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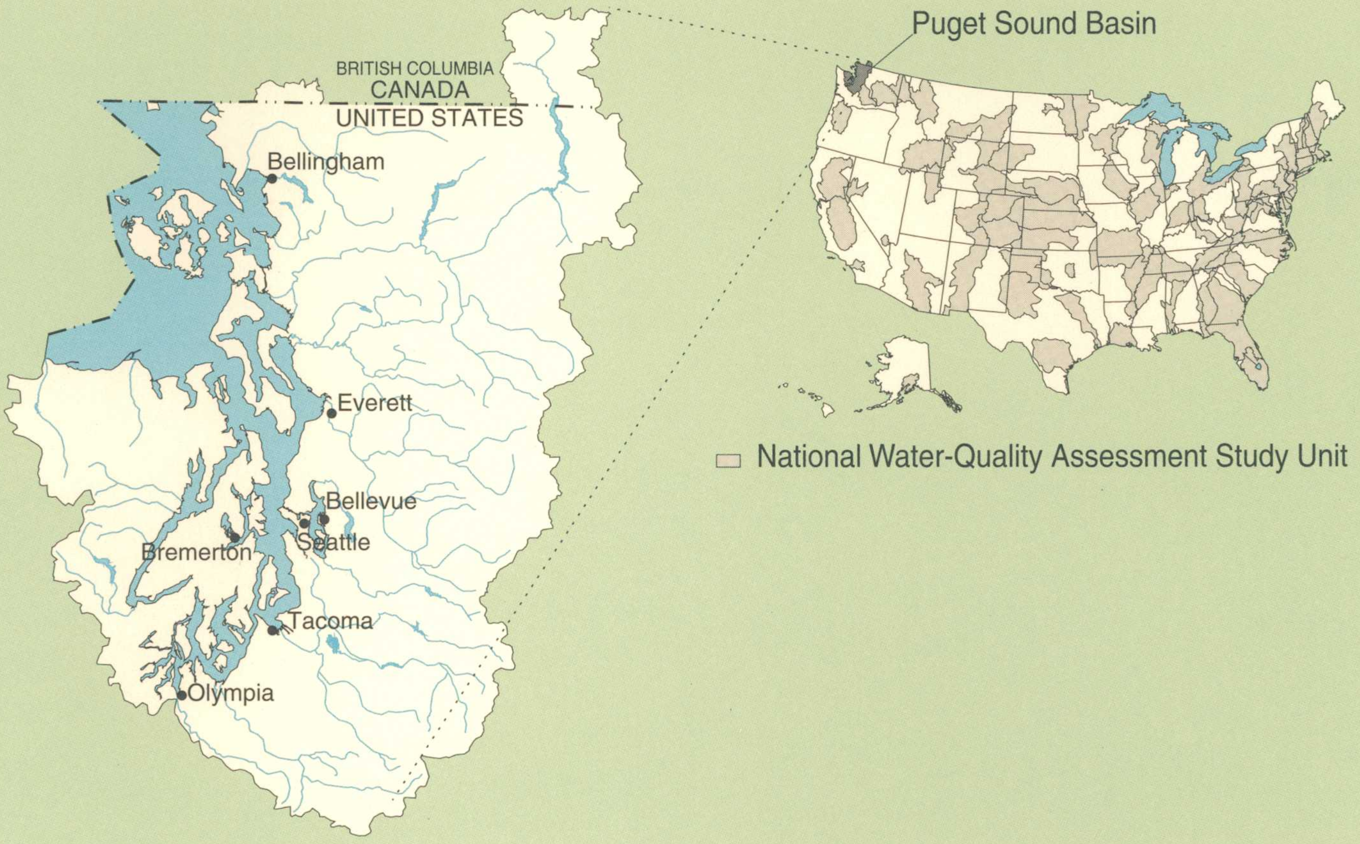
Pesticides Detected in Urban Streams During Rainstorms in King and Snohomish Counties, Washington, 1998

Prepared in cooperation with
WASHINGTON STATE DEPARTMENT
OF ECOLOGY

By Frank D. Voss and Sandra S. Embrey



U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 00-4098

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Tacoma, Washington
2000

U.S. DEPARTMENT OF THE INTERIOR
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FOREWORD

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

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

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

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

•Describe how water quality is changing over time.

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

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

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of more than 50 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within these study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

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

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

Robert M. Hirsch
Chief Hydrologist

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Pesticides Detected in Urban Streams During Rainstorms in King and Snohomish Counties, Washington, 1998

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ABSTRACT

The U.S. Geological Survey and the Washington State Department of Ecology cooperated in sampling 13 sites in 10 urban watersheds during 3 storms in King County, Wash., in the spring of 1998. Twenty-six of the 98 pesticides and transformation products sampled for were detected. Twenty-three of the 26 were pesticides (17 herbicides, 5 insecticides, and 1 fungicide), and 3 were transformation products. The pesticides dichlobenil, 2,4-D, MCPP, Diazinon, and pentachlorophenol were detected at all of the urban study sites.

Samples of 5 of 14 detected pesticides with maximum concentration limits exceeded those limits–the insecticides carbaryl, chlorpyrifos, Diazinon, Lindane, and Malathion. The concentrations of 3 of 11 pesticides with chronic aquatic-life criteria exceeded the limits–Lindane, Diazinon, and carbaryl.

Twelve pesticides detected in stream-water samples were sold in retail stores. Several of these pesticides–2,4-D, dichlobenil, Diazinon, and MCPP–were detected in all the sampled streams, possibly because of their high retail sales. Retail sales might also explain why other pesticides (such as prometon and triclopyr) are frequently detected.

Five pesticides were sold in retail stores but were not detected in stream-water samples–two insecticides (*cis*-permethrin and disulfoton), two fungicides (chlorothalonil and triadimefon), and one herbicide (pendimethalin).

The pesticides not sold in retail stores but detected in stream-water samples probably originate from applications to nonresidential areas (roadsides, playing fields, and parks) by local governments. Detected pesticides sold in a small number of units (prometon, triclopyr, MCPA) also may be from nonresidential rather than residential applications.

INTRODUCTION

Each year in the Puget Sound Basin, urban and residential areas are treated with a variety of pesticides. Storm-water runoff transports these pesticides to streams, sometimes causing pesticide concentrations to reach levels that may cause adverse ecological effects.

As the population of the Puget Sound Basin increases and urban and residential areas expand, pesticides will probably be used increasingly. However, understanding how pesticide usage affects water quality and potentially affects aquatic habitat can lead to managing pesticide applications better and minimizing potential adverse impacts on streams in urban watersheds.

Purpose and Scope

This report presents the results of a study to assess the occurrence and concentrations of pesticides in urban stream-water sampled during spring storms and to infer sources of pesticides by

- sampling for 98 pesticides and pesticide transformation products during rain storms in April and May of 1998 at 13 sites in 11 watersheds in western King and Snohomish Counties;
- compiling sampling data into a database and examining where pesticides were detected;
- examining the concentrations of pesticides in stream-water and comparing these concentrations with criteria for the protection of aquatic life set by the National Academy of Sciences and the National Academy of Engineering (NAS/NAE), the U.S. Environmental Protection Agency (USEPA), and other agencies; and
- comparing the sample data to pesticide sales data and land-use information to try to determine possible sources of pesticides found in stream water.

Description of the Study Area

This study was conducted in western King and south Snohomish Counties, both located in western Washington (fig. 1). Western King and south Snohomish Counties are in a heavily developed urban/

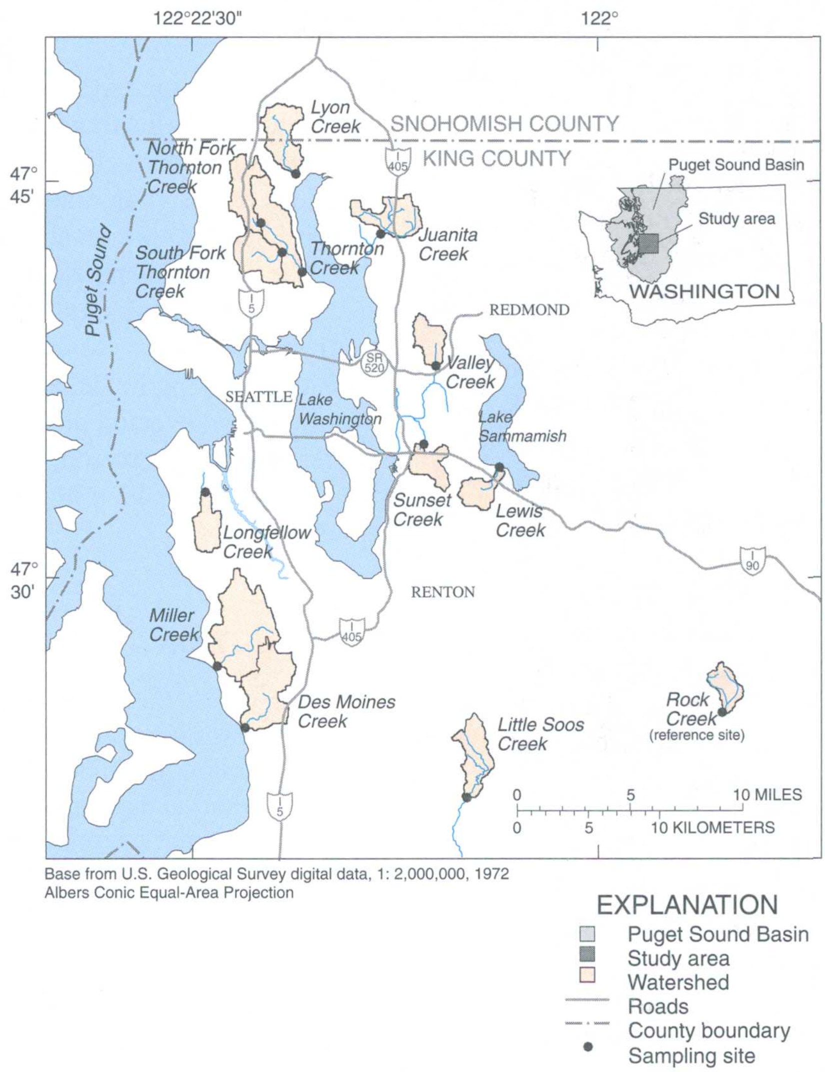


Figure 1. Locations of sampling sites within watersheds, King and Snohomish Counties, Washington.

suburban environment that includes much of the greater Seattle metropolitan area. Temperatures are fairly mild throughout the year. The average daily high and low temperatures in January are 45°F (degrees Fahrenheit) and 35.1°F, and the average daily high and low temperatures in July are 75.2°F and 55.2°F (Beautiful Seattle.com, 1999). The mean annual precipitation in Seattle is 37 inches per year.

