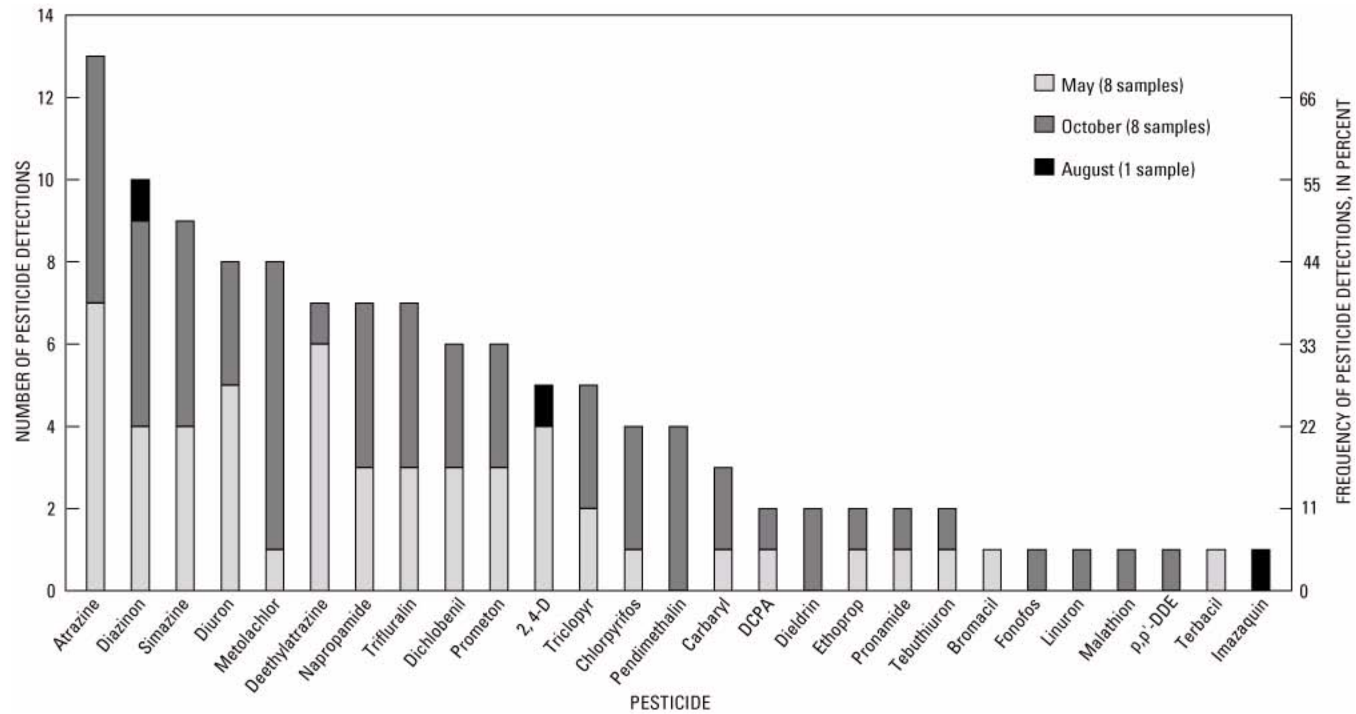


Figure 4. Pesticide detections in the Clackamas River Basin, Oregon, 2000–01 (includes 119 detections in 13 tributary and 4 main-stem Clackamas River samples; no pesticides were detected in untreated or treated water in January).

Rapid runoff of storm water from impervious surfaces (roofs, roads, and driveways) may transport pesticides to streams via storm drains in urban areas or through tile drainage on farms. Together, these transport mechanisms produce high streamflows in these lower basin tributaries during storms. Previous studies (Clackamas County Soil and Water Conservation District, 2002; Carpenter, 2003) have found other indications of degraded water quality in these four streams, including elevated concentrations of nitrogen and phosphorus, and high pH.

Pesticide concentrations were generally highest in Sieben and Rock Creeks due to the combined effects of draining relatively greater amounts of urbanized area and farmland, and to their relatively low streamflows, which afforded less dilution compared with the other tributaries. In contrast, higher streamflow in Deep Creek (fig. 3) probably resulted in lowering pesticide concentrations through dilution, although the actual amounts (loads) were generally higher in Deep Creek.

Most of the highest pesticide concentrations were observed in Sieben Creek, where the herbicides dichlobenil, napropamide, and triclopyr were found at concentrations ranging from about 1 to 16.8 µg/L (micrograms per liter, or parts per billion; fig. 5). All of these herbicides are applied in urban areas or along roads and other right-of-ways. Napropamide and dichlobenil also are used on nursery and greenhouse crops, hazelnuts, and cane berries, and triclopyr is one of the ingredients (along with 2,4-D) in Crossbow™, a potent herbicide that is widely used to control blackberries and other brush.

Nearly half of the pesticides applied to agricultural lands in Clackamas County are used for nursery and greenhouse crops.

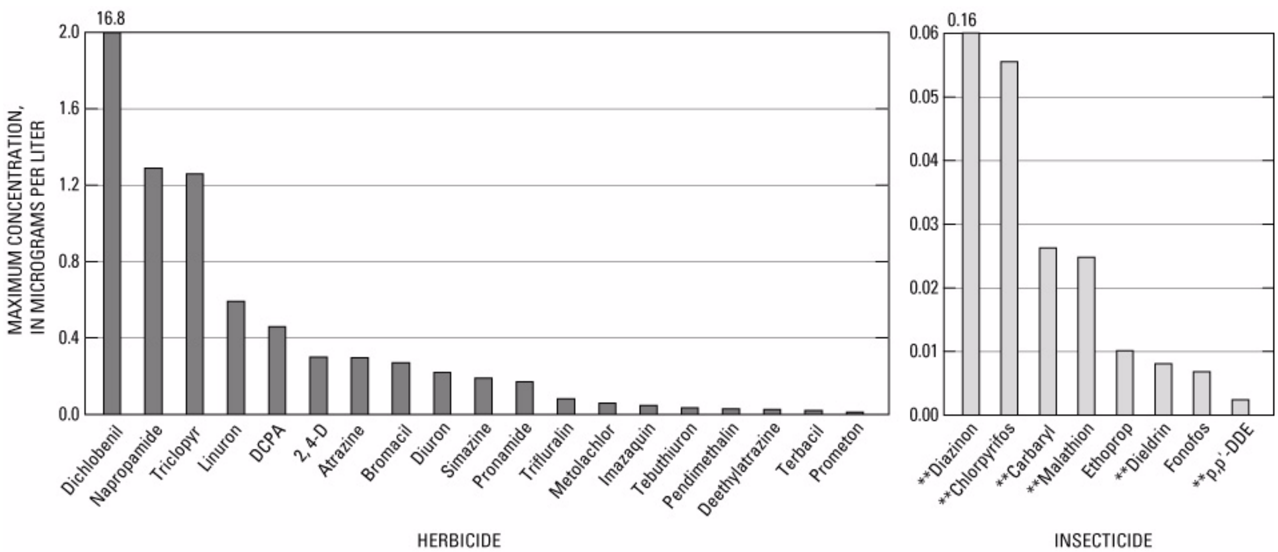


Figure 5. Maximum concentrations of herbicides and insecticides in the Clackamas River Basin, May and October 2000. (** Indicates value equal to or exceeding an aquatic-life criterion. Quality-control data indicate a high bias [323% recovery] for carbaryl, see table A-2 in appendix.)

Spot applications may help reduce the amount of pesticides that eventually enter streams.

