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Squalicum Creek Toxics Screening Study

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Squalicum Creek
Toxics Screening Study

by
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January 2004

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Abstract

The Washington State Department of Ecology Environmental Assessment Program conducted water and sediment sampling in the Squalicum Creek watershed in Whatcom County between November 2002 and June 2003. This study prioritized pollution sources and chemicals of concern in the watershed. Results from the study will be used by the Whatcom Watersheds Pledge program to educate residential, commercial, and industrial groups and to reduce pollution sources.

Water was analyzed at seven sites for a suite of pesticides and herbicides, five metals (arsenic, copper, lead, mercury, zinc), pH, temperature, conductivity, hardness, and total suspended solids. Fourteen pesticides and breakdown products were detected among the sampling sites; two pesticides exceeded water quality criteria for the protection of aquatic life. All five metals were detected at all sites, with two metals exceeding criteria.

Sediment was analyzed at five sites for semi-volatile organic carbon compounds (SVOCs), #2 diesel, lube oil, five metals (arsenic, copper, lead, mercury, zinc), grain size, and total organic carbon. Thirty-three SVOCs were detected in sediments; five of these SVOCs were above the recommended freshwater sediment quality values for the protection of aquatic life. High concentrations of lube oil were found at a majority of the sampling sites. All five metals were detected at all sites, with zinc exceeding its recommended sediment quality value at two stations.

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Introduction

The city of Bellingham is drained via three major streams: Whatcom Creek, Padden Creek, and Squalicum Creek.

In 1998 community organizers created the Whatcom Watersheds Pledge (Pledge) program with the goal of reducing nonpoint pollution from residential and commercial sources. The Pledge program is a collaborative effort among the Port of Bellingham, RE Sources, Sustainable Connections, Whatcom County Solid Waste Division, Whatcom County Health Department, Washington State Department of Ecology, Western Washington University, and the cities of Bellingham, Blaine, Everson, and Sumas. These entities work together to identify pollutants in local waterbodies and provide educational materials and technical assistance to Whatcom County businesses and residents to help them identify and implement actions they can take to reduce water pollution. The Pledge program has been implemented in watersheds throughout Whatcom County.

Water, sediment, and fish sampling conducted on Whatcom Creek helped identify contaminants of concern. The Pledge program then recommended specific actions residents could take to reduce those pollutants. Residents pledged to reduce or eliminate detrimental activities or use safer alternatives.

Sampling activities in the Padden Creek watershed examined pesticides and herbicides in water. A progress report was published in 2001 (Seiders 2001), and the final report was released in late October 2003 (Seiders 2003). Pledge program managers desired to conduct a comprehensive examination of potential contaminations in Squalicum Creek, which is the focus of this report.

The Squalicum Creek watershed drains 6,750 hectares of land. The combined creeks and tributaries create 84 kilometers of stream habitat that drain water from land of varying uses (Downen 1999). The creek provides habitat for five salmonid species including chum, chinook, coho, steelhead trout, and sea-run cutthroat trout (Washington Department of Fish and Wildlife 1998). Agriculture and forest lands are the predominant land use in the upper portion of the watershed. Land use in the lower portion is mainly commercial, industrial, and residential.

Although there have been previous studies on Squalicum Creek, little data have been generated regarding the presence and concentration of toxic contaminants. In order to fill in these data gaps, sediment and water from the Squalicum Creek watershed were collected and analyzed for a range of potential contaminants.

Study Objectives

The objectives of the Squalicum Creek monitoring program were to:

- Characterize baseline concentrations of pesticides, herbicides, and breakdown products of oil, gas, and diesel in Squalicum Creek and its tributaries.
- Identify chemicals of concern in the Squalicum Creek watershed.
- Prioritize drainage basins to the Squalicum Creek watershed for source control and education efforts by the Whatcom Watersheds Pledge program.

Methods

Sampling Design

The Squalicum Creek watershed was split into six regions for a risk assessment completed by Chen (2001). Each region boundary was defined by similarities in land use types, topography, and hydrology (Chen 2001). The six land use regions are shown in Table 1 and Figure 1.

Table 1. Land use, topography, and hydrology of the six land use regions.

Region	Land Use	Topography and Hydrology
1	Port facilities, residential, park, and transportation	Lower portion of Squalicum Creek
2	Commercial, heavy industrial, agricultural, and undeveloped	One natural lake, two constructed lakes, and middle section of both Squalicum and Baker
3	Commercial, residential, golf course, and undeveloped	Middle section of Baker Creek
4	Forested, undeveloped, agricultural, and residential	Two natural lakes and a section of Squalicum Creek headwaters
5	Agricultural, residential, and forested	Section of Squalicum Creek headwaters
6	Agricultural, residential, forested, and undeveloped	Upstream portion of Baker Creek

Ecology collected water and sediment from four of the six regions to screen for potential sources of contaminants.

Water samples were collected at seven stations (Figure 2 and Appendix Table A1) during three storm events. The stations were spread across the watershed to characterize varying land use types. Four of the sites were on the mainstem of Squalicum Creek, and the remaining sites were on major tributaries. Analysis included zinc, lead, mercury, arsenic, copper, total suspended solids (TSS), hardness, pesticides, and herbicides.