The land use in 10 of the 11 watersheds selected for pesticide sampling consists of varying mixtures of dense urban housing, tracts of suburban single-family housing, commercial strips and malls, and industrial complexes. One of the 11 watersheds (Rock Creek) is forested and was sampled to test for pesticides in an undeveloped watershed. Natural drainage in most of the watersheds has been altered for storm-water management, making it difficult to delineate exact drainage areas. Estimated watershed areas in this study (table 1) range from approximately 1.8 square miles (Rock Creek) to 11.3 square miles (Thornton Creek).

Acknowledgments

We acknowledge and thank the following people for their contributions to this study. Dale A. Davis from the Washington State Department of Ecology (Ecology) and Jim Ebbert and Sandra Embrey from the U.S. Geological Survey (USGS) performed site reconnaissance. Bob Black, Jim Ebbert, Sandra Embrey, Ralph Embrey (volunteer), Joe Gilbert, Kathy Greene, Allan Haggland, Gary Holloway, Emily Inkpen, Greg Justin, Stephanie Leisle, Ann Vanderpool from the USGS and Dale A. Davis, Art Johnson, Art Larson, Pam Marti, Dave Serdar from Ecology performed storm sampling, often working under adverse conditions. James Lyles, Deanna Walth, Connie Dean, and Ginger Renslow from the USGS performed editing and report publication.

METHODS

The following section discusses USGS and Ecology methods for collecting and processing field samples, processing samples in the laboratory, and collecting pesticide retail sales data.

Table 1. Land use in study watersheds, King and Snohomish Counties, Washington
[NF, north fork; SF, south fork; Built-up, comprised of areas of intensive use with much of the land covered by structures (Anderson and others, 1976)]

Watershed name	Station identifier	Watershed area (square miles)	Percent land use in watershed			
			Built-up	Agri-culture	Wooded	Water
Des Moines Creek	12103324	6.0	98.3	0.0	1.3	0.3
Miller Creek	12103326	8.6	97.2	0.0	2.1	0.7
Little Soos Creek	12109550	3.4	60.2	1.0	37.8	1.1
Longfellow Creek	12113488	2.2	100.0	0.0	0.0	0.0
Rock Creek	12117695	1.8	0.0	0.0	100.0	0.0
Valley Creek	12119795	2.1	86.5	0.0	13.5	0.0
Sunset Creek	12119900	2.1	100.0	0.0	0.0	0.0
Juanita Creek	12120480	3.4	100.0	0.0	0.0	0.0
Lewis Creek	12121750	1.9	36.8	0.0	63.2	0.0
Lyon Creek	12127290	3.6	99.5	0.0	0.0	0.5
NF Thornton Creek	12127700	3.1	100.0	0.0	0.0	0.0
SF Thornton Creek	12127800	3.4	100.0	0.0	0.0	0.0
Thornton Creek	12128000	11.3	100.0	0.0	0.0	0.0

[1] Land-use categories assigned following the method of Hitt, 1995.

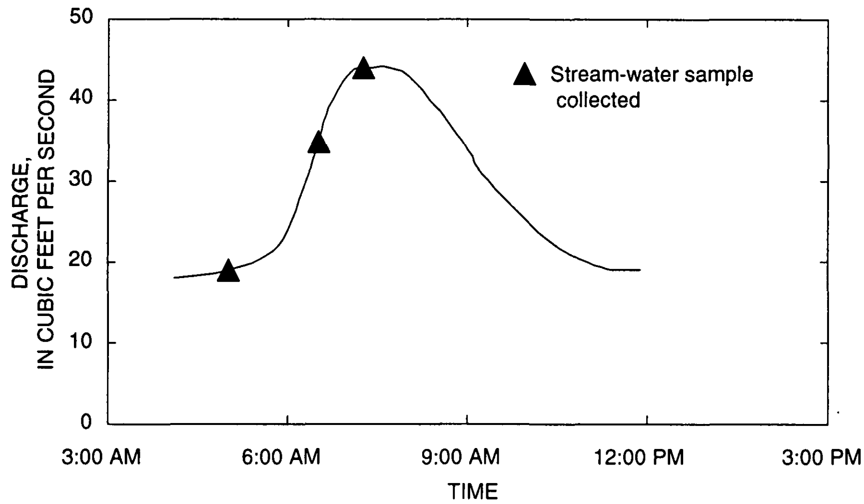


Figure 2. Conceptual diagram of desired relation between discharge and sample collection.

Sample Collection and Processing

The USGS and Ecology cooperated in sampling 13 sites in 11 watersheds during storms in the spring of 1998. Streams were sampled during spring because it was believed that more pesticides would be detected and their concentrations would be higher than at other times of the year. This assumption was based on pesticide sales data from King County showing that pesticide sales were highest during the spring (Market Trends Incorporated, 1996). From these sales statistics, it was assumed that these pesticides were being purchased for immediate use. It was also assumed that the number of pesticides detected and their concentrations would be the highest during storms. This assumption was based on previous sampling of Thornton Creek (sampled about 40 times from March 1996 through May 1998) showing that the number of pesticides detected and their concentrations often were higher during periods of storm runoff.

The study team determined that taking three samples per stream was the best compromise between characterizing pesticide concentrations in streams and staying within the study's budget. The study design specified collecting the three samples while the stream was rising during storms, thus capturing the storm runoff believed to carry the greatest amount of transportable pesticides. Figure 2 depicts the desired relation between the amount of discharge and the times when samples should be collected. As shown in this figure, the samplers should arrive while the stream is at base flow. As the flow in the stream increases slightly due to inflow from runoff, the first sample should be collected. Another sample should be collected as the flow continues to increase. Finally, the last sample is collected at the storm-runoff peak.

In this study, samples were collected within the watersheds during three storms. Table 2 shows the locations and dates. While three samples were taken at most of the study sites, varying storm intensity and the timing of the resulting storm runoff caused variations in the numbers of samples taken at some sites (figs. 3, 4, and 5). For example, two samples were taken at Lyon Creek, Thornton Creek, and South Fork Thornton Creek, and four samples were taken at Des Moines Creek and Little Soos Creek. Single samples were taken at Sunset Creek and Lewis Creek on April 10, 1997, because the storm failed to produce significant runoff. A single sample was also taken at the reference site, Rock Creek.

Table 2. Sampling locations and storm dates, King and Snohomish Counties, Washington, 1998

Sampling locations	Storm date
Juanita Creek, Sunset Creek, Valley Creek, and Lewis Creek	April 23, 1998
Lyon Creek, North Fork Thornton Creek, South Fork Thornton Creek, and Thornton Creek	May 14, 1998
Des Moines Creek, Miller Creek, Longfellow Creek, Little Soos Creek, and Rock Creek	May 14, 1998