Rock Creek contained the greatest number of pesticides—18 (table 2 and table 3). The highest concentration of atrazine (0.30 µg/L) and triclopyr (1.3 µg/L) were found in Rock Creek, and one highly turbid sample collected from Rock Creek in October contained 15 pesticides. Twelve pesticides were found in Richardson Creek, and concentrations were somewhat lower than in Sieben, Rock, and Deep Creeks.

Fifteen compounds were detected in Deep Creek, with the herbicides bromacil, diuron, atrazine, napropamide, metolachlor, and 2,4-D occurring at the highest concentrations, ranging from 0.06 to 0.27 µg/L (table 3). The breakdown product of the banned insecticide DDT (*p,p'*-DDE) was found only at this site in October, at a concentration of 0.002 µg/L. Other USGS studies have shown high concentrations of *p,p'*-DDT and its breakdown products in nearby Johnson Creek, possibly due to erosion of sediments in agricultural areas (Edwards, 1994).

Eagle and Clear Creeks, which drain larger watersheds consisting mostly of forestland, Christmas tree plantations, and some rural residential land, contained fewer pesticides (from 2 to 5 pesticides each) at lower concentrations compared with the other lower-basin tributaries (table 3). Atrazine, an herbicide commonly applied to conifer trees, and its breakdown product deethylatrazine, were detected in both Eagle and Clear Creeks. Another herbicide that is applied to Christmas trees, pendimethalin (Oregon State University, 2001b), also was detected in Clear Creek. Due to their higher streamflows, these two streams had pesticide loads that were sometimes high, particularly for atrazine in May and metolachlor in October.

Herbicides are used for weed control in Christmas tree plantations.

Potential Pesticide Source Areas

In order to examine the potential sources of pesticides detected in the Clackamas River, the relative pesticide load from each of the sampled tributaries was determined for each of the pesticides detected in the main stem. This approach estimates the relative amounts, calculated as the instantaneous pesticide loads (in grams per day [g/d]) that, in theory, could be contributed by each of the tributaries during sampling.

Several factors, however, contribute uncertainty in such analyses, including the dynamic nature of streamflow during storms, determined largely by the timing and spatial pattern in rainfall and runoff. Heavy precipitation may transport pesticides and other chemicals to streams initially, but continued runoff may actually lower pesticide concentrations in the streams through dilution after a period of sustained rainfall. Additional uncertainty complicates the relationship between pesticide loads in the tributaries with those in the main stem, including unknown travel times from sampling locations in the tributaries to those in the main stem, and in the reporting accuracy of pesticide concentrations by the laboratory.

Of the 20 pesticides detected in the tributaries during the May storm, only atrazine and diuron were detected in the main-stem Clackamas River (table 3), where the high streamflow (more than 7,000 cfs) provided a high degree of dilution. Two of the top three loads for pesticides detected from all tributaries combined were from atrazine and diuron, making up 34% of the total (table 4). Only bromacil had a higher load—143 g/d or about 25% of the total pesticide load, all from Deep Creek. Bromacil, which was found only in Deep Creek, was not detected in the main-stem Clackamas River due to a combination of dilution (75% of the flow originated from forestland in the upper basin) and a relatively high laboratory detection limit for bromacil (0.04 μg/L; table 1).

More than 80% of the total pesticide load from the six tributaries combined during the May storm was attributable to inputs from Deep and Rock Creeks, and nearly 90% of the total pesticide load during the October storm was attributable to Sieben Creek (fig. 6).

In May, the herbicides atrazine and diuron were detected in the Clackamas River at Carver and in each of the four lowermost tributaries (table 3). Deep Creek accounted for 53% of the atrazine and 94% of the diuron load measured in the tributaries in May (fig. 7), which by calculation accounted for 33% of the atrazine and 33% of the diuron load in the main-stem Clackamas River. Eagle, Clear, and Rock Creeks also were important contributors of atrazine. Atrazine is used to control broadleaf and grassy weeds in corn, Christmas trees, and other crops. It is also used as a nonselective herbicide on noncroplands, golf courses, and on urban landscaping (Extoxnet, 1996).

Diuron is used to kill moss and broadleaf and grassy weeds in urban areas and is also used on a variety of agricultural crops—especially grass seed, hay, and hazelnuts (Oregon State University, 2001b). Diuron is also applied along roads to control vegetation in a formulation called Krovar™ that also contains the herbicide bromacil (Robert Edgar, Oregon Department of Transportation, written commun., 2000). Concentrations of diuron and bromacil were both high in Deep Creek relative to concentrations in most other streams (table 3). The higher concentrations

Table 4. Pesticide loads from the main-stem Clackamas River and lower-basin tributaries, May and October 2000

[Pesticide load in grams per day (g/d) is the product of streamflow (in cubic feet per second) and pesticide concentration (in micrograms per liter, or parts per billion); pesticide loads are estimates due to the combined variation in streamflow and pesticide concentrations during storms; nd, not detected in the main stem; 2,4-D, 2,4-dichlorophenoxyacetic acid; DCPA, dimethyl-2,3,5,6-tetrachloroterephthalate; DDE, dichlorodiphenyldichloroethylene]

May				October			
Pesticide or breakdown product	Percentage of total load from tributaries[a]	Tributary load (g/d)[b]	Main-stem load (g/d)[c]	Pesticide or breakdown product	Percentage of total load from tributaries[a]	Tributary load (g/d)[b]	Main-stem load (g/d)[c]
Bromacil	24.6	143	nd	Dichlobenil	76.8	799	792
Atrazine	20.1	117	187	Triclopyr	13.8	144	nd
Diuron	14.9	86.6	239	Diuron	1.9	19.6	54
2,4-D	10.7	61.9	nd	Linuron	1.4	14.7	nd
Napropamide	6.3	36.7	nd	Napropamide	1.3	13.8	nd
Metolachlor	5.5	32.0	nd	DCPA	1.1	11.4	nd
Simazine	4.5	26.3	nd	Trifluralin	.6	6.6	6.0
Deethylatrazine	3.9	22.9	nd	Pendimethalin	.6	5.9	nd
Terbacil	2.4	13.9	nd	Diazinon	.4	4.5	9.1
Dichlobenil	1.7	9.7	nd	Pronamide	.4	4.3	nd
Diazinon	1.3	7.8	nd	Metolachlor	.4	4.0	12
Triclopyr	1.2	7.1	nd	Chlorpyrifos	.3	3.4	nd
Trifluralin	1.1	6.4	nd	Simazine	.3	2.7	9.6
Ethoprop	.8	4.5	nd	Atrazine	.2	2.0	nd
Tebuthiuron	.3	1.7	nd	Ethoprop	.1	.9	nd
DCPA	.2	1.3	nd	Tebuthiuron	.1	.9	nd
Prometon	.2	1.0	nd	Carbaryl	.1	.9	nd
Pronamide	.1	.7	nd	Prometon	.1	.6	nd
Carbaryl	.1	.3	nd	Deethylatrazine	.04	.5	nd
Chlorpyrifos	.1	.3	nd	Dieldrin	.03	.3	nd
				Malathion	.02	.2	nd
				p,p'-DDE	.02	.2	nd
				Fonofos	.01	.1	nd

[a]Percentage of the total instantaneous pesticide load (all pesticides) from all measured tributaries for each storm combined.
[b]Total measured load of each pesticide from all measured tributaries combined for each storm.
[c]Sample was collected from the Clackamas River at Carver in May, and therefore does not include contributions from downstream tributaries, including Rock and Sieben Creeks; October sample was collected from a water-treatment-plant intake in the lower river, but streamflow was measured upstream at Carver.