Sediment was collected from four stormwater catch basins and ditches entering Squalicum Creek (Figure 2 and Appendix Table A2). The catch basins were located in developed urban areas. A fifth background station was located in an undeveloped rural area in the upper watershed. The background station was in Squalicum Lake, a natural surface waterbody. Analysis of sediments included semi-volatile organic carbon compounds (SVOCs), zinc, lead, mercury, arsenic, copper, grain size, total organic carbon (TOC), lube oil, and #2 diesel.

Water results were compared to Washington State Water Quality Standards (WAC 1997), U.S. Environmental Protection Agency's Quality Criteria for Water (EPA 1986), and any other applicable water quality standards. Sediment results were compared to recommended freshwater sediment quality values (FSQVs) for Washington State (SAIC and Avocet 2002, SAIC and Avocet 2003).

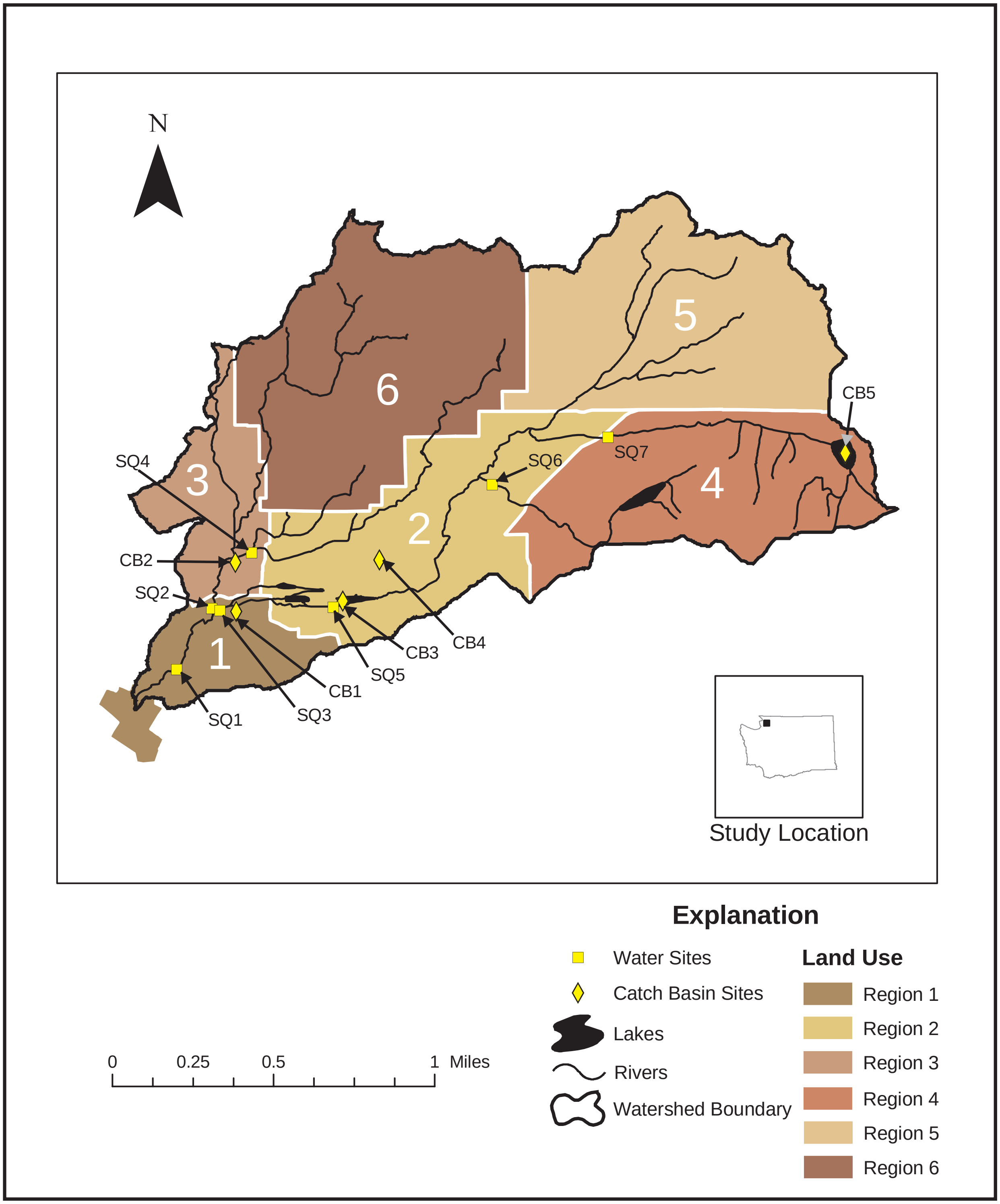

Figure 1. Land use regions for the Squalicum Creek watershed.