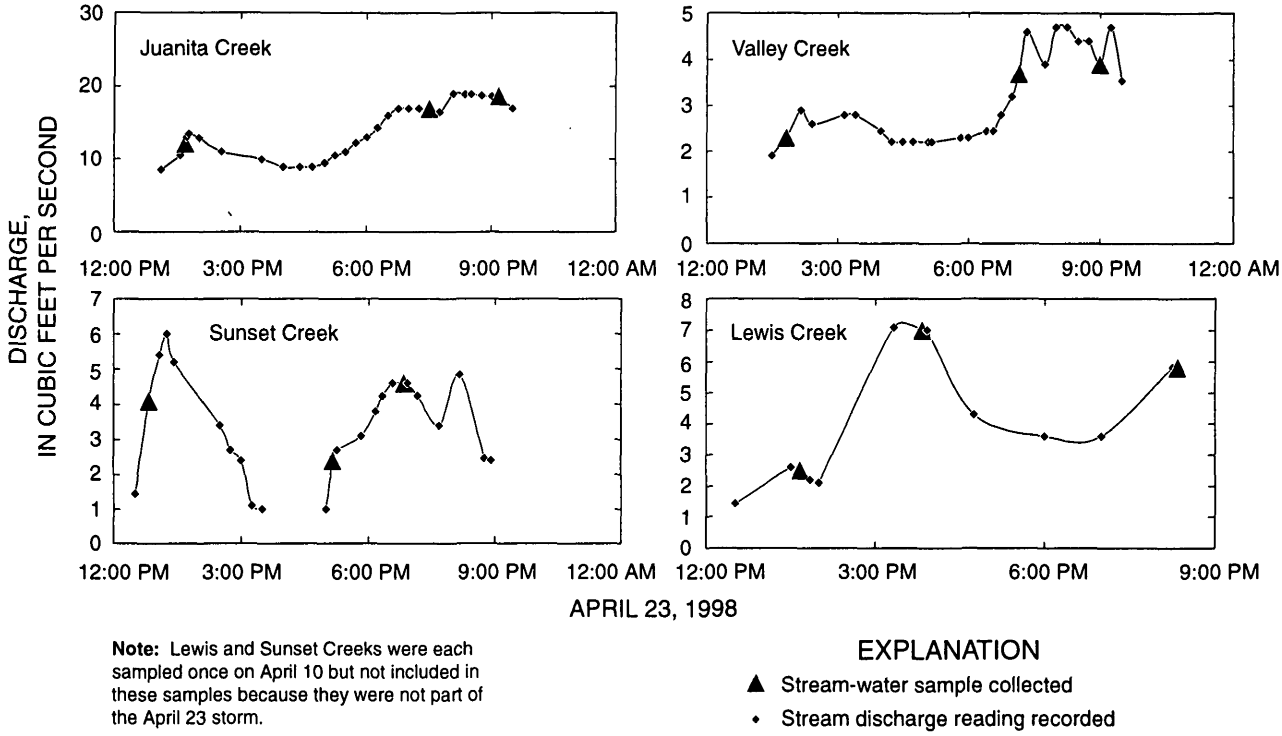


Figure 3. Hydrographs for streams sampled during the storm on April 23, 1998, King County, Washington.

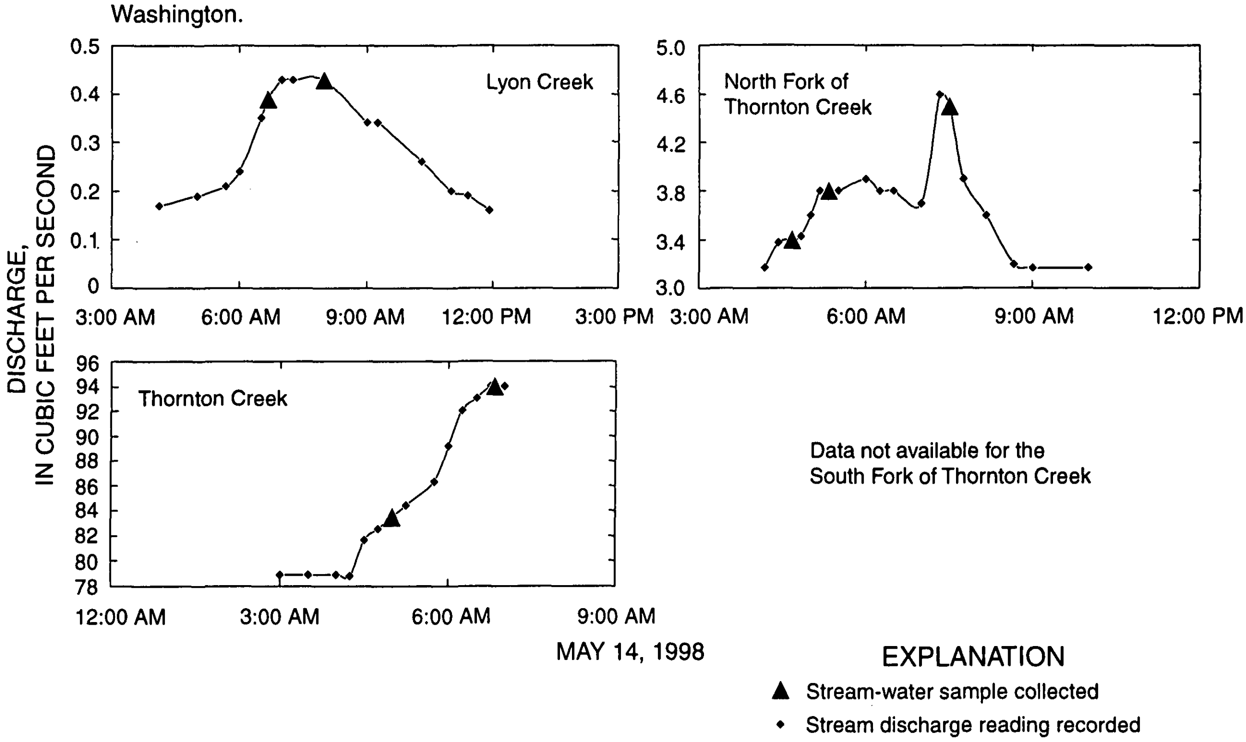


Figure 4. Hydrographs for streams sampled during the storm on May 14, 1998, King and Snohomish Counties, Washington.

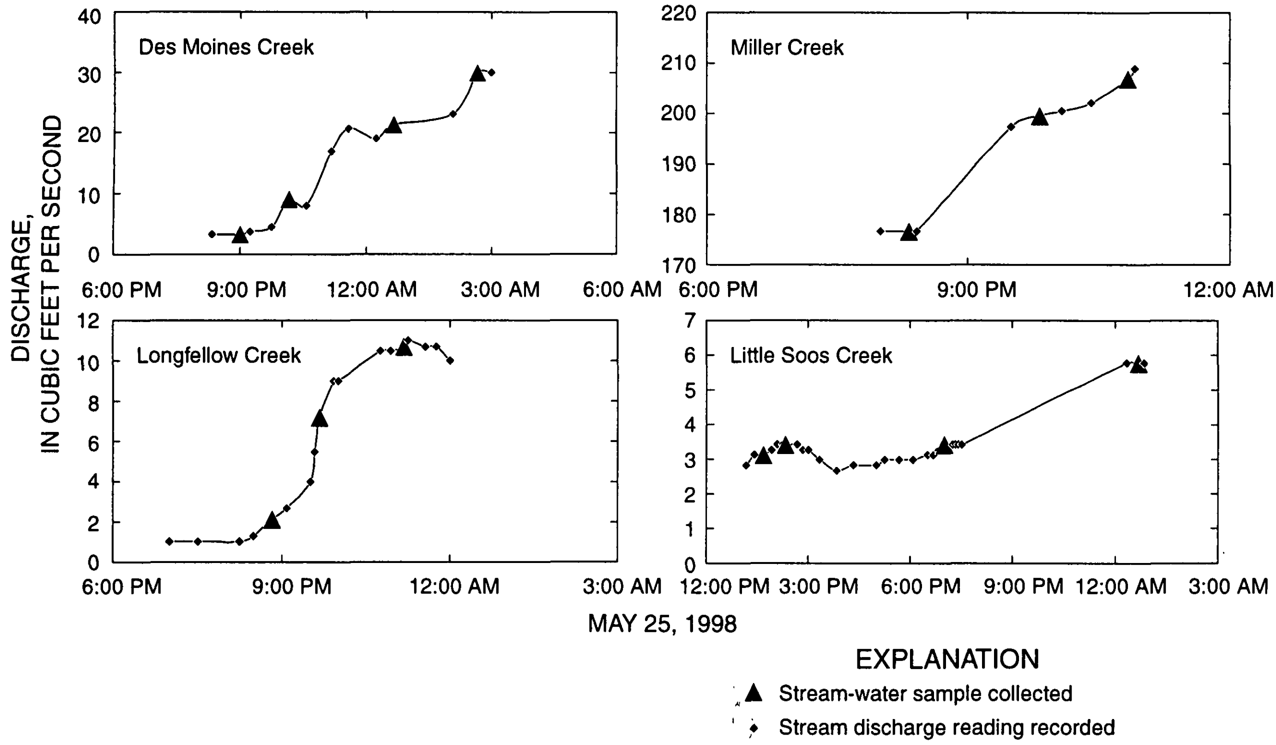


Figure 5. Hydrographs for streams sampled during the storm on May 25, 1998, King County, Washington.

A sample representative of the flow in the stream cross-section was obtained by mixing depth-integrated samples collected at equally spaced verticals across the stream in a glass carboy. Samples were collected using the U.S. DH-81 sampler as described by Edwards and Glysson (1988) and Shelton (1994). The sampler holds a 3-liter Teflon sample bottle, and all parts of the sampler coming into contact with sample water are constructed of Teflon. All equipment used to collect and process samples was cleaned with a 0.2-percent nonphosphate detergent, rinsed with deionized water, rinsed with pesticide-grade methanol, air dried, wrapped in aluminum foil, and stored in a dust-free environment prior to sample collection (Shelton, 1994). The composite sample in the glass carboy was split into individual samples for analysis at the USGS and Ecology laboratories using a Teflon cone splitter (Shelton, 1994).

One of the split samples was filtered through a 0.7-μm (micrometer) glass-fiber filter and passed through a C-18 solid-phase extraction (SPE) cartridge to extract pesticide compounds. The SPE cartridge was stored in amber pesticide-free vials at less than 4 degrees Celsius and shipped to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. The equipment required and the procedures used to collect, process, and extract the sample using the SPE method are described in Shelton (1994) and Sandstrom and others (1992).