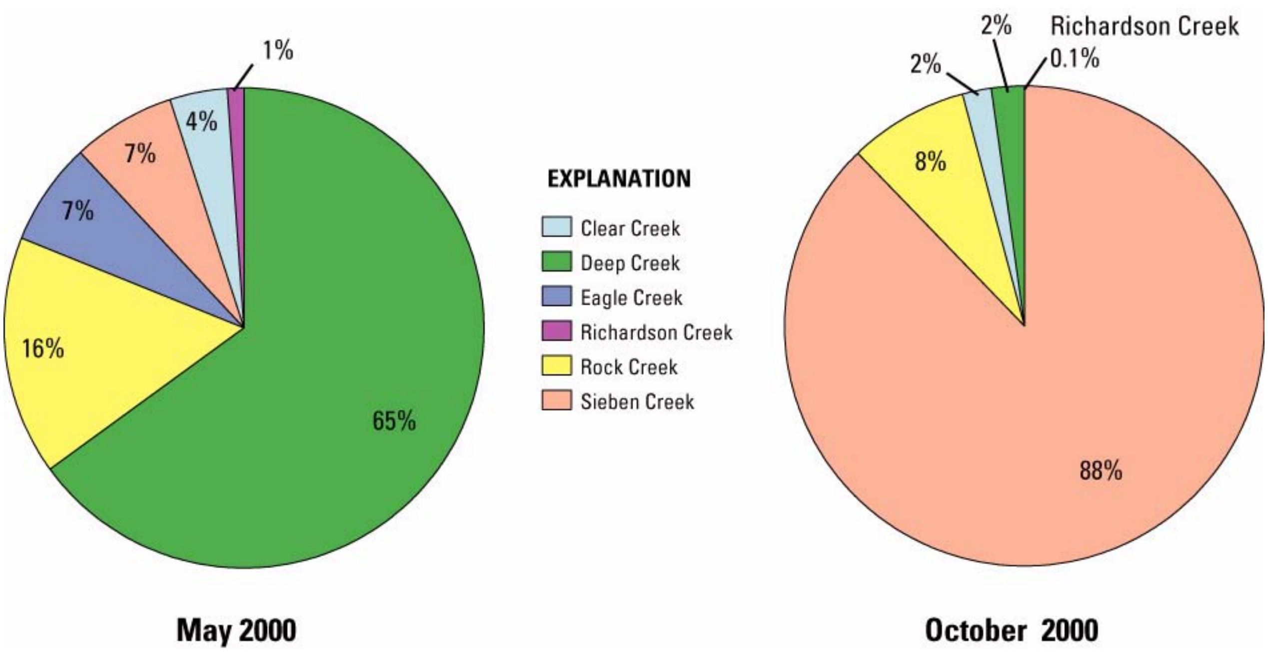


Figure 6. Relative pesticide loads from the lower-basin tributaries, May and October 2000. (Percentage of total load for all pesticides, for all streams sampled).

of these herbicides in Deep Creek may be related to the greater number of road miles in the Deep Creek Basin relative to the other basins. Further, both diuron and bromacil appear to be relatively persistent; Wood (2001) found both herbicides in a roadside drainage ditch that received an experimental application of Krovar after more than 3 months and 20 inches of rain, indicating a long-term residual for these compounds. The aquatic-life criterion for bromacil—the concentration of pesticide above which aquatic organisms might be adversely affected—is 5 µg/L (table 5), or 18 times higher than the concentration in Deep Creek. The possible effect of the diuron concentration in Deep Creek (0.150 µg/L) is difficult to evaluate because no aquatic-life criterion exists for diuron. Extoxnet (1996), however, reports that diuron is moderately toxic to fish and highly toxic to aquatic invertebrates.

Six pesticides were detected in the lower Clackamas River during the October storm (table 3). At this time, most of the measured pesticide load from the tributaries was from Sieben Creek (fig. 8). The highest

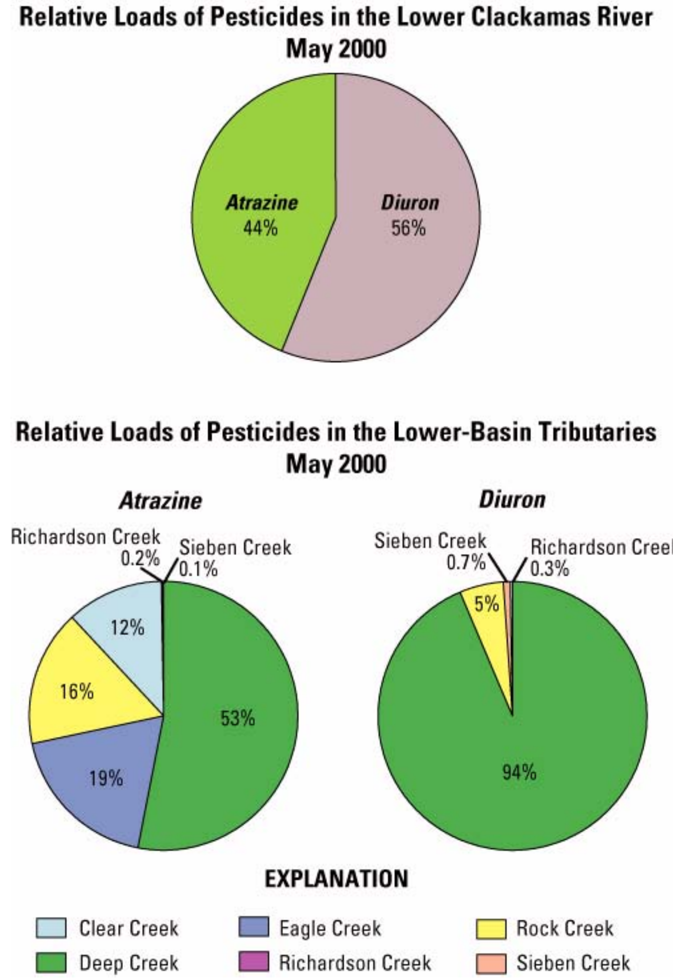


Figure 7. Relative pesticide loads in the main-stem Clackamas River and lower-basin tributaries, May 2000. (Relative loads from the tributaries are the percentage of total load, by mass, of each pesticide from all the measured tributaries combined.)

measured load of metolachlor, however, came from Clear Creek, with lesser contributions from each of the other four tributaries. Metolachlor is a preemergent herbicide used to control broadleaf weeds and annual grasses on nursery and field crops, including grass seed, sweet corn, beans, and peas. It also is applied to woody ornamentals and along right-of-ways (Extoxnet, 1996).

Most (about 80%) of the measured simazine load from the tributaries came from Deep and Sieben Creeks during the October storm (fig. 8). Simazine is a selective herbicide used to control broadleaf weeds and annual grasses on nursery and field crops, including Christmas trees, hazelnuts, and cane berries. Simazine also may be used to control aquatic plant growth in farm ponds, swimming pools, and fish hatcheries (Extoxnet, 1996).

Herbicides are applied to Clackamas River Basin roadsides for vegetation control; shown here is U.S. Highway 26 in the Deep Creek Basin.