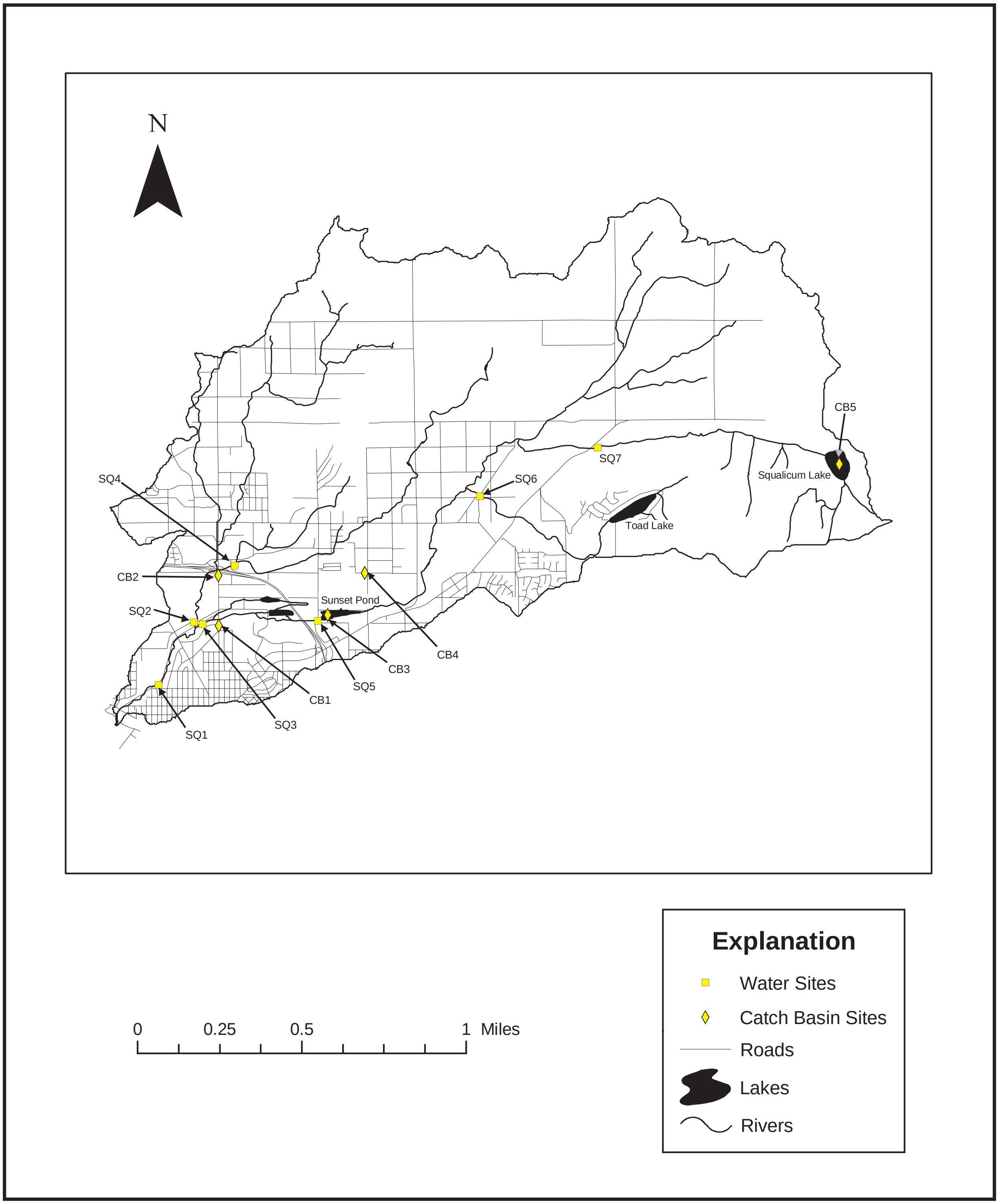

Figure 2. Water and catch basin sampling sites in the Squalicum Creek watershed.

Data generated from this project were used to produce a list of chemicals of concern prioritized by sampling locations. A chemical was considered of concern if it exceeded applicable water or sediment quality values. The information generated was also used to prioritize drainage basins for educational and source-control efforts.

Water Sampling

Surface water was collected during storm events preceded by several days of dry weather. Samples were collected using a U.S. Geological Survey (USGS) depth-integrating sampler when stream depth was greater than one foot. A hand held bottle was used to collect samples where the water depth was less than one foot. Samples were collected at three points (quarter point transect) across the stream at each site to create a single composite sample. These sub-samples were then split into one-gallon glass sample containers. Dissolved metal sampling followed EPA method 1669 (EPA 1996).

All sampling equipment was cleaned prior to use. Cleaning consisted of scrubbing with Liquinox® detergent followed by sequential rinses with tap water, 10% nitric acid, deionized water, and pesticide grade acetone. All cleaned equipment was wrapped in aluminum foil to prevent contamination. Sample bottles were supplied by Manchester Environmental Laboratory (MEL) and were specially cleaned by the manufacturer according to EPA (1990) specifications.

All sample containers were placed on ice in coolers immediately after collection. Samples then were transported to Ecology headquarters where they were stored in a refrigerator at 4˚C until transport to MEL by Ecology's courier. Chain-of-custody procedures were used for all samples.

Temperature, pH, and conductivity were measured at the time of sampling. Flow was also measured, but only one measurement was usable. All measurements were missing from the first sampling event, and several measurements were incomplete from the third event. As a result, flow was not used in the data analysis. Temperature was measured with an alcohol thermometer. pH was measured with an Orion Model 250 temperature-compensating pH meter. Specific conductance was measured using a YSI Model 33 S-C-T meter. Sample locations were recorded with a Magellan GPS 320 global positioning receiver.