Samples analyzed by Ecology's Manchester Environmental Laboratory were collected from the cone splitter in glass bottles, but were not filtered. They were stored on ice during transport to the laboratory in Manchester, Wash.

Three field blanks (one per storm) were collected for quality assurance of the stream-water samples. No pesticides were detected in the field blanks.

Laboratory Procedures

Samples were analyzed for 98 pesticides and pesticide transformation products, which required three different analytical methods. The USGS laboratory analyzed for several types of pesticides (Appendix

A) using gas chromatography/mass spectrometry (Zaugg and others, 1995). The Ecology laboratory analyzed for 73 chlorinated herbicides and nitrogen-containing pesticides (Appendices B and C). Chlorinated herbicides and nitrogen-containing pesticides were analyzed using Draft EPA Method 8085, which uses capillary column GC analysis with an atomic emission detector (AED) and ion-trap GC/MS confirmation (Davis, 1998).

No analytes of interest were detected in any of the method blanks at the USGS and Ecology laboratories. Precision data were obtained for a set of replicate samples. Concentration differences ranged from 0.0 to 40.0 percent as measured by relative percent difference. No modifications were made to the data set based on these results. Surrogate recoveries for pesticide analysis by GC/MS indicate that the process was acceptably precise and accurate for the pesticide families represented. Quality-control methods for the USGS and Ecology laboratories are documented by Wagner and others, 1996, and by Davis, 2000.

There was some overlap of compounds analyzed by the USGS and Ecology laboratories, which provided additional quality assurance. In cases of overlap, the value reported by the USGS laboratory was included in the database for analysis because of lower reporting levels.

Data returned from the laboratories were aggregated into a database and analyzed by the USGS. The original data sets can be accessed at http://wa.water.usgs.gov/ps.data.html.

Method for Collecting Pesticide Retail Sales Data

Data for 1997 pesticide sales were purchased by the King County Hazardous Waste Management Program from a firm that collects marketing information from home and garden stores in western Washington. All the large home and garden stores (nine stores) in western King County and one store in south Snohomish County were selected. The stores are widely distributed throughout the study area.

GENERAL WATER-QUALITY FINDINGS

The following section discusses the pesticides detected in stream-water samples and how the concentrations relate to criteria to protect aquatic life.

Pesticides Detected in Stream-Water Samples

Twenty-six of the 98 pesticides and transformation products sampled for were detected (table 3). Three of the 26 compounds detected were transformation products of other pesticides (desethylatrazine is a transformation product of atrazine, 4-nitrophenol is a transformation product of methyl parathion, and 2,6-dichlorobenzamide is a transformation product of dichlobenil). In this report a transformation product is not counted as a detected pesticide because it cannot be directly related to the pesticide sales database. Of the 23 detected pesticides, 17 were herbicides, 5 were insecticides, and 1 was a fungicide. The herbicides 2,4-D, dichlobenil, MCPP, and prometon; the insecticide Diazinon; and the fungicide pentachlorophenol were detected at all of the urban sites. The watershed with the greatest number of pesticides detected (17) was Juanita Creek. The watershed with the least number of pesticides detected was Little Soos Creek, with eight pesticides detected. The reference site, Rock Creek, was sampled to show which pesticides would be found in stream water if urban development was absent. None of the pesticides studied were detected in Rock Creek.

Pesticide Concentrations and Aquatic Criteria

Table 4 lists the concentrations of pesticides and pesticide transformation products detected by watershed and sample. Figure 6 shows concentrations of detected pesticides and their relation to criteria to protect aquatic life. Criteria are not established for the transformation products. Fourteen of the pesticides detected in this study have maximum recommended concentration limits for the protection of aquatic life established by the National Academy of Sciences and National Academy of Engineering (1973) or the Ministers of Health Canada and Environment Canada (1995). The limits were exceeded in sample concentrations of five insecticides–carbaryl, chlorpyrifos, Diazinon, Lindane, and Malathion (fig. 6). Eleven of the pesticides detected in this study have chronic aquatic-life criteria recommended by Norris and Dost (1991), the U.S. Environmental Protection Agency (1998), and others. These limits were exceeded by concentrations of Lindane, Diazinon, and carbaryl. The aquatic-life

SAMPLE SITES

PESTICIDES	*Juanita Creek*	*Lyon Creek*	*Sunset Creek*	*Des Moines Creek*	*North Fork Thornton Creek*	*Valley Creek*	*Lewis Creek*	*Miller Creek*	*Longfellow Creek*	*Thornton Creek*	*South Fork Thornton Creek*	*Little Soos Creek*
2,4-D	X	X	X	X	X	X	X	X	X	X	X	X
4-Nitrophenol*	X	X	X	X	X	X	X	X	X	X	X	X
Diazinon	X	X	X	X	X	X	X	X	X	X	X	X
Dichlobenil	X	X	X	X	X	X	X	X	X	X	X	X
MCPP (Mecoprop)	X	X	X	X	X	X	X	X	X	X	X	X
Pentachlorophenol	X	X	X	X	X	X	X	X	X	X	X	X
Prometon	X	X	X	X	X	X	X	X	X	X	X	X
Trichlopyr	X	X	X	X	X	X		X	X	X	X	X
MCPA	X	X	X	X	X	X	X		X		X	
Atrazine	X	X	X	X	X		X	X		X		
Benzamide, 2,6-dichloro-*		X	X	X	X		X	X		X	X	
Carbaryl	X	X	X		X	X		X		X	X	
Simazine	X	X	X	X	X		X			X	X	
Dicamba	X	X		X					X			
Lindane	X		X			X						X
Malathion	X	X				X		X				
Dichlorprop		X		X					X			
Metolachlor	X					X		X				
Trifluralin	X		X	X								
Desethylatrazine*			X				X					
EPTC	X						X					
Napropamide		X	X									
Acetochlor									X			
Chlorpyrifos						X						
Oxadiazon				X								
Tebuthiuron					X							

X - compound was detected

* - pesticide transformation product

Table 3. Pesticides and pesticide transformation products detected at sample sites, King and Snohomish Counties, Washington, 1998.

Table 4. Concentrations of all pesticides and pesticide transformation products detected in stream-water samples, King and Snohomish Counties, Washington, 1998

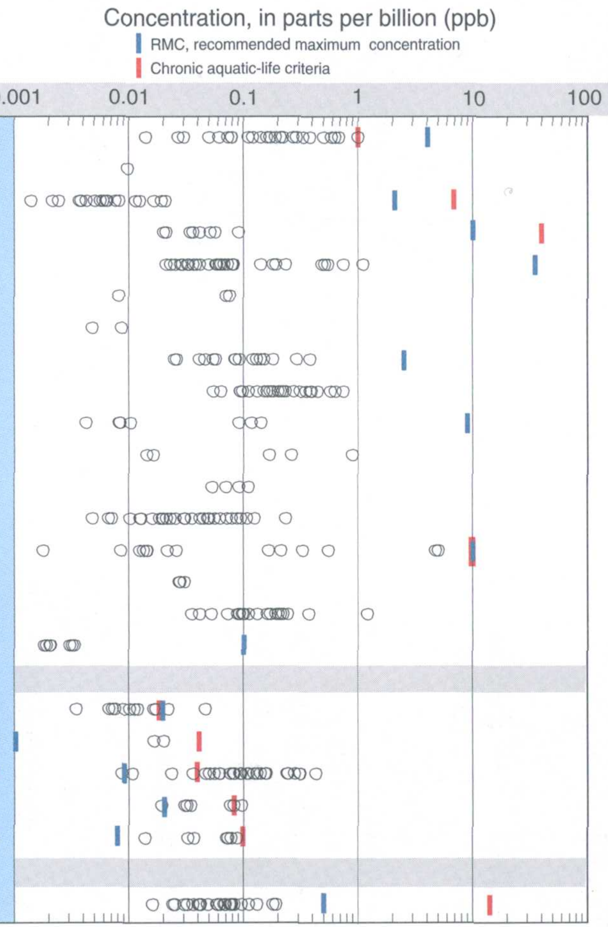
[J, Estimated value, Ecology; E, Estimated value, USGS; *, pesticide transformation product; --, no data. All values are in micrograms per liter, µg/L]