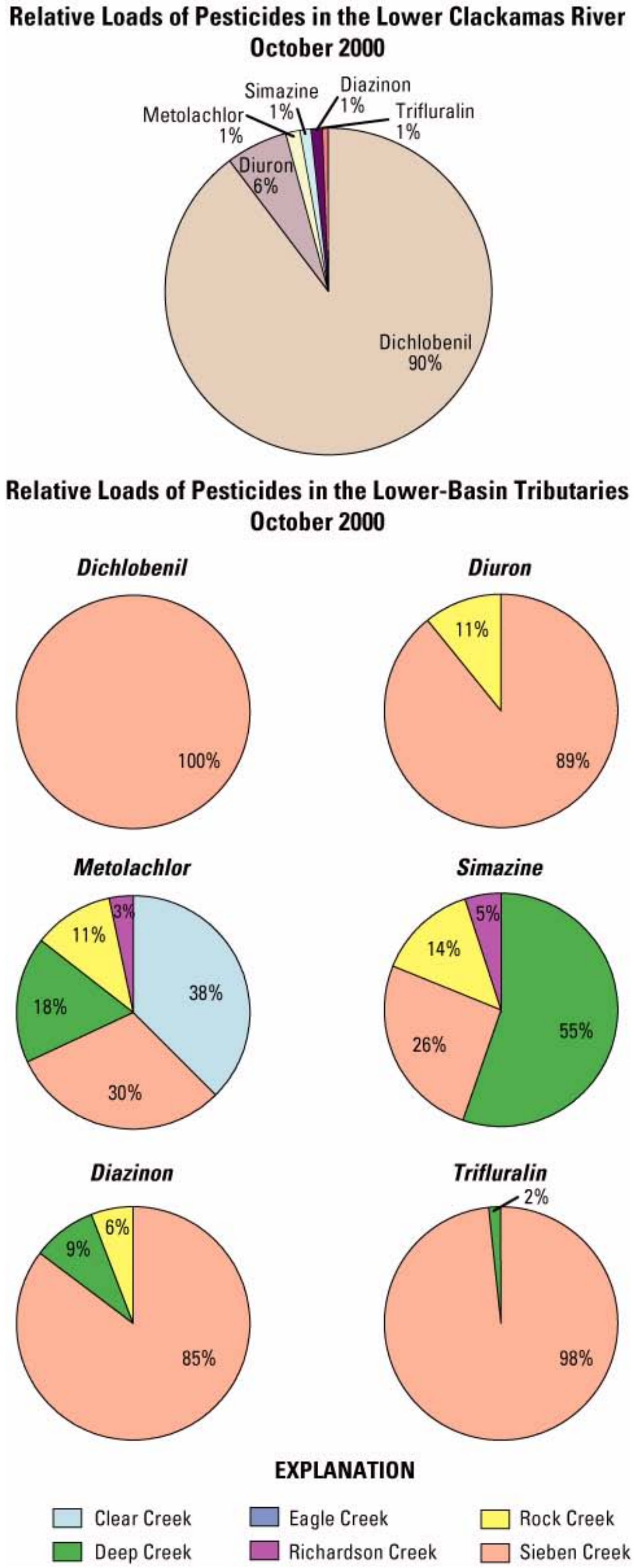


Figure 8. Relative pesticide loads in the main-stem Clackamas River and lower-basin tributaries, October 2000. (Relative loads from tributaries are the percentage of total load, by weight, of each pesticide from all the measured tributaries combined.)

Pesticide Concentrations Relative to Water-Quality Standards and Suggested Guidelines to Protect Human Health and Aquatic Life

Despite the detection of nine pesticides in the Clackamas River and untreated drinking water, no pesticides were detected in three samples of treated drinking water collected during this study. None of the pesticides detected in the Clackamas River exceeded U.S. Environmental Protection Agency (USEPA) drinking-water standards (table 5), although no standards exist for two of the compounds detected in the main stem, dichlobenil and imazaquin (U.S. Environmental Protection Agency, 2000a).

Aquatic-life criteria exist for 17 of the 27 pesticides or breakdown products detected in the Clackamas River Basin (table 5). Multiple guidelines are presented in table 5 due to the large range of values among the different agencies. Concentration criteria suggested by the National Academy of Sciences/National Academy of Engineering (NAS/NAE), for example, are lower than those of other agencies because NAS/NAE criteria incorporate a 100-fold safety factor, thereby providing a greater amount of protection for aquatic life. Some of the rationale for this “safety buffer” includes the fact that criteria are typically developed for single pesticides and do not account for exposure to multiple compounds or repeated exposures. Studies by the USGS in agricultural and urban watersheds throughout the United States since the early 1990s found that more than half of the streams sampled contained pesticides at concentrations that exceeded aquatic-life criteria (U.S. Geological Survey, 1999). Although biological communities in many of these streams were impaired or otherwise degraded, it is difficult to isolate the effects of pesticides from other impacts, such as sedimentation, nutrient enrichment, and habitat degradation.

Six compounds (all insecticides), including carbaryl, chlorpyrifos, diazinon, dieldrin, malathion, and the breakdown product of DDT (*p,p’*-DDE), were found at concentrations that exceeded an aquatic-life criterion (fig. 5 and table 5), sometimes for multiple pesticides in one sample. Each of the four lowermost tributaries (Deep, Rock, Richardson, and Sieben Creeks) contained at least one pesticide at a concentration that equaled or exceeded a criterion. Rock and Sieben Creeks each contained three pesticides at concentrations that exceeded aquatic-life criteria (table 3 and table 5). Concentrations of the organophosphate insecticides chlorpyrifos and diazinon exceeded their aquatic-life criteria by several-fold in these streams. Diazinon was detected in each of the four lowermost tributaries, and concentrations exceeded the NAS/NAE aquatic-life criterion in all samples collected from Sieben and Rock Creeks. The highest diazinon concentration (0.160 µg/L, measured in Sieben Creek in May) exceeded its aquatic-life criteria by a factor of 1.5–18, depending on which criterion is applied (table 5). Diazinon and chlorpyrifos are restricted-use insecticides that were commonly found together in urban streams during a survey of pesticides in streams across the country (U.S. Geological Survey, 1999), although both may have agricultural uses (table 7). The Koc values of these compounds range from 1,000 to 6,070 (table A-1 in the appendix), indicating a relatively strong tendency to adsorb to soil particles. It is likely that soil erosion is an important transport process for mobilizing diazinon and chlorpyrifos, which is consistent with the high turbidity values in Rock and Sieben Creeks, particularly during the October sampling. As mentioned previously, because water samples were filtered prior to analysis, it is likely that concentrations reported here are lower than what aquatic organisms are exposed to.

Potential Effects of Pesticides on Aquatic Life

Many pesticides have the potential to harm aquatic life, especially benthic macroinvertebrates, fish, amphibians, and various stream microbes (Nowell and others, 1999) that are exposed to high concentrations of pesticides. The Clackamas River and some of its tributaries support a variety of anadromous and resident fish species, although declines in some populations, including winter steelhead trout, spring Chinook, and coho salmon, have resulted in their being on the Endangered Species List. Potential explanations for such declines include overharvesting of fish, dams, degraded water quality, and poor stream habitat, but the effects of pesticides have not been fully evaluated.

One of the complicating factors in determining safe exposure levels for aquatic life to pesticides is that laboratory studies typically involve only a single compound and do not consider additive or possibly synergistic effects of exposing aquatic life to multiple pesticides at once. While it is logical to assert that two pesticides with the same mode of action would act in an additive fashion (such as the organophosphate insecticides chlorpyrifos and diazinon, which both inhibit the nervous system enzyme acetylcholine esterase), certain pesticides may increase the toxicity of others through various physiological mechanisms that are just beginning to be understood. For example, the toxicity of organophosphate insecticides to chironomid midge larvae can increase markedly by simultaneous exposure to the herbicide atrazine (Pape-Lindstrom and Lydy, 1997). Kao and others (1995) demonstrated that this occurs because atrazine stimulates cytochrome P450 and general esterase activity in insects, which increases the conversion of organophosphates into oxon breakdown products, such as diazoxon and malaoxon, which are more toxic than the parent pesticide compounds (diazinon and malathion).