Sediment Sampling

Sediment was collected once from catch basins that drain to Squalicum Creek. Samples were collected using a 0.02 m^2 stainless steel Petite Ponar grab sampler. The top 2 cm of sediment in the grab was removed using stainless steel spoons, placed in a stainless steel bowl, and homogenized by stirring. Homogenized sediment was placed in glass jars with Teflon lid liners cleaned to EPA QA/QC specifications (EPA 1990).

All sample containers were placed on ice in coolers immediately after collection. After collection, the samples were transported to the Ecology headquarters building where they were stored in a refrigerator at 4˚C until transport to MEL by Ecology's courier. Chain-of-custody procedures were used for all samples.

Data Quality

MEL employed standard quality assurance/quality control (QA/QC) procedures throughout analysis of the project samples. These QA/QC procedures are documented in MEL's Quality Assurance Manual (MEL 2001). All sample extraction and analysis was conducted within recommended method holding times. No analytes were detected in laboratory method blanks. Table 2 shows the analytical methods with their respective detection limits for each parameter by matrix.

Overall, quality assurance results led to estimated data qualifiers for several compounds, most notably herbicides. Low recoveries and matrix interferences have also adversely impacted some results. However, with the data qualifiers given, the data appear suitable for prioritizing pollutant sources.

Surrogate recoveries were within acceptable limits for all parameters except for four pesticide samples in water (468109, 468110, 468111, and 508111) that had recoveries below the acceptable limits of 30-130%. Laboratory control samples (LCS) were within acceptable limits for all parameters analyzed for water and sediment except herbicides. The fortified blank spike for the first sampling event (11/12/02) had low recoveries of picloram and acifluorfen. As a result, the compounds were qualified as estimates in the samples.

Matrix spike and duplicates were within acceptable quality control limits for all water parameters except pesticides. The majority of the samples from the first event (11/12/02) had high matrix interference which may have caused lower recoveries for several compounds. Bromacil was particularly affected, and all detections were qualified as estimates. Some of the samples from the December 10, 2002 had a problem with moderate matrix interference.

Laboratory and field replicates were within acceptable limits for all parameters analyzed for water and sediment. Laboratory replicate results showed a relative percent difference (RPD) ranging from 0-0.63% which demonstrates that there was excellent analytical precision present at the time of analysis. A single field replicate sample was analyzed for water only. The results showed moderate precision for pesticides with a RPD of 35% on a single detection (0.020 and 0.014), good precision for herbicides with a RPD range of 3.5-22% for five detections, and excellent precision for metals with a RPD range of 0-5.4% for six detections.

Table 2. Analytical methods for water and sediment laboratory analysis.

Parameter	Analytical Method	Detection Limit
Water		
Conventionals		
Total Suspended Solids	Gravimetric EPA 160.2	1 mg/L
Hardness	ICP EPA 200.7	200 µg/L
Metals		
Arsenic	ICP/MS EPA 200.8	0.1 µg/L
Copper	ICP/MS EPA 200.8	0.1 µg/L
Lead	ICP/MS EPA 200.8	0.1 µg/L
Zinc	ICP/MS EPA 200.8	5 µg/L
Low Level Mercury	CVAFS EPA 245.7	0.005 µg/L
Organics		
Pesticide Screen[1]	GC/AED 8085	0.010 - 0.10 µg/L
Herbicide Screen	GC/AED 8085	0.09 - 0.70 µg/L
Sediment		
Conventionals		
Grain Size	Sieve and Pipet	n/a
TOC	Combustion/CO_2 Generation EPA 415.1	1 mg/L
Percent Solids	Gravimetric EPA 160.3	1 mg/Kg, dry
Metals		
Arsenic	ICP/MS EPA 200.8	0.2 mg/Kg, dry
Copper	ICP/MS EPA 200.8	0.1 mg/Kg, dry
Lead	ICP/MS EPA 200.8	0.1 mg/Kg, dry
Zinc	ICP/MS EPA 200.8	5.0 mg/Kg, dry
Mercury	CVAA EPA 245.5	0.05 mg/Kg, dry
Organics		
Diesel Extended Range	GC/FID Diesel Extended Range	50 mg/Kg
BNA - no TIC	GC/MS EPA 625	200 µg/Kg, dry

[1]nitrogen containing, organophosphate, chlorinated
CVAA - cold vapor atomic absorption
CVAFS - cold vapor atomic fluorescence spectrometry
GC/AED - gas chromatography/atomic emission detection
GC/FID - gas chromatography/flame ionization detector
GC/MS - gas chromatography/mass spectrometry
ICP - inductively coupled plasma
ICP/MS - inductively coupled plasma/mass spectrometry

Results

Water

The results of conventional analysis of water samples collected during the three rounds of storm sampling are shown in Table 3. Temperature, pH, and specific conductance appear to be consistent with expected conditions during the time of year each sampling round occurred.

Measurements for temperature and pH are similar between stations during particular rounds with one exception. Temperature measured at the Squalicum Creek station at the outlet of Sunset Pond (SQ5) during the third round was more than 7˚C higher than the lowest measured temperature (Table 3). This is likely due to the location of the station, downstream of Sunset Pond.