Sample site name	Sample	2,4-D	2,6-Dichloro-benzamide*	4-Nitro-phenol*	Aceto-chlor	Atrazine	Carbaryl	Chlor-pyrifos	Desethyl-atrazine*	Diaz-inon	Dicamba	Dichlo-benil	Dichlor-prop	EPTC
Des Moines Creek	1	--	J0.01	J0.04	--	0.006	--	--	--	0.009	--	J0.03	--	--
	2	0.29	J0.01	0.07	--	E0.004	--	--	--	0.036	0.06	J0.04	0.07	--
	3	0.11	--	J0.05	--	0.012	--	--	--	--	--	0.05	--	--
	4	0.22	--	0.12	--	0.008	--	--	--	0.036	J0.02	0.07	--	--
Miller Creek	1	J0.01	J0.04	--	--	0.006	--	--	--	--	--	J0.03	--	--
	2	0.05	J0.05	J0.05	--	0.008	--	--	--	0.011	--	J0.03	--	--
	3	0.06	--	0.08	--	--	E0.046	--	--	0.108	--	0.06	--	--
Little Soos Creek	1	--	--	--	--	--	--	--	--	--	--	--	--	--
	2	--	--	--	--	--	--	--	--	--	--	--	--	--
	3	--	--	--	--	--	--	--	--	--	--	--	--	--
	4	J0.01	--	J0.06	--	--	--	--	--	0.157	--	0.14	--	--
Longfellow Creek	1	0.21	--	J0.05	--	--	--	--	--	--	0.05	0.06	--	--
	2	0.17	--	J0.06	0.01	--	--	--	--	--	--	J0.03	--	--
	3	0.27	--	0.12	--	--	--	--	--	0.046	--	J0.04	0.08	--
Valley Creek	1	0.38	--	--	--	--	--	--	--	0.05	--	0.07	--	--
	2	0.33	--	--	--	--	--	0.02	--	0.061	--	0.51	--	--
	3	0.68	--	0.16	--	--	E0.007	0.02	--	0.055	--	0.19	--	--
Sunset Creek	1	0.19	J0.02	0.4	--	--	--	--	--	0.08	--	0.23	--	--
	2	0.59	J0.02	0.24	--	0.011	E0.017	--	E0.005	0.122	--	1.1	--	--
	3	0.50	--	0.24	--	0.006	E0.01	--	--	0.13	--	0.74	--	--
Juanita Creek	1	1.0	--	0.29	--	--	--	--	--	0.242	0.09	J0.08	--	--
	2	0.63	--	0.25	--	0.004	E0.022	--	--	0.276	J0.03	0.54	--	--
	3	0.59	--	0.22	--	--	E0.017	--	--	0.309	0.04	0.18	--	0.009
Lewis Creek	1	J0.03	--	0.07	--	--	--	--	--	0.238	--	J0.02	--	0.005
	2	--	J0.02	J0.02	--	E0.002	--	--	--	0.105	--	J0.02	--	--
	3	0.12	J0.04	J0.05	--	E0.002	--	--	E0.002	0.094	--	J0.04	--	--
Lyon Creek	1	0.29	J0.03	--	--	0.019	E0.012	--	--	0.305	J0.04	0.06	--	--
	2	0.14	J0.03	J0.04	--	0.021	E0.011	--	--	0.425	J0.02	0.06	J0.01	--
Thornton Creek Golf Course	1	0.16	J0.02	J0.04	--	0.005	--	--	--	0.092	--	J0.03	--	--
	2	0.08	J0.03	--	--	0.006	E0.003	--	--	0.076	--	J0.03	--	--
	3	0.07	--	J0.03	--	0.006	--	--	--	0.061	--	J0.04	--	--
Thornton Creek South Fork	1	0.08	J0.02	0.08	--	--	E0.008	--	--	0.094	--	J0.03	--	--
	2	0.11	--	0.08	--	--	E0.009	--	--	0.154	--	0.06	--	--
Thornton Creek	1	0.11	J0.02	J0.06	--	--	--	--	--	0.139	--	0.08	--	--
	2	0.12	J0.02	0.08	--	E0.004	E0.007	--	--	0.152	--	0.08	--	--

Table 4. Concentrations of all pesticides and pesticide transformation products detected in stream-water samples, King and Snohomish Counties, Washington, 1998--Continued

Sample site name	Sample	Lindane	Mala-thion	MCPA	MCPP	Metol-achlor	Naprop-amide	Oxa-diazon	Penta-chloro-phenol	Prometon	Simazine	Tebu-thiuron	Trichlopyr	Trifluralin
Des Moines Creek	1	--	--	--	--	--	--	J0.07	0.18	0.035	--	--	--	--
	2	--	--	--	0.17	--	--	0.05	0.069	0.233	--	--	0.1	--
	3	--	--	--	0.18	--	--	0.09	0.082	0.106	0.026	--	0.19	E0.002
	4	--	--	0.09	0.27	--	--	J0.11	0.095	0.124	--	--	1.2	E0.003
Miller Creek	1	--	--	--	--	0.116	--	--	J0.016	0.02	--	--	0.09	--
	2	--	--	--	0.2	0.09	--	--	0.075	0.02	--	--	0.1	--
	3	--	0.078	--	0.21	0.141	--	--	0.076	0.055	--	--	0.05	--
Little Soos Creek	1	--	--	--	--	--	--	--	--	--	--	--	--	--
	2	--	--	--	--	--	--	--	--	--	--	--	--	--
	3	--	--	--	--	--	--	--	--	--	--	--	--	--
	4	--	--	--	0.09	--	--	--	0.025	E0.016	--	--	0.05	--
Longfellow Creek	1	--	--	0.29	0.18	--	--	--	0.04	--	--	--	0.13	--
	2	--	--	J0.06	0.23	--	--	--	0.062	0.124	--	--	0.19	--
	3	--	--	--	0.35	--	--	--	0.19	0.049	--	--	0.09	--
Valley Creek	1	0.095	0.014	--	0.27	0.01	--	--	0.11	E0.013	--	--	--	--
	2	0.082	--	0.08	0.22	0.008	--	--	0.059	E0.01	--	--	0.21	--
	3	0.019	--	0.09	0.38	0.008	--	--	0.13	E0.013	--	--	0.24	--
Sunset Creek	1	--	--	0.18	0.31	--	0.167	--	--	--	--	--	0.2	E0.002
	2	0.032	--	0.15	0.63	--	0.884	--	0.067	0.03	0.008	--	0.1	E0.002
	3	0.076	--	0.13	0.57	--	0.260	--	0.079	0.025	--	--	0.11	--
Juanita Creek	1	--	0.087	0.38	0.74	--	--	--	--	0.05	--	--	--	E0.002
	2	0.034	0.073	0.12	0.39	--	--	--	0.076	0.087	0.014	--	0.17	E0.003
	3	0.03	0.071	0.14	0.44	0.004	--	--	0.077	0.078	0.026	--	0.1	E0.003
Lewis Creek	1	--	--	--	0.06	--	--	--	J0.016	--	--	--	--	--
	2	--	--	J0.04	0.11	--	--	--	--	E0.007	E0.002	--	--	--
	3	--	--	--	0.13	--	--	--	--	E0.007	--	--	--	--
Lyon Creek	1	--	0.033	--	0.15	--	0.02	--	0.036	0.031	4.73	--	0.13	--
	2	--	0.037	J0.03	0.13	--	0.01	--	0.042	0.042	4.99	--	0.09	--
Thornton Creek Golf Course	1	--	--	J0.05	0.16	--	--	--	0.032	0.019	0.013	0.028	0.04	--
	2	--	--	--	0.1	--	--	--	0.024	0.021	0.014	0.027	--	--
	3	--	--	J0.05	0.11	--	--	--	0.048	0.062	0.022	0.03	0.04	--
Thornton Creek South Fork	1	--	--	--	J0.05	--	--	--	0.03	0.023	0.211	--	0.07	--
	2	--	--	J0.03	J0.06	--	--	--	0.041	0.094	0.164	--	0.16	--
Thornton Creek	1	--	--	--	0.09	--	--	--	0.058	0.071	0.326	--	0.22	--
	2		--	--	0.11	--	--	--	0.078	0.045	0.549	--	0.37	--

Active ingredient and trade name[1] example in parentheses	Freshwater aquatic-life criteria, in parts per billion (-- no aquatic-life criteria exist)		
	Acute	Chronic	RMC
Herbicide			
2,4-D (Weedone)	[4]10	[4]1	[5,2]4
Acetochlor (Guardian)	--	--	--
Atrazine (AAtrex)	[4]70	[4]7	[5]2
Dicamba (Banvel)	[4]390	[4]39	[5]10
Dichlobenil (Casoron)	--	--	[2]37
Dichlorprop (2,4-DP)	--	--	--
EPTC (Eptam)	--	--	--
MCPA (Kilsem)	--	--	[5]2.6
MCPP (Mecoprop)	--	--	--
Metolachlor (Dual)	--	--	[5]8
Napropamide (Devrinol)	--	--	--
Oxadiazon (Ronstar)	--	--	--
Prometon (Pramitol)	--	--	--
Simazine (Princep)	[4]100	[4]10	[2,5]10
Tebuthiuron (Spike)	--	--	--
Triclopyr (Garlon)	[4]5,600	[4]560	--
Trifluralin (Treflan)	--	--	[5]0.1
Insecticide			
Carbaryl (Sevin)	[4]0.17	[4]0.017	[2]0.02
Chlorpyrifos (Dursban)	[3,7]0.083	[3,7]0.041	[2]0.001
Diazinon (Diazinon)	[6]0.16	[6]0.04	[2]0.009
gamma-HCH (Lindane)	[3]0.95	[7]0.08	[2]0.02
Malathion (Malathion)	--	[3]0.1	[2]0.008
Fungicide			
Pentachlorophenol (Penta)	[3,8]19	[3,8]15	[5]0.5



1 Use of trade names is for descriptive purposes and does not imply endorsement by the U.S. Geological Survey, the Department of Ecology, or King County
2 *National Academy of Sciences and National Academy of Engineering*, 1973
3 U.S. Environmental Protection Agency, 1998
4 Norris and Dost, 1991, Table 3
5 Ministers of Health Canada and Environment Canada, 1995
6 Menconi and Cox, 1994
7 State of Washington, 1992
8 Criteria are pH dependent; values shown calculated at pH of 7.8

Figure 6. Concentrations of detected pesticides and their relations to criteria to protect aquatic life.

criteria indicate concentrations that may adversely affect aquatic organisms. However, the ecological effects in the streams sampled are unknown because the duration of exposure to the concentrations observed and the combined effects of many pesticides in stream water are unknown.