In addition, toxicity tests in the past were most often designed to detect effects on growth and survival rates, not on developmental or reproductive attributes. New research suggests that exposure to environmentally relevant pesticide concentrations may cause such effects. Laboratory experiments by Hayes and others (2002a), for example, showed that exposure to the herbicide atrazine produced developmental deformities in frog gonads in 20% of male frogs studied at concentrations as low as 0.10 µg/L. This concentration is 30 times lower than the USEPA maximum contaminant level allowable in drinking water (3 µg/L; table 5). However, because the results of Hayes and others contradict studies used to develop drinking-water standards, and also because those results have not yet been replicated, more study is needed. This is particularly true considering that atrazine is the most widely used pesticide in the world and is the most frequently detected pesticide in streams nationwide (U.S. Geological Survey, 1999). Atrazine was the most frequently detected pesticide in the Clackamas River Basin, occurring in all of the tributaries sampled, with the highest concentrations occurring in Rock and Deep Creeks (0.30 and 0.12 µg/L, respectively).

Sublethal effects on aquatic life from exposure to pesticides, such as impaired reproduction and development, have been documented by numerous laboratory and field studies. Cope and others (1970) showed delayed fish spawning from exposure to 2,4-D.

Table 5. Pesticide concentrations relative to human health standards and aquatic-life criteria

[Pesticide concentrations in micrograms per liter (µg/L), or parts per billion; USEPA, U.S. Environmental Protection Agency; CCME, Canadian Council of Ministers of the Environment; NAS/NAE, National Academy of Sciences/ National Academy of Engineering; USGS, U.S. Geological Survey; ** concentration exceeds a criterion; ns, no standard available; 2,4-D, 2,4-dichlorophenoxyacetic acid; DCPA, dimethyl-2,3,5,6-tetrachloroterephthalate; DDE, dichlorodiphenyldichloroethylene]

	Clackamas River Basin		USEPA human health standards[a]		Aquatic-life criteria/guidelines/recommendations/benchmark					
Pesticide or breakdown product	Number of detections	Maximum concentration	Value	Type	USEPA acute[b]	USEPA chronic[c]	Canada CCME[d]	Great Lakes Water-Quality Objectives[e]	NAS/NAE[f]	USGS[g]
Atrazine	13	0.30	3	MCL	350[h]	12[h]	1.8	ns	ns	1.8
Diazinon	10	.16**	.6	HAL	.1[h]	.1[h]	ns	0.08	0.009	.08
Simazine	9	.19	4	MCL	ns	ns	10	ns	10	10
Diuron	8	.22	10	HAL	ns	ns	ns	ns	1.6	ns
Metolachlor	8	.06	100	HAL	ns	ns	7.8[i]	ns	ns	7.8
Deethylatrazine	7	.021	ns	ns	ns	ns	ns	ns	ns	ns
Napropamide	7	1.3	ns	ns	ns	ns	ns	ns	ns	ns
Trifluralin	7	.082	5	HAL	ns	ns	.20	ns	ns	.20
Dichlobenil	6	16.8	ns	ns	ns	ns	ns	ns	37	ns
Prometon	6	.012	100	HAL	ns	ns	ns	ns	ns	ns
2,4-D	5	.3	70	MCL	ns	ns	4.0[j]	ns	3	4.0[j]
Triclopyr	5	1.3	ns	ns	ns	ns	ns	ns	ns	ns
Chlorpyrifos	4	.056**	20	HAL	.083	.041	.0035	ns	.001	.041
Pendimethalin	4	.03	ns	ns	ns	ns	ns	ns	ns	ns
Carbaryl	3	.026**	700	HAL	ns	ns	.20	ns	.02	.20
DCPA	2	.46	70	HAL	ns	ns	ns	ns	ns	ns
Dieldrin	2	.008**	.02	RSD5	.24	.056	ns	ns	.005	.056
Ethoprop	2	.01	ns	ns	ns	ns	ns	ns	ns	ns
Pronamide	2	.17	1	HAL	ns	ns	ns	ns	ns	ns
Tebuthiuron	2	.034	500	HAL	ns	ns	1.6[i]	ns	ns	1.6
Bromacil	1	.27	90	HAL	ns	ns	5.0[i]	ns	ns	5.0
p,p'-DDE	1	.002**	1	RSD5	1.1[k]	.001[k]	ns	ns	ns	.001[k]
Fonofos	1	.007	10	HAL	ns	ns	ns	ns	ns	ns
Imazaquin	1	.047	ns	ns	ns	ns	ns	ns	ns	ns
Linuron	1	.59	ns	ns	ns	ns	7.0[i]	ns	ns	7.0
Malathion	1	.025**	100	HAL	ns	.1	ns	ns	.008	.1
Terbacil	1	.026	90	HAL	ns	ns	ns	ns	ns	ns

[a] USEPA maximum contaminant level (MCL), lifetime health advisory (HAL), or risk-specific dose at a cancer risk level of 1 in 100,000 (RSD5) allowable in drinking water (U.S. Environmental Protection Agency, 2000a).

[b] Criterion maximum (acute) concentration—the highest concentration that organisms can be exposed to for a short (1-hour) period; protects 95% of a diverse group of genera; should not occur more than once every 3 years (U.S. Environmental Protection Agency, 1999).

[c] Criterion continuous (chronic) concentration—the highest concentration that organisms can be exposed to for an extended period; protects 95% of a diverse group of genera; should not occur more than once every 3 years (U.S. Environmental Protection Agency, 1999).

[d] Intended to protect all aquatic life and should not be exceeded at any time (Canadian Council of Ministers of the Environment, 2001).

[e] Represents the maximum allowable concentration in the boundary waters between the United States and Canada to protect recognized, most sensitive uses (International Joint Commission Canada and the United States, 1978).

[f] Recommended maximum concentrations in all waters at all times (National Academy of Sciences/National Academy of Engineering, 1973).

[g] "Preferred" ecological benchmark adopted by the USGS National Water-Quality Assessment Program to evaluate pesticide concentrations in streams nationwide (U.S. Geological Survey, 1999).

[h] Draft guideline (U.S. Environmental Protection Agency, 2000; 2001a; 2001b).

[i] Interim guidelines (Canadian Council of Ministers of the Environment, 2001).

[j] Sum of phenoxy herbicides.

[k] Based on the total concentration of the parent compound *p,p'*-DDT plus metobolites (*p,p'*-DDE and others).

Von Westernhagen and others (1989) showed reduced fish fertilization from exposure to dieldrin. Choudhury and others (1993) and Baatrup and others (2001) showed reproductive system disruption in fish from exposure to carbaryl and *p,p'*-DDE, respectively. Hayes and others (2002b) showed developmental irregularities in frogs from low-level exposure to atrazine. Colborn and others (1993) reported endocrine system disruption in wildlife and humans. Exposure to pesticides also may affect fish behaviors, including predator avoidance and homing (Scholz and others, 2000), swimming (Matton and Laham, 1969), and feeding (Bull, 1974). Many pesticides thought to elicit such sublethal effects, including 2,4-D, atrazine, carbaryl, dieldrin, and *p,p'*-DDE, were found in the Clackamas River or its tributaries during this study, but their effects on aquatic life in the Clackamas River Basin are not yet known.