Table 3. Temperature, pH, conductivity, and total suspended solids (TSS) results for Squalicum Creek.

Station	Time	Sample No.	Temperature (˚C)	pH	Conductivity (µmhos/cm)	TSS (mg/L)
November 12, 2002						
SQ1	0815	468105	10.6	7.10	110	3
SQ2	0745	468106	10.2	7.20	100	1
SQ3	0845	468107	10.1	7.33	125	6
SQ4	0700	468108	9.2	7.36	235	2
SQ5	0945	468109	10.9	7.14	45	15
SQ6	1045	468110	9.7	7.40	140	37
SQ7	1015	468111	9.2	7.02	90	2
December 10, 2002						
SQ1	1045	508105	7.4	7.25	278	4
SQ2	0950	508106	7.4	7.44	201	6
SQ3	1015	508107	7.7	6.85	102	1
SQ4	1130	508108	5.8	7.29	347	2
SQ5	1200	508109	6.5	7.23	194	2
SQ5 (rep)	1200	508112	nd	nd	nd	2
SQ6	1530	508110	6.5	7.39	197	1
SQ7	1430	508111	5.9	6.58	143	1 U
June 30, 2003						
SQ1	1600	274061	16.2	7.38	162	12
SQ2	1540	274060	16.0	7.31	172	6
SQ3	1635	274062	15.6	7.47	138	32
SQ4	1700	274063	15.9	7.34	141	12
SQ5	1730	274064	21.6	7.81	164	15
SQ6	1815	274065	15.9	8.01	151	45
SQ7	1900	274066	14.3	8.06	97	8

nd - no data collected.
U - the analyte was not detected at or above the reported result.

Conductivity was variable between stations and sampling rounds. The Squalicum Creek station at the outlet of Sunset Pond (SQ5) was particularly different than the other stations during the first round of sampling. Again this difference may be attributed to the proximity to Sunset Pond.

TSS rounds one and two were low except for the Squalicum Creek stations at the outlet of Sunset Pond (SQ5) and Toad Lake drainage (SQ6) during the first round (Table 3). Round 3 had TSS values closer to what is expected for a storm event, with the exception of the station at the mouth of Baker Creek (SQ2) and the station furthest upstream of Squalicum Creek (SQ7) (Table 3).

Metals

All five target analytes, except for zinc, were detected during all three sampling events at all seven stations (Table 4). Zinc was not detected at the upstream Squalicum Creek station (SQ7) during the last two sampling events. The majority of the detections were low. Mercury and zinc were exceptions; they had four high concentrations. The results for all analytes were variable between sites and between sampling events, making comparisons difficult.

Pesticides

Fourteen pesticides were detected in water. Most of the detected pesticides were found in the last sampling round on June 30, 2003. All detections for each station by sample event are shown in Table 5.

Eleven of the 14 pesticides detected were herbicides: atrazine, bromacil, dichlobenil, diuron, prometon, 2,4-D, dicamba, MCPA, MCPP (mecoprop), pentachlorophenol, and triclopyr. One was an herbicide breakdown product: 2,3,4,5-tetrachlorophenol. One was a fungicide breakdown product: 4-nitrophenol. One was an insecticide: diazinon. Caffeine also was detected during the first storm event at two stations.

All stations, except for the most upstream station on Squalicum Creek (SQ7), had similar detection frequencies and types of compounds. The most frequently detected pesticides were MCPP, pentachlorophenol, triclopyr, bromacil, dichlobenil, and 2,4-D. Diuron, atrazine, and MCPA were also detected frequently but only during the last sampling event. Although the above pesticides were detected frequently, the majority of the detections were at or near the method detection limit.

Most of the pesticides were detected in the lower part of the creek from the mouth to the outlet of Sunset Pond (SQ1 – SQ5). Stations SQ1 through SQ3 had eleven detections, and stations SQ4 and SQ5 had ten detections. The two stations in the upper Squalicum Creek basin (SQ6 and SQ7) had eight and three detections, respectively. There were only a few detections at the most upstream station on Squalicum Creek. This may be due, in part, to its location in a rural area where there is little residential or agricultural influence.

The majority of the pesticide detections occurred in the lower part of the watershed (regions 1 – 3). This part of the watershed is mainly made up of urban and residential areas. The remainder of the detections and violations occurred in the upper part of the watershed which primarily has rural and agricultural land uses (region 4).

Table 4. Dissolved metals concentrations and hardness values in water samples from seven Squalicum Creek stations, and hardness corrected water quality values for copper, lead, and zinc (µg/L).