RELATING GENERAL WATER-QUALITY FINDINGS TO RETAIL SALES OF PESTICIDES

The following section discusses how pesticides sold in 10 home and garden stores located in urban and suburban areas in King and Snohomish Counties relate to pesticide detections in the study area watersheds.

The Retail Sales Database

In 1997, King County assembled a database of retail pesticide sales to study the pesticides that King County residents were purchasing and applying to their lawns and gardens. Sales data for 61 pesticides were obtained from 10 home and garden stores located in urban and suburban areas in King and south Snohomish Counties. It was assumed that the sales numbers represent pesticide sales throughout western King County because according to a 1996 survey of 1,200 King County residents (Market Trends Incorporated, 1996), two-thirds of retail pesticide sales are from home and garden stores.

The measured quantity was a "unit" or package of active ingredient sold. Often two or more active ingredients are combined in a package of pesticide. For example, if a package contains the active ingredients 2,4-D and MCPP, these pesticides would be counted in the retail pesticide database as one unit sold of 2,4-D and one unit sold of MCPP. The total units sold from the 10 stores are shown in figure 7.

Estimating the amounts of pesticides applied in watersheds was not possible because of two limitations in the 1997 retail sales data. First, the counted packages (units) varied in size and in concentration of active ingredients. Second, some active ingredients were not counted because only the first two active ingredients listed on a package were recorded into the database even though the product might contain several more active ingredients. One known instance is for the herbicide dicamba, which is listed as the third active ingredient in some products. However the number of packages (units) sold do indicate consumer preference and thus is some indication of how widely the active ingredient is used in residential areas.

The rest of this report compares data in the pesticide retail sales database with pesticides detected in the stream-water samples collected for this study. The studied pesticides are grouped in the following categories:

- pesticides sold in retail stores and detected in stream-water samples,
- pesticides sold in retail stores but not detected,
- pesticides not sold in retail stores but detected,
- pesticides not sold in retail stores and not detected, and
- pesticides sold in retail stores but not sampled for.

Pesticides Sold in Retail Stores and Detected in Stream-Water Samples

Twelve pesticides detected in stream-water samples were sold in retail stores (table 5). High retail sales of several of these pesticides probably contribute to their being detected. This assumption was made because the pesticides 2,4-D, MCPP, and Diazinon (which had the highest unit sales of the pesticides sampled for) were detected at 100 percent of the sampling sites.

Table 5. Pesticides with retail sales and detected in stream-water samples, King and Snohomish Counties, Washington, 1998

Pesticide	Units sold, 1997	Percent of sites detected
2,4-D	47,950	100
carbaryl	2,722	67
chlorpyrifos	15,830	8
Diazinon	18,695	100
dichlobenil	16,652	100
EPTC	138	16
Malathion	1,335	33
MCPA	5,112	73
MCPP	52,673	100
prometon	6,051	100
triclopyr	4,918	91
trifluralin	5,803	25

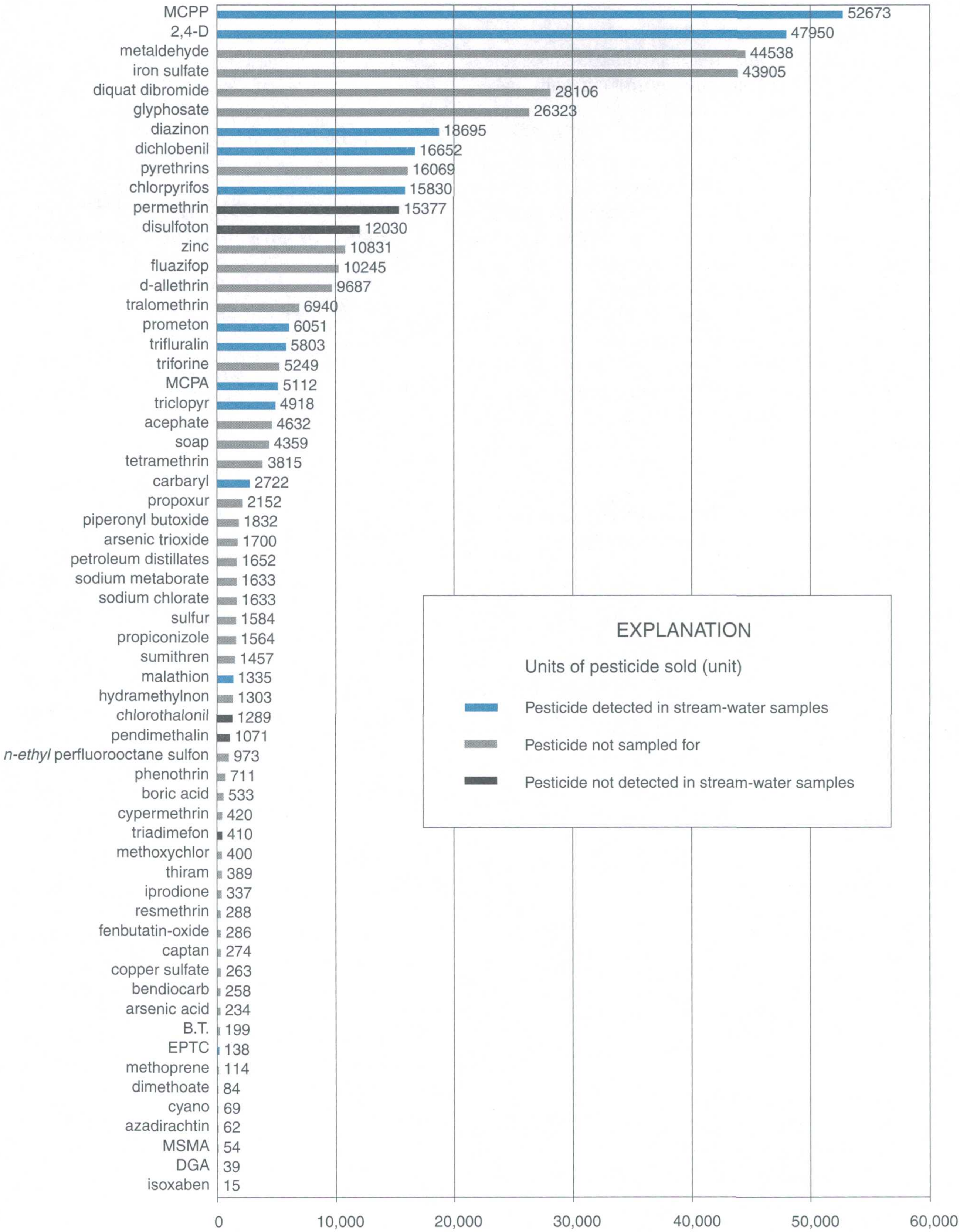


Figure 7. Units of pesticide sold in 1997 at 10 home and garden stores located in western King and south Snohomish Counties (Market Trends, Incorporated, 1996).

Application of pesticides sold in retail outlets is a possible source of other frequently detected pesticides (such as dichlobenil and chlorpyrifos) that also have relatively high unit sales (fig. 8).

Relating pesticide concentrations found in stream water to the number of units of pesticides sold in home and garden stores was not attempted because tracking the many factors that influence pesticide distribution, degradation, and transport was beyond the scope of this study. Although this study did not determine how pesticides sold in home and garden stores are related to concentrations in urban streams, it is a starting point to determine which pesticides are found in urban streams and to determine whether the detected concentrations are exceeding aquatic-health criteria. It is hoped that this report will suggest ideas for further studies.

Pesticides Sold in Retail Stores but Not Detected in Stream-Water Samples

Five pesticides were sold in retail stores but were not detected in stream-water samples (table 6). They include two insecticides (permethrin, 15,377 units sold, and disulfoton, 12,030 units sold), two fungicides (chlorothalonil, 1,289 units sold, and triadimefon, 410 units sold), and one herbicide (pendimethalin, 1,071 units sold).

Table 6. Pesticides with retail sales and not detected in stream-water samples, King and Snohomish Counties, Washington, 1998

Pesticide	Units sold, 1997
Permethrin	15,377
Disulfoton	12,030
Chlorothalonil	1,289
Pendimethalin	1,071
Triadimefon	410

A plausible explanation for not detecting the insecticides is that they might not be widely distributed in the sampled watersheds. This is because insecticides tend to be applied to small areas of insect infestation, whereas herbicides are believed to be combined with fertilizer and applied to entire lawns periodically through the growing season. The fungicides have lower sales than the insecticides and are also believed to be applied to problem areas.