To address the problem of evaluating the effects of exposure to multiple pesticide compounds, Munn and Gilliom (2001) developed a pesticide toxicity index (PTI) that combines pesticide exposure (measured concentrations of pesticides in stream water) with toxicity estimates from laboratory studies (typically 96-hour LC50 values, the lethal concentration for 50 percent of the test population for a 96-hour chemical exposure). The PTI is the sum of toxicity quotients for each pesticide compound measured in a stream:

$$PTI = \left(\sum_{i = 1}^{n} {}_{i} \right) \frac{E_i}{MTC_{x,\, i}}$$

where:

E_i = concentration of pesticide i

$MTC_{x,\, i}$ = median toxicity concentration for the pesticide i for taxonomic group x

n = number of pesticides, and

E and MTC are expressed in the same units

Although the PTI does not determine whether water in a sample is toxic, its values can be used to rank or compare the toxicity of samples on a relative basis. The PTI approach may be useful for comparing the significance of pesticides in different streams on a common basis, for evaluating relations between pesticide exposure and observed biological conditions, and for prioritizing future studies. PTI values for samples collected in the Clackamas River Basin were calculated for both benthic invertebrates and fish (table 6).

In all samples, the PTI values were higher for benthic invertebrates than for fish, indicating a greater risk to invertebrates. Moreover, EPT taxa richness (the number of mayfly, stonefly, and caddisfly taxa in a sample, an index often used to indicate the health of the benthic invertebrate community) declined steadily, from 31 EPT taxa in Eagle Creek to 1 in Sieben Creek, as the PTI values increased (fig. 9). Dewberry and others (1999) found a low diversity of aquatic insects in both Rock and Sieben Creeks and attributed the poor community condition to habitat impairment. In light of this study's findings, pesticide exposure also may be a factor affecting aquatic life in these and other tributaries in the Clackamas River Basin.

One of the potential explanations for the low EPT taxa richness in Rock and Sieben Creeks is the occurrence of the insecticides diazinon and chlorpyrifos, which were found in both streams at concentrations exceeding their aquatic-life criteria (table 5). Both of these organophosphorus insecticides impair nervous system function through inhibition of the enzyme acetylcholinesterase (AChE) (Nowell and others, 1999). Exposure to these compounds may inhibit AChE activity in aquatic life such as benthic invertebrates. Studies also have found that diazinon impairs predator avoidance behavior and homing ability in Chinook salmon at concentrations of 1 and 10 µg/L, respectively (Scholz and others, 2000). Although these concentrations are much higher than those found in the Clackamas River Basin, diazinon was detected in the main-stem Clackamas River twice (table 3), the effects of sustained or multiple exposures to diazinon are not known. The recent cancellation order for all products containing diazinon (U.S. Environmental Protection Agency, 2003), however, should help reduce the occurrence of this pesticide in the environment and subsequent exposure to aquatic life.

Table 6. Pesticide toxicity index (PTI) values for fish and benthic invertebrates for samples collected in the Clackamas River Basin, May 2000–August 2001

[Larger PTI values indicate greater relative toxicity; nd, no pesticides detected]

Sample	Date	PTI-Fish	Rank, in order of descending toxicity
Rock Creek	October 2000	3.4×10^{-3}	1
Sieben Creek	9 October 2000	3.4×10^{-3}	2
Sieben Creek	20 October 2000	2.5×10^{-3}	3
Sieben Creek	May 2000	1.2×10^{-3}	4
Richardson Creek	October 2000	8.5×10^{-4}	5
Rock Creek	May 2000	2.4×10^{-4}	6
Deep Creek	May 2000	1.9×10^{-4}	7
Clackamas River untreated water	August 2001	1.5×10^{-4}	8
Richardson Creek	May 2000	8.1×10^{-5}	9
Deep Creek	October 2000	5.7×10^{-5}	10
Clackamas River untreated water	October 2000	5.7×10^{-5}	11
Clear Creek	October 2000	4.4×10^{-5}	12
Clackamas River at Carver	May 2000	3.3×10^{-6}	13
Clear Creek	May 2000	1.1×10^{-6}	14
Eagle Creek	May 2000	8.7×10^{-7}	15
Eagle Creek	October 2000	nd	nd
Clackamas River at Estacada	May 2000	nd	nd
Clackamas River			
Treated drinking water	October 2000	nd	nd
Treated drinking water	January 2001	nd	nd
Treated drinking water	August 2001	nd	nd

Sample	Date	PTI-Benthic invertebrates	Rank, in order of descending toxicity
Rock Creek	October 2000	1.1×10^{-1}	1
Sieben Creek	20 October 2000	5.3×10^{-2}	2
Sieben Creek	May 2000	5.2×10^{-2}	3
Sieben Creek	9 October 2000	3.2×10^{-2}	4
Rock Creek	May 2000	2.9×10^{-3}	5
Deep Creek	May 2000	9.8×10^{-4}	6
Deep Creek	October 2000	9.4×10^{-4}	7
Richardson Creek	May 2000	8.6×10^{-4}	8
Richardson Creek	October 2000	3.5×10^{-4}	9
Clear Creek	October 2000	3.5×10^{-4}	10
Clackamas River un treated water	October 2000	1.6×10^{-4}	11
Clackamas River untreated water	August 2001	1.3×10^{-4}	12
Clackamas River at Carver	May 2000	1.6×10^{-5}	13
Clear Creek	May 2000	1.9×10^{-6}	14
Eagle Creek	May 2000	1.4×10^{-6}	15
Eagle Creek	October 2000	nd	nd
Clackamas River at Estacada	May 2000	nd	nd
Clackamas River			
Treated drinking water	October 2000	nd	nd
Treated drinking water	January 2001	nd	nd
Treated drinking water	August 2001	nd	nd

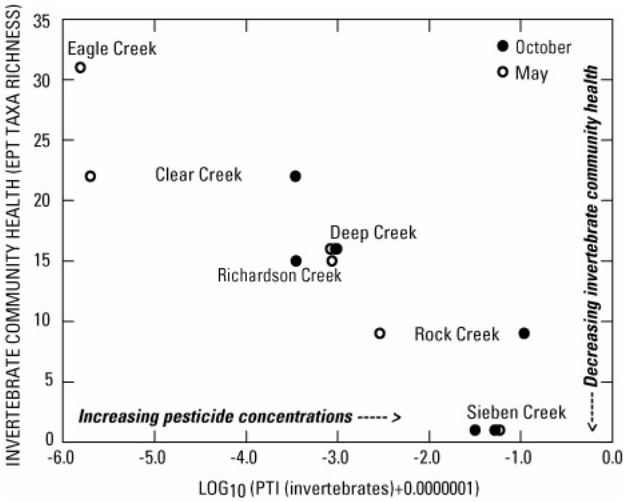


Figure 9. Pesticide toxicity index (PTI) values compared with EPT taxa richness for samples collected from tributaries in the Clackamas River Basin, Oregon. (Pesticide samples were collected from sites in May and October 2000; invertebrate data in September 1999 [USGS, unpublished data] and August/September 1997 [Dewberry and others, 1999]. No pesticides were detected in Eagle Creek in October.)

Potential Uses of Pesticides in the Clackamas River Basin

According to the USEPA, most (77% by volume) of the national pesticide use occurs on agricultural land, about 11% is used in homes and gardens, and 12% is used by industries, commercial operations, and governments (U.S. Environmental Protection Agency, 1997). Identifying the sources of pesticides detected in the Clackamas River Basin is difficult because most of the pesticides detected have multiple uses, and all of the sampled streams drain areas of mixed land use. Of the 25 parent compounds detected, 22 have agricultural applications, 24 have urban applications, 16 are approved for application to golf courses, 11 are approved for application along right-of-ways, and 5 have or once had forestry applications (table 7). Thirteen of the pesticides were previously banned or have some form of restricted use.