Parameter	Sample Date	Station						
		SQ1	*SQ2*	*SQ3*	*SQ4*	*SQ5*	*SQ6*	*SQ7*
Metals								
Arsenic	11/12/02	0.43	0.40	0.68	0.54	0.64	0.59	0.60
	12/10/02	0.68	0.45	1.54	0.49	1.31	0.42	0.42
	6/30/03	0.81	0.67	1.13	0.86	1.19	0.87	0.69
Copper	11/12/02	2.35	2.68	1.58	1.91	2.90	3.30	1.72
	Criteria	*6.78*	*6.33*	*7.54*	*12.89*	*3.20*	*9.12*	*6.22*
	12/10/02	1.97	3.04	0.97	1.29	1.58	1.46	1.31
	Criteria	*11.01*	*8.43*	*8.91*	*13.85*	*8.17*	*8.63*	*5.88*
	6/30/03	3.46	3.13	2.95	2.65	1.42	4.04	1.40
	Criteria	*6.75*	*7.86*	*5.79*	*7.64*	*7.00*	*7.43*	*5.03*
Lead	11/12/02	0.213	0.235	0.147	0.075	0.405	0.506	0.179
	Criteria	*1.30*	*1.19*	*1.49*	*2.96*	*0.49*	*1.90*	*1.16*
	12/10/02	0.13	0.270	0.053	0.037	0.19	0.060	0.062
	Criteria	*2.12*	*1.72*	*1.85*	*3.23*	*1.65*	*1.77*	*1.08*
	6/30/03	0.307	0.229	0.296	0.17	0.070	0.080	0.089
	Criteria	*1.29*	*1.57*	*1.06*	*1.51*	*1.35*	*1.46*	*0.88*
Mercury (total)	11/12/02	0.0066	0.0085	0.0082	0.0047	**0.012**	**0.013**	0.011
	12/10/02	0.0044 J	0.0063 J	0.0079 J	0.0047 J	0.0088 J	0.0079 J	0.0086 J
	6/30/03	0.0084 J	0.0072 J	0.0094 J	0.0084 J	0.0041 J	**0.014**	0.0081 J
Zinc	11/12/02	9.1	22.4	6.4	8.7	**53.2**	4.0	2.1
	Criteria	*62.68*	*58.58*	*69.70*	*118.51*	*29.75*	*84.12*	*57.60*
	12/10/02	6.6	16.4	3.7	9.5	4.9	1.3	-
	Criteria	*101.4*	*77.8*	*82.2*	*127.1*	*75.5*	*79.67*	-
	6/30/03	11.7	16.7	7.2	13.8	2.4	1.9	-
	Criteria	*62.39*	*72.55*	*53.63*	*70.56*	*64.72*	*68.65*	-
Hardness								
	11/12/02	54.7	50.5	62.0	116	22.7	77.4	49.5
	12/10/02	96.5	70.6	75.3	126	68.1	72.6	46.3
	6/30/03	54.4	65.0	45.5	62.9	56.8	60.9	38.6

Bold indicates the numerical value was at or exceeded the water quality criteria for the protection of aquatic life.

Table 5. Nitrogen pesticides, caffeine, organophosphorus pesticides, and chlorophenoxy herbicides detected in water samples from seven Squalicum Creek stations (µg/L).

Parameter	Sample Date	Station						
		SQ1	SQ2	SQ3	SQ4	SQ5	SQ6	SQ7
Nitrogen pesticides								
Atrazine	11/12/02	-	-	-	-	-	-	-
	12/10/02	-	-	-	-	-	-	-
	6/30/03	0.018 J	0.025 J	-	0.033 J	-	0.049 J	-
Bromacil	11/12/02	0.030 J	-	0.67 J	0.15 J	-	0.14 J	-
	12/10/02	-	0.042 J	0.095 J	0.23 J	-	-	-
	6/30/03	0.10 J	-	-	0.473 J	0.010 J	0.076 J	-
Dichlobenil	11/12/02	0.059	0.24	-	0.23	-	-	-
	12/10/02	-	0.15	-	0.077	-	-	-
	6/30/03	0.025 J	0.043 J	0.026 J	0.038 J	0.027 J	0.11 J	-
Diuron	11/12/02	-	-	-	-	-	-	-
	12/10/02	-	-	-	-	-	-	-
	6/30/03	0.144 NJ	0.14 NJ	-	0.100 NJ	0.189 NJ	0.214 NJ	-
Prometon (Pramitol 5P)	11/12/02	-	-	-	-	-	-	0.091
	12/10/02	-	-	-	-	0.020	-	-
	6/30/03	-	-	0.01 J	-	-	-	-
Organophosphorus pesticides								
Diazinon	11/12/02	-	**0.13**	-	-	-	-	-
	12/10/02	-	-	-	-	-	-	-
	6/30/03	**0.15 J**	**0.134 J**	-	-	-	-	-
Chlorophenoxy herbicides								
2,3,4,5 Tetrachlorophenol	11/12/02	-	-	0.25	-	-	-	-
	12/10/02	-	-	0.092 J	-	-	-	-
	6/30/03	-	-	-	-	-	-	-
2,4-D	11/12/02	0.14 J	0.14 J	0.088 J	0.084 J	-	0.065 NJ	-
	12/10/02	0.11 J	0.098 J	0.0097 J	0.039 J	0.041 J	0.0043 J	-
	6/30/03	0.45	0.35	0.29	0.36	-	1.4	-
4-Nitrophenol	11/12/02	-	-	0.058 J	-	0.4	-	-
	12/10/02	-	-	-	-	-	-	-
	6/30/03	-	-	-	-	-	-	-
Dicamba I	11/12/02	-	-	-	0.022 NJ	-	-	-
	12/10/02	-	-	0.0050 NJ	-	0.011 NJ	-	-
	6/30/03	-	-	-	-	-	-	-
MCPA	11/12/02	0.031 NJ	0.033 NJ	-	-	-	-	-
	12/10/02	-	-	-	-	-	-	-
	6/30/03	0.21 J	0.16 J	0.31 J	0.070 J	-	-	-
MCPP (Mecoprop)	11/12/02	0.051 NJ	**0.13 NJ**	0.019 J	0.049 NJ	-	0.064 NJ	-
	12/10/02	-	**0.15 NJ**	0.019 J	0.023 J	0.012 J	0.0050 NJ	-
	6/30/03	**0.18 J**	**0.24 J**	**0.22 J**	**0.16 J**	0.044 J	**0.45**	-
Pentachlorophenol	11/12/02	0.20	0.075	-	0.024 J	0.34	0.070 J	0.016 J
	12/10/02	0.16	0.081 J	-	0.041 J	0.061 J	0.039 J	0.0069 J
	6/30/03	0.11 J	0.069 J	0.12	0.060 J	0.031 J	0.060 J	0.017 J
Trichlopyr	11/12/02	0.057 J	0.074 J	-	0.052 J	0.026 NJ	0.17	-
	12/10/02	0.10 J	0.071 J	0.021 J	0.049 J	0.28	0.12 J	-
	6/30/03	0.26	0.18	0.27	0.31	0.068 J	0.98	0.059 J
Caffeine	11/12/02	0.21 J	0.44 J	-	-	-	-	-
	12/10/02	-	-	-	-	-	-	-
	6/30/03	-	-	-	-	-	-	-