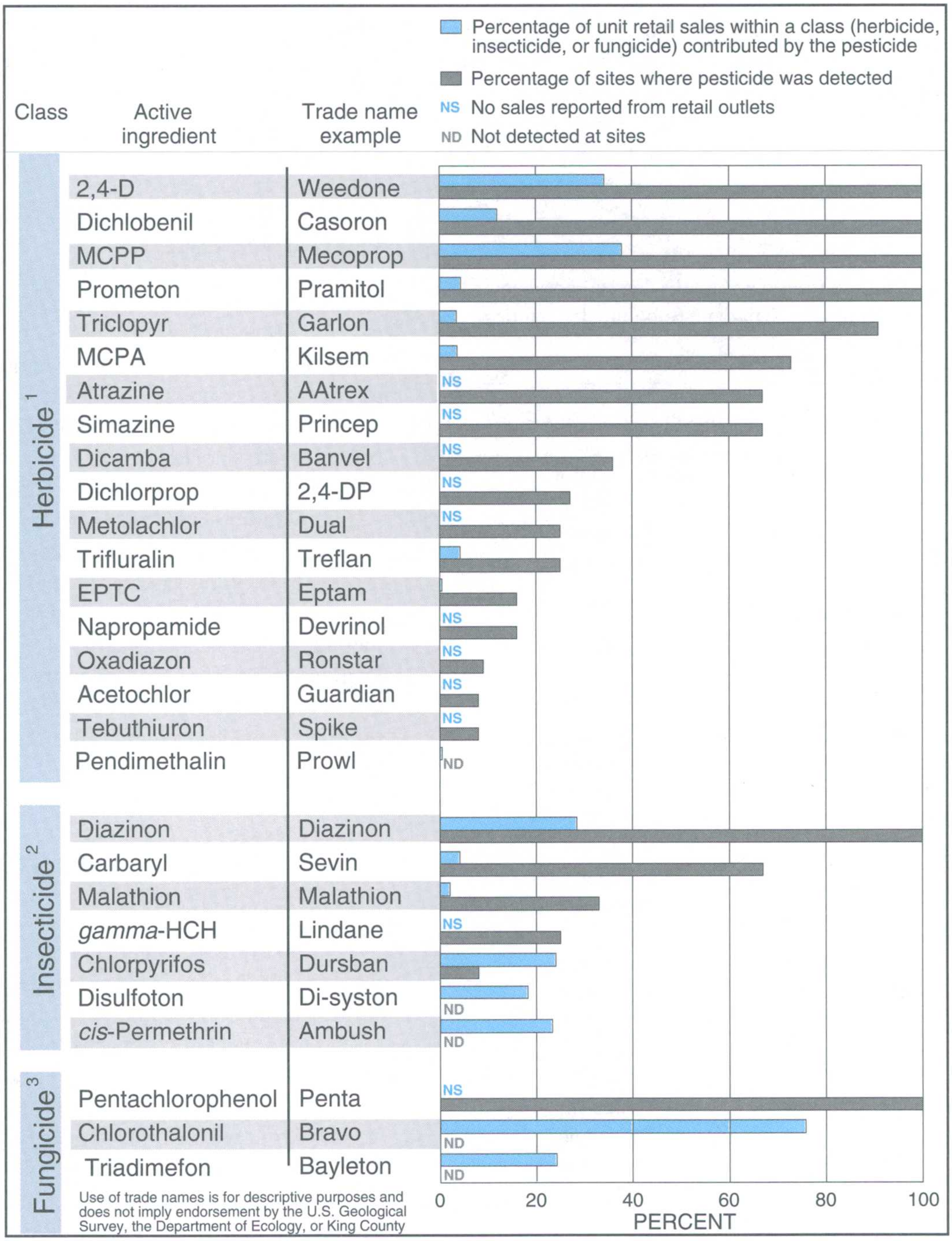
Pesticides Not Sold in Retail Stores but Detected in Stream-Water Samples

Pesticides not sold in retail stores but detected in stream-water samples (table 7) probably originate from applications to nonresidential areas. Detected pesticides with a relatively small number of units sold (prometon, triclopyr, MCPA–see table 5) also may possibly be from nonresidential rather than residential applications.

Table 7. Pesticides with no retail sales but detected in stream-water samples, King and Snohomish Counties, Washington, 1998

Pesticide	Percent of sites detected
Acetochlor	8
Atrazine	67
Dicamba	36
Dichlorprop	27
gamma-HCH (Lindane)	25
Metolachlor	25
Napropamide	16
Oxadiazon	9
Pentachlorophenol	100
Simazine	67
Tebuthiuron	8

It should be noted that detections of pesticides with little or no reported retail sales could still result, in part, from residential sales if one or more active ingredients mixed in the formulation were not reported. For example, dicamba, detected at nearly 40 percent of the study sites, is the third active ingredient listed in some combined fertilizer-pesticide products sold in home and garden stores. Also, pentachlorophenol was not shown in the database as being sold in retail stores, but it was detected in all the basins. It is a popular wood preservative.



[1] Unit retail sales for these herbicides total to 140,000 units
[2] Unit retail sales for these insecticides total to 66,000 units
[3] Unit retail sales for these fungicides total to 1,700 units

Figure 8. Comparisons of units of pesticides sold with the percentage of study watersheds where pesticide detections occurred, King and Snohomish Counties, Washington, 1998.

Pesticides Not Sold in Retail Stores and Not Detected in Stream-Water Samples

Sixty-six pesticides sampled for but not sold in retail stores were not detected (table 8). For the most part, the fact that these pesticides were not sold or detected indicates little usage in urban watersheds. This conclusion is consistent with findings based on samples from 58 rivers and streams across the United States (Larson and others, 1996). Several of the pesticides not detected in samples collected during this study were either not detected or detected infrequently in samples from urban streams across the United States. Examples are the herbicides terbacil and triallate and the insecticides azinphos-methyl and carbofuran.

Table 8. Pesticides with no retail sales and not detected in stream-water samples, King and Snohomish Counties, Washington, 1998

Pesticides	
2,3,4,5-tetrachlorophenol	Fenarimol
2,3,4,6-tetrachlorophenol	Fluridone
2,4,5-T	Fonofos
2,4,5-TB	Hexazinone
2,4,5-TP	Ioxynil
2,4,5-trichlorophenol	Linuron
2,4,6-trichlorophenol	Metalaxyl
2,4-DB	Metribuzin
3,5-dichlorobenzoic acid	MGK264
Acifluorfen	Molinate
Alachlor	Norflurazon
Alpha-HCH	Oxyfluorfen
Ametryn	*p,p'*-DDE
Atraton	Parathion
Azinphos-methyl	Parathion-methyl
Benfluralin	Pebulate
Bentazon	Phorate
Bromacil	Picloram
Bromoxynil	Profluralin
Butachlor	Prometryn
Butylate	Propachlor
Carbofuran	Propanil
Carboxin	Propargite
Chlorpropham	Propazine
Cyanazine	Propyzamide
Cycloate	Terbacil
DCPA	Terbufos
Diallate	Terbutryn
Diclofop-methyl	Thiobencarb
Dieldrin	Triallate
Dinoseb	Vernolate
Diphenamid	
Diuron	
Ethalfluralin	
Ethoprophos	

Pesticides Sold in Retail Stores but Not Assessed

Sixty-one active ingredients were listed as sold in retail home and garden stores. Seventeen of the 61 were sampled for, leaving 44 pesticides (table 9) sold in retail stores but not sampled for.

Pesticides routinely analyzed at the USGS NWQL were selected because they are most frequently sold in the United States and are fairly easy to extract (Gilliom and others, 1995). Thus, there was a gap between what was sold and what was sampled for.

Some of the sales of the pesticides not sampled were relatively large. For example, 44,538 units of metaldehyde and 26,323 units of glyphosate were sold. Pesticides that were sold in equivalent numbers (52,673 units of MCPP and 47,950 of 2,4-D) and sampled for were found in all of the sample sites (except the reference site).

IMPLICATIONS OF THIS STUDY FOR FUTURE RESEARCH

This study is valuable as an exploratory study for future work in measuring pesticide concentrations in surface water and has many implications for further research. A weak relation was found between pesticide sales and some pesticide concentrations in stream water. This does not necessarily imply that pesticides are not being washed into the surface water. In fact, there are many intervening variables that could contribute to these weak relations, and these variables need further study before any definitive conclusions can be drawn.

In this study, it was assumed that most pesticides were purchased in the spring for immediate use. This might not necessarily be the case. Pesticides might be purchased in the spring for use throughout the spring and summer. If this is the case, sampling of surface water in the spring might measure only initial applications. It would therefore be interesting to study the

Table 9. Pesticides and other compounds with retail sales that were not sampled for, King and Snohomish Counties, Washington, 1998

Pesticide	Units sold, 1997	Pesticide	Units sold, 1997
Acephate	4,632	Metaldehyde	44,538
Arsenic Acid	234	Methoprene	114
Arsenic trioxide	1,700	Methoxychlor	400
Azadirachtin	62	MSMA	54
B.T.	199	*N-ethyl* perfluorooctane sulfon	973
Bendiocarb	258	Petroleum distillates	1,652
Boric Acid	533	Phenothrin	711
Captan	274	Piperonyl butoxide	1,832
Copper sulfate	263	Propiconizole	1,564
Cyano	69	Propoxur	2,152
Cypermethrin	420	Pyrethrins	16,069
D-allethrin	9,687	Resmethrin	288
DGA	39	Soap	4,359
Dimethoate	84	Sodium chlorate	1,633
Diquat dibromide	28,106	Sodium metaborate	1,633
Fenbutatin-oxide	286	Sulfur	1,584
Fluazifop	10,245	Sumithren	1,457
Glyphosate	26,323	Tetramethrin	3,815
Hydramethylnon	1,303	Thiram	389
Iprodione	337	Tralomethrin	6,940
Iron sulfate	43,905	Triforine	5,249
Isoxaben	15	Zinc	10,831

concentrations of pesticides in surface water throughout the spring and summer to determine if any relations could be found.

This study serves as a general survey of pesticide concentrations during a limited time frame. However, not all pesticides are the same–they have different properties. Some pesticides are transformed faster in the environment than others. Pesticides also have different transport times and different solubilities in water. Again, a study that encompasses a larger time frame and that measures and analyzes each pesticide concentration within the context of its unique properties (such as transformation time, transformation products, and transport time) would be useful.