Agricultural uses—Approximately 100,000 acres of land is used for agriculture in Clackamas County. Pastureland, hay fields (mostly alfalfa), nurseries, and greenhouses make up about 60% of the agricultural land in the basin (fig. 10). In 2000, the top agricultural commodity in Oregon was production from nurseries and greenhouses. Nursery and greenhouse sales have steadily increased in Oregon, from $347 million in 1993 to $642 million in 2000 (Oregon Department of Agriculture, 2001). Clackamas County, which was the leading county for nursery sales in Oregon, had approximately 21,370 acres in nursery and greenhouse production in 1997. Clackamas County also is one of the top Christmas tree producing counties in the country. According to the National Agricultural Statistics Service (2002), 18 herbicides, 12 insecticides, and 4 fungicides are used on Christmas trees in Oregon, and several of these were detected in the Clackamas River Basin (table 7).

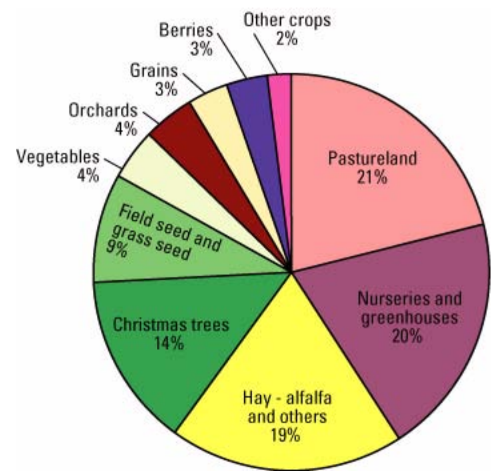


Figure 10. Top agricultural crops and commodities grown in Clackamas County, Oregon, 1997 (by percentage of total acreage). (Source: Oregon Department of Agriculture, 1997.)

Of the estimated agricultural applications in Clackamas County, most of which is in the Clackamas River Basin, the highest amounts of pesticides (49%) are applied to nursery and greenhouse crops, with lesser amounts, ranging from 4 to 15%, applied to pastureland, Christmas trees, hay fields, hazelnuts, and grass seed fields (fig. 11). These estimates were calculated using crop acreage obtained from the Oregon Department of Agriculture (1997) and average pesticide application rates obtained from Oregon State University Extension Services (2001a, b) and from the National Agricultural Statistics Service (2002). It is important to note, however, that the application rates used here are approximations and assume a single application per year, which may not be the case for crops receiving multiple pesticide applications in a season, such as strawberries and fruit trees. Therefore, these estimates may differ considerably from what is actually applied.

Table 7. Potential uses of pesticides detected in the Clackamas River Basin, Oregon, 2000–01

[H, herbicide; I, insecticide; IBP, insecticide breakdown product; N, nematocide; X, indicates likely use; DCPA, dimethyl-2,3,5,6-tetrachloroterephthalate; 2,4-D, 2,4-dichlorophenoxyacetic acid; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane]

Compound	Type	Agriculture[a]	Urban[b]	Golf courses[c]	Right-of-ways[d]	Forestry[e]	Top agriculture uses[a]	Restricted pesticides[f]
Atrazine	H	X	X	X		X	Christmas trees, sweet corn	all States
Bromacil	H		X		X		None reported	Washington
Carbaryl	I	X	X				Pastureland, hay, cane berries, wheat, sweet corn	
Chlorpyrifos	I	X	X	X			Nurseries, hazelnuts, sweet corn, Christmas trees, strawberries	most uses
2,4-D	H	X	X	X	X	X	Pastureland, hay, grass seed, hazelnuts, wheat	
DCPA	H	X	X	X			Nurseries, cucumbers, strawberries, squash, snap beans	Washington
p,p'-DDE[g]	IBP	X	X	X		X	DDT was once used on numerous crops	all States[g]
Diazinon	I	X	X	X			Grass seed, cane berries, fescue seed, nurseries, squash	all States
Dichlobenil	H	X	X	X	X		Nurseries, hazelnuts, cane berries, cauliflower, blueberries	
Dieldrin	I		X				None reported	all States
Diuron	H	X	X		X		Grass seed, hay, hazelnuts, fescue seed, cane berries	Washington
Ethoprop	N	X	X	X			Sweet corn, snap beans	most uses
Fonofos	I	X	X	X			Nurseries, sweet corn, snap beans, broccoli, strawberries	most uses
Imazaquin[h]	H		X				Cottonwood trees grown for pulp and grass turf	
Linuron	H	X					Garden crops such as corn, potatoes, fruit trees, wheat, oats, and barley	
Malathion	I	X	X	X		X	Pastureland, hay, cane berries, hazelnuts, wheat	
Metolachlor	H	X	X	X	X		Nurseries, grass seed, sweet corn, snap beans, green peas	Washington
Napropamide	H	X	X		X		Nurseries, hazelnuts, cane berries, strawberries, rhubarb	
Pendimethalin	H	X	X	X	X		Nurseries, Christmas trees, grass seed, snap beans, grapes	
Prometon	H		X				None reported	all States
Pronamide	H	X	X	X			Nurseries, Christmas trees, cane berries, grass seed, alfalfa	all States
Simazine	H	X	X	X	X		Nurseries, Christmas trees, hazelnuts, cane berries, blueberries	
Tebuthiuron	H	X	X		X		Pastureland	
Terbacil	H	X					Grass seed, cane berries, alfalfa, apples, peaches	
Triclopyr	H	X	X	X	X	X	Pastureland, hay, Christmas trees, clearing heavy brush	
Trifluralin	H	X	X	X	X		Nurseries, wheat, alfalfa, cucumbers, cauliflower	

[a]Agricultural uses estimated from average pesticide application rate for crops in the Pacific Northwest (Oregon State University, 2001a; 2001b) and from estimated crop acreage for Clackamas County (Oregon Department of Agriculture, 1997).

[b]Anderson and others (1996); Krastzer, C.R. (1998); Panshin and others (1998); U.S. Geological Survey (1999).

[c]Pesticides used on and detected in ground water beneath golf courses (Jack Barbash, U.S. Geological Survey, Web page http://ca.water.usgs.gov/pnsp/golf.html, accessed 7/9/02).

[d]Roadside applications (Rob Edgar, Oregon Department of Transportation, written commun., 2002; Ron Buck, Clackamas County Department of Public Works, written commun., 2002).

[e]Cramer (1974).

[f]Oregon State University (2001a; 2001b).

[g]*p,p'*-DDE is one of several breakdown products of *p,p'*-DDT, an organochlorine insecticide. Estimated use is for *p,p'*-DDT, not *p,p'*-DDE.

[h]Imazaquin is applied to hybrid cottonwood trees grown for pulp and on grass turf.

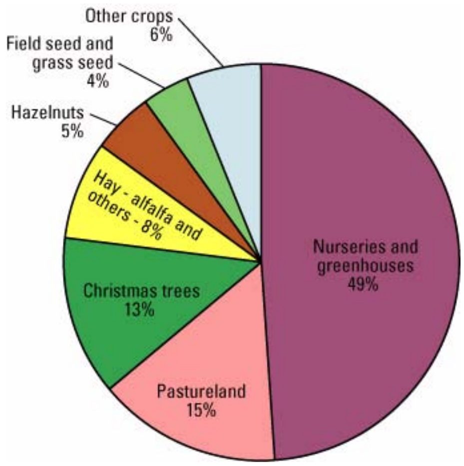


Figure 11. Percentage of total estimated pesticide applications to agricultural crops grown in Clackamas County, Oregon, 1997. [Source: Pesticide application estimates from Oregon State University Extension Services (2001) and from grower surveys published by the National Agricultural Statistics Service, 2002. Crop acreage for Clackamas County from the Oregon Department of Agriculture (1997).]