"-" The analyte was not detected.
J - The analyte was positively identified. The associated numerical result is an estimate.
NJ - There is evidence that the analyte is present. The associated number is an estimate.
Bold indicates the numerical value was at or exceeded a water quality value for the protection of aquatic life.

Sediment

Conventionals data on sediments collected from catch basins on December 11, 2002 are shown in Table 6. Total organic carbon (TOC) is low for all stations except Squalicum Lake (CB5) which exceeded 15% in both replicates. The stations on Meridian Street (CB1 and CB2) have a high percentage of solids, while Squalicum Lake (CB5) has a low percent solids. The Meridian Street and Sunset Pond (CB3) stations were composed of primarily coarse material (sand and gravel). The Irongate industrial area station (CB4) was evenly distributed, and the Squalicum Lake station (CB5) was primarily made up of fine grain materials (silt and clay).

Table 6. Total organic carbon (TOC), percent solids, and grain size results for catch basin sediment entering Squalicum Creek, December 11, 2002.

Station	Time	Sample No.	Solids (%)	TOC (%)		% Gravel (>2 mm)	% Sand (2 mm-62 µm)	% Silt (62-4 µm)	% Clay (<4 µm)
				104˚C	70˚C				
CB1	0800	508120	60.8	4.0	3.8	9.9	65.9	23.3	0.9
CB2	0900	508121	62.7	6.0	6.0	13.3	74.8	11.2	0.7
CB3	1530	508122	38.8	2.9	2.8	16.9	41.0	31.5	10.6
CB4	0945	508123	32.4	5.0	4.9	14.2	38.0	39.4	8.4
CB5	nd	508124	10.2	21.3	21.6	0.1	25.9	37.3	36.7
CB5 (rep)	nd	508125	10.3	15.6	16.1	0.1	22.7	37.8	39.5

nd - not data collected.

Metals

In general, concentrations of metals, with the exception of copper, were highest at the Meridian Street stations (CB1 and CB2). Copper appeared to be elevated at all stations. Arsenic, copper, lead, mercury, and zinc were detected at all stations. Detections were variable betweens stations; therefore, it was difficult to make comparisons. The majority of highest detections were at the upper Meridian Street station (CB2), and the majority of the lowest detections were at the Sunset Pond station (CB3).

Semi-Volatile Organic Carbon

Thirty-three SVOC compounds were detected at one or more of the five sampling stations (Table 7). Most of the detections occurred at the Meridian Street stations (CB1 and CB2) and the station at the Irongate industrial area (CB4). The two remaining stations, Sunset Pond (CB3) and Squalicum Lake (CB5), had only 9 and 5 detections, respectively.

Most of the detections were either polynuclear aromatic hydrocarbons (PAHs) or phthalates. Many of the identified compounds are routinely detected in the environment. Three compounds were found at high concentrations: bis (2-ethylhexl) phthalate, dimethylphthalate, di-n-octyl phthalate (Table 7). About 80% of all the phthalates manufactured are used as plasticizers.

Plasticizers make plastics flexible (American Chemistry Council 2003); their chief use is in the manufacture of vinyl.

Lube oil was found at four of the five sampling stations (Table 7). The Irongate industrial area (CB4) was the only one of the five stations to have #2 diesel detected.

The majority of the detections of SVOCs occurred in the lower part of the watershed in land use regions 1 through 3 (Figure 1). This part of the watershed is primarily made up of urban and residential areas. Urban and residential areas tend to have high volumes of car and truck traffic. Most of the PAH's detected are associated with incomplete combustion of fossil fuels as well as urban street dust (Cubbage 1994). One source of this incomplete combustion is emissions from motorized vehicles. The remainder of the detections occurred in the upper part of the watershed (region 4) which is made up of mainly rural and agricultural land uses (Figure 1).

Table 7. Semi-volatile organic carbons (SVOC), petroleum products, and metals detected in sediment collected from five catch basins near Squalicum Creek on December 11, 2002.

Parameter	Station					
	CB1	CB2	CB3	CB4	CB5	CB5 (rep)
Metals (mg/Kg dw)						
Mercury	0.0371	0.029	0.050	0.0821	0.24	0.24
Copper	41.5	72.3	28.0	43.8	34.6	33.7
Zinc	**200**	**371**	67.2	114	111	77.7
Arsenic	3.18	3.37	3.49	8.71	5.38	5.24
Lead	36.6	53.4	6.2	12.4	14.5	14.5
SVOCs (µg/Kg dw)						
Naphthalene	79	117	-	32	-	-
Acenaphthylene	-	21	-	-	-	-
Acenaphthene	35	44	-	-	-	-
Fluorene	91	68	-	-	-	-
Phenanthrene	820	772	30	134	45	52 J
Anthracene	101	115	8.1 J	-	-	-
Total LPAH	1100	1100	38	170	45	52
Fluoranthene	1390	1270	71	189	45 J	39 J
Pyrene	1450	1470	51	349	48 J	26 J
Benzo(a)anthracene	410	387	-	61	-	-
Benzo(a)pyrene	376	413 J	-	47	-	-
Indeno(1,2,3-cd)pyrene	-	292 J	-	-	-	-
Benzo(ghi)perylene	458	485 J	-	-	-	-
Benzo(b)fluoranthene	-	1020 J	22 J	94	-	-
Benzo(k)fluoranthene	-	-	-	82	-	-
Chrysene	757	809	24 J	154	-	-
Total HPAH	4800	5800	170	980	93	65
Dimethylphthalate	**3110**	**56**	-	**196**	-	-
Di-N-Butylphthalate	**153**	**188**	-	-	-	-
Butylbenzylphthalate	-	-	-	**584**	-	-
Bis(2-Ethylhexyl) Phthalate	**7660**	**15100 J**	-	**4020**	-	-
Di-N-Octyl Phthalate	-	**1070**	-	-	-	-
Phenol	-	312	55	374	231	272
2-Methylphenol	-	41	-	-	-	-
4-Methylphenol	2260	416	-	447	-	-
Pentachlorophenol	305	-	-	-	-	-
2-Methylnaphthalene	100	120	-	36	-	-
1-Methylnaphthalene	50	50	-	22	-	-
Aniline	-	-	96	-	-	-
Benzyl Alcohol	-	201	-	-	-	-
Benzoic Acid	858 J	937 J	-	711 J	1560 J	1670 J
Dibenzofuran	-	38	-	25 J	-	-
N-Nitrosodiphenylamine	-	76	-	-	-	-
Carbazole	154	120	-	-	-	-
Retene	-	-	72	1860	-	-
Petroleum Products (mg/Kg dw)						
#2 Diesel	-	-	-	580 J	-	-
Lube Oil	6500	6300	130	3800 J	nd	nd

"-" The analyte was not detected.

nd - No data was reported.

J - The analyte was positively identified. The associated numerical result is an estimate.

Bold indicates the numerical value was at or exceeded a sediment quality value for the protection of aquatic life (Table 8).

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Discussion

Comparison to Environmental Quality Standards

Water

Two metals exceeded applicable water quality criteria. Mercury exceeded the Washington State chronic water quality standard of 0.012 µg/L during the November 12 and December 10, 2002 sampling events at two stations (WAC 1997). A recent regional assessment by USGS has been conducted to determine possible sources. The study is expected to be released in late January 2004. Zinc exceeded its hardness corrected water quality criteria for the protection of aquatic life of 29.75 µg/L on a single occasion on Squalicum Creek at the outlet of Sunset Pond (SQ 5). Zinc is typically found in urbanized areas as a constituent of road runoff. While both these metals are above criteria, there is no apparent link between station location and land use patterns.

Two pesticides exceeded criteria for the protection of aquatic life. The herbicide MCPP (Mecoprop) exceeded the Netherlands ecotoxicological value of 0.11 µg/L (Stortelder et al. 1989) at five stations during the last sampling event on 30 June 2003. Diazinon, an insecticide, exceeded a California Department of Fish and Game chronic criterion of 0.04 µg/L (Menconi and Cox 1994). Both MCPP and diazinon exceeded their respective water quality values on several occasions at several stations. Most of the violations were found at the mouth of Baker Creek (SQ2).

Diazinon is a non-systemic organophosphate insecticide that functions as an acetylcholinesterase inhibitor (Extoxnet 1996a). It is used on home gardens and farms to control a wide variety of sucking and leaf eating insects. Diazinon is also used as an ingredient in pest strips. Mecoprop is a selective, post-emergence, hormone-type herbicide (Extoxnet 1996b). It is used on ornamentals, sports turf, forest site preparation, and on drainage ditches to control ground-creeping, broadleaf weeds.

Sediment

At this time (2004) the Washington State Department of Ecology (Ecology) is updating the recommended freshwater sediment quality values (FSQVs) for use in Washington State. Pending the