Future studies relating sales data to pesticide concentrations might also benefit from standardizing and quantifying unit sales, such as pounds of active ingredients. Unfortunately, for this study, unit sales could not be broken down into quantifiable units that could be compared across pesticides or meaningfully compared to pesticide concentrations found in surface water. Ranking pesticides by their toxicity to aquatic life would also help assess the relative environmental impact of pesticides. Future studies could focus on these problems in the data-collection phase.

SUMMARY

In Spring 1998, the U.S. Geological Survey and the Washington State Department of Ecology cooperated in sampling 13 sites in 11 watersheds during storms, when more pesticides and higher concentrations might be detected than at any other time of the year.

Ninety-eight pesticides and pesticide transformation products were sampled for at each site. The USGS used the 2010 laboratory schedule, and Ecology used the chlorinated herbicide and nitrogen-containing laboratory schedules.

Twenty-six of the 98 pesticides and pesticide transformation products were detected–23 pesticides (17 herbicides, 5 insecticides, and 1 fungicide) and 3 transformation products. The herbicides dichlobenil, 2,4-D, MCPP, the insecticide Diazinon, and the fungicide pentachlorophenol were detected at all of the urban study sites.

Five insecticides–carbaryl, chlorpyrifos, Diazinon, Lindane, and Malathion exceeded maximum concentration limits for the protection of aquatic life established by the National Academy of Sciences and National Academy of Engineering (NAS/NAE) or the Ministers of Health Canada and Environment Canada. Lindane, Diazinon, and carbaryl exceeded chronic aquatic-life criteria recommended by Norris and Dost, the U.S. Environmental Protection Agency, and others.

Sales data for 61 pesticides were obtained from 10 home and garden stores located in urban and suburban areas in King and south Snohomish Counties. Estimating the amounts of pesticides applied in watersheds was not possible because of two limitations in the 1997 retail sales data. First, the counted packages (units) varied in size and in concentration of active ingredient. Second, some active ingredients were not counted. However, the number of packages (units) sold did indicate consumer preference and thus is some indication of how widely the active ingredient is used in residential areas.

Twelve pesticides detected in stream-water samples were sold in retail stores. High retail sales of 2,4-D, MCPP, and Diazinon probably contributed to their being detected at 100 percent of the sampling sites. Application of pesticides sold in retail outlets was a possible source of other frequently detected pesticides (such as dichlobenil and chlorpyrifos) that also have relatively high unit sales.

Five pesticides sold in retail stores were not detected in stream-water samples–two insecticides (*cis*-permethrin and disulfoton), two fungicides (chlorothalonil and triadimefon), and one herbicide (pendimethalin). Possibly they were not detected because some of them are relatively insoluble in water and are not likely to be transported in runoff. Alternately, some of them might not be widely distributed in the sampled watersheds.

Pesticides not sold in retail stores but detected in stream-water samples probably originate from applications to nonresidential areas. Detected pesticides with a small number of units sold (prometon, triclopyr, MCPA) also may be from nonresidential rather than residential applications.

This study is valuable as an exploratory study for future work in measuring pesticide concentrations in surface water and has many implications for further research. A weak relation was found between pesticide sales and some pesticide concentrations in stream water. This does not necessarily imply that pesticides are not being washed into the surface waters. In fact, there are many intervening variables that could contribute to these weak relations, and these variables must further be studied before any definitive conclusions can be drawn.

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APPENDICES

Appendix A. Pesticides analyzed by the USGS in this study and their method detection limits
[Abbreviations: H, herbicide; I, insecticide; µg/L, microgram per liter]

Chemical Abstract Service (CAS) identification number	Pesticide name	Pesticide type	Method detection limit (µg/L)
579-66-8	2,6-Diethylaniline*	H	0.003
34256-82-1	Acetochlor	H	0.002
15972-60-8	Alachlor	H	0.002
319-84-6	*alpha*-HCH	I	0.002
1912-24-9	Atrazine	H	0.001
86-50-0	Azinphos-methyl	I	0.001
1861-40-1	Benfluralin	H	0.002
2008-41-5	Butylate	H	0.002
63-25-2	Carbaryl	I	0.003
1563-66-2	Carbofuran	I	0.003
2921-88-2	Chlorpyrifos	I	0.004
21725-46-2	Cyanazine	H	0.004
1861-32-1	DCPA	H	0.002
6190-65-4	Desethylatrazine*	H	0.002
333-41-5	Diazinon	I	0.002
60-57-1	Dieldrin	I	0.001
298-04-4	Disulfoton	I	0.017
759-94-4	EPTC	H	0.002
55283-68-6	Ethalfluralin	H	0.004
13194-48-4	Ethoprophos	I	0.003
944-22-9	Fonofos	I	0.003
58-89-9	Lindane	I	0.004
330-55-2	Linuron	H	0.002
121-75-5	Malathion	I	0.005
51218-45-2	Metolachlor	H	0.002
21087-64-9	Metribuzin	H	0.004
2212-67-1	Molinate	H	0.004
15299-99-7	Napropamide	H	0.003
56-38-2	Parathion	I	0.004
298-00-0	Parathion-methyl	I	0.006
1114-71-2	Pebulate	H	0.004
40487-42-1	Pendimethalin	H	0.004
5264-55-3	*cis*-permethrin	I	0.005
298-02-2	Phorate	I	0.002
72-55-9	*p,p'*-DDE	I	0.006
1610-18-0	Prometon	H	0.018
1918-16-7	Propachlor	H	0.007
709-98-8	Propanil	H	0.004
2312-35-8	Propargite	I	0.013
23950-58-5	Propyzamide	H	0.003
122-34-9	Simazine	H	0.005
34014-18-1	Tebuthiuron	H	0.01
5902-51-2	Terbacil	H	0.007
13071-79-9	Terbufos	I	0.013
28249-77-6	Thiobencarb	H	0.002
2303-17-5	Triallate	H	0.001
1582-09-8	Trifluralin	H	0.002

* Pesticide transformation product.

Appendix B. Nitrogen-containing pesticides analyzed by the Washington State Department of Ecology in this study and their quantitation limits
[µg/L, micrograms per liter]

Chemical Abstract Service (CAS) identification number	Analyte	Quantitation limit [1] (µg/L)
15972608	Alachlor	0.26
834128	Ametryn	0.071
1610179	Atraton	0.21
1912249	Atrazine	0.071
1861401	Benefin	0.11
2008584	Benzamide, 2,6-dichloro-	0.081
314409	Bromacil	0.28
23184669	Butachlor	0.25
2008415	Butylate	0.14
5234684	Carboxin	0.78
1897456	Chlorothalonil	0.17
101213	Chlorpropham	0.028
21725462	Cyanazine	0.11
1134232	Cycloate	0.14
2303164	Diallate	0.27
1194656	Dichlobenil	0.16
957517	Diphenamid	0.21
330541	Diuron	0.48
759944	EPTC	0.14
55283686	Ethalfluralin	0.11
60168889	Fenarimol	0.21
59756604	Fluridone	0.43
51235042	Hexazinone	0.11
57837191	Metalaxyl	0.48
51218452	Metolachlor	0.28
21087649	Metribuzin	0.071
113484	MGK264	0.50
2212671	Molinate	0.14
15299997	Napropamide	0.21
27314132	Norflurazon	0.14
19666309	Oxadiazon	0.04
42874033	Oxyfluorfen	0.28
1114712	Pebulate	0.14
40487421	Pendimethalin	0.11
26399360	Profluralin	0.17
1610180	Prometon	0.071
7287196	Prometryn	0.071
23950585	Pronamide	0.28
1918167	Propachlor	0.17
139402	Propazine	0.071
122349	Simazine	0.072
34014181	Tebuthiuron	0.11
5902512	Terbacil	0.21
886500	Terbutryn	0.071
43121433	Triadimefon	0.18
2303175	Triallate	0.18
1582098	Trifluralin	0.11
1929777	Vernolate	0.14

[1] Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample.

Appendix C. Chlorinated herbicides analyzed for by the Washington State Department of Ecology in this study and their quantitation limits
[µg/L, micrograms per liter]

Chemical Abstract Service (CAS) identification number	Analyte	Quantitation limit [1] (µg/L)
4901513	2,3,4,5-Tetrachlorophenol	0.023
58902	2,3,4,6-Tetrachlorophenol	0.023
93765	2,4,5-T	0.033
93801	2,4,5-TB	0.038
93721	2,4,5-TP (Silvex)	0.033
95954	2,4,5-Trichlorophenol	0.025
88062	2,4,6-Trichlorophenol	0.025
94757	2,4-D	0.042
94826	2,4-DB	0.050
51365	3,5-Dichlorobenzoic Acid	0.042
100027	4-Nitrophenol	0.073
62476599	Acifluorfen (Blazer)	0.17
25057890	Bentazon	0.063
1689845	Bromoxynil	0.042
1861321	DCPA	0.033
1918009	Dicamba	0.042
120365	Dichlorprop	0.046
51338273	Diclofop-methyl	0.063
88857	Dinoseb	0.063
1689834	Ioxynil	0.042
94746	MCPA	0.083
93652	MCPP	0.083
87865	Pentachlorophenol	0.021
1918021	Picloram	0.042
55335063	Trichlopyr	0.035

[1] Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample.

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