Urban uses—Pesticides are used in urban areas to control weeds and insect pests on lawns, gardens, and ornamental trees and plants, and in homes to control pests such as ants and fleas. Nearly all of the pesticides detected in the Clackamas River Basin have urban uses, and several herbicides also are applied along right-of-ways such as roads, utility lines, and fences (table 7). The two streams draining the largest proportion of urban land in this study—Rock and Sieben Creeks—contained the greatest number and highest concentrations of pesticides (table 3). Several herbicides were found in all four of the lowermost tributaries in the Clackamas River Basin, many of which, including atrazine, metolachlor, simazine, prometon, diuron, and 2,4-D, are the most commonly detected herbicides in urban streams nationwide (U.S. Geological Survey, 1999).

Pesticide Management and Future Studies

Pesticide occurrence in streams is directly related to their use in upstream areas (U.S. Geological Survey, 1999). The transport of pesticides from their target areas to streams and ground water depends on several factors, some of which are listed in table A-1 in the appendix. These include their solubility in water, half-lives (rate of breakdown in the environment), and physical or hydrologic characteristics of the watershed. Reducing pesticide contamination may be achieved through educating the public on the use of alternatives to pesticides (see Northwest Coalition for Alternatives to Pesticides, http://www.pesticide.org); avoiding application to areas adjacent to waterbodies; avoiding applications during windy periods or prior to rainfall; taking care when cleaning pesticide application apparatus; and controlling soil erosion from application areas. Developing and implementing other best management practices also may reduce the transport of pesticides to streams and ground water.

From October 2002–September 2003, the USGS collected monthly samples of the lower Clackamas River for 234 contaminants, including pesticides, pharmaceuticals, fuel oxygenates, and other compounds as part of the National Water-Quality Assessment Program's Source Water Assessment. These data will help characterize the temporal variations in contaminants in the main-stem Clackamas River. Additional sampling for pesticides in the lower-basin tributaries might be used to identify areas where pesticides are already contaminating streams and/or ground water.

Future studies in the basin could also include land use or crop studies whereby smaller streams that drain areas with more homogeneous land uses are sampled for pesticides. Small-scale land use/land cover data also would facilitate future study design by identifying subbasins with a large percentage of a particular crop or land use. Such studies would benefit from pesticide use data, which would help determine which areas to focus on and which pesticides to test for. Follow-up studies could include evaluation of the benthic ecosystem (invertebrates and algae) or examination of potential reproductive, developmental, or behavioral effects on fish caused by exposure to pesticides.

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APPENDIX

APPENDIX TABLE A-1. Properties of pesticides detected in the Clackamas River Basin, Oregon, 2000–01

[Pesticide movement rating is derived from empirical data on pesticide half-life and soil Koc from the Oregon State University Extension Pesticide Properties Database (P.A. Vogue, written commun., 1994); H, herbicide; I, insecticide; N, nematocide; HBP, herbicide breakdown product; IBP, insecticide breakdown product; nd, no data]

Compound	Type	Pesticide movement rating	Water solubility (mg/L)	Soil half-life (days)	Soil Koc[a]
Atrazine	H	high	33.0	60	100
Bromacil	H	very high	700.0	60	32
Carbaryl	I	low	120.0	10	300
Chlorpyrifos	I	very low	0.4	30	6,070
2,4-D	H	moderate	900.0	10	20
DCPA	H	very low	.5	100	5,000
p,p'-DDE	IBP	extremely low	.1	1,000	50,000
Deethylatrazine	HBP	nd	nd	nd	nd
Diazinon	I	low	60.0	40	1,000
Dichlobenil	H	moderate	21.0	60	400
Dieldrin	I	extremely low	.2	1,000	12,000
Diuron	H	moderate	42.0	90	480
Ethoprop	N	high	750.0	25	70
Fonofos	I	low	17.0	40	870
Imazaquin	H	very high	60.0	60	20
Linuron	H	moderate	75.0	60	400
Malathion	I	extremely low	130.0	1	1,800
Metolachlor	H	high	530.0	90	200
Napropamide	H	moderate	74.0	70	700
Pendimethalin	H	very low	.3	90	5,000
Prometon	H	very high	720.0	500	150
Pronamide	H	low	15.0	60	800
Simazine	H	high	6.2	60	130
Tebuthiuron	H	very high	2,300.0	360	80
Terbacil	H	very high	710.0	120	55
Triclopyr	H	very high	430.0	46	20
Trifluralin	H	very low	.3	60	8,000

[a]Organic carbon and sorption coefficient. Compounds with higher values have relatively greater affinity to adhere to sediment than those with lower values.

Evaluation of quality-control data—No pesticides were detected in the blank samples, and the split sample contained similar concentrations of both atrazine and diuron (table A-2). Replicate samples collected from the Clackamas River at Carver in May also were similar, with only atrazine and its breakdown product deethylatrazine being detected at similar concentrations. The second set of replicate samples collected from Clear Creek in October showed greater variation. Metolachlor was detected in both samples at similar concentrations, but three compounds—atrazine, triclopyr, and pendimethalin—were detected in just the first sample. Concentrations of these compounds were less than the detection limit and therefore had a 50% probability of being detected, which is consistent with finding them in only one of the two samples. Differences between these replicate samples also may have resulted from real temporal variations in pesticide concentrations, because replicate samples were collected about 15 minutes apart near the peak of the storm hydrograph (fig. 2). No pesticides were detected in either replicate sample of treated drinking water collected in January. The spike sample indicated that most of the detected pesticides had acceptable recoveries—the median recovery for all pesticides was 111%. A few compounds (carbaryl, terbacil, and linuron) exhibited a high bias with recoveries of between 174 and 330%. A low bias (recovery of 65 and 83%, respectively) was found for the breakdown products *p,p'*-DDE and deethylatrazine.

APPENDIX TABLE A-2. Quality-control data

[Pesticide concentrations in micrograms per liter (μg/L), or parts per billion; e, estimated value; spike data reported for only those compounds that were detected]

Quality–assurance sample	Pesticides detected	Sample concentration	Replicate/split concentration	Relative percent difference
Equipment blank—May 2000	None			
Laboratory blank—October 2000	None			
Equipment blank—January 2001	None			
Split—May 2000	Atrazine	0.0109	e0.0106	3
	Diuron	e.0133	e.0142	6
Replicate—October 2000	Metolachlor	e.005	.004	--
	Atrazine	e.002	<.001	--
	Triclopyr	e.040	<.25	--
	Pendimethalin	e.008	<.01	20
Replicate—January 2001	None	None detected	None detected	0

Quality–assurance sample	Pesticide or breakdown product	Calculated spike	Reported concentration	Percent recovery
Spike—May 2000	Atrazine	0.113	0.120	107
	Deethylatrazine	.105	e.088	83
	Carbaryl	.100	e.323	323
	Chlorpyrifos	.100	.106	106
	DCPA	.100	.111	111
	p,p'-DDE	.100	.065	65
	Diazinon	.100	.106	106
	Dieldrin	.100	.108	108
	Ethoprop	.100	.111	111
	Fonofos	.100	.106	106
	Linuron	.100	.174	174
	Malathion	.100	.130	130
	Metolachlor	.100	.117	117
	Napropamide	.100	.117	117
	Pendimethalin	.100	.126	126
	Prometon	.100	.105	105
	Simazine	.100	.117	117
	Tebuthiuron	.100	.129	129
	Terbacil	.100	e.330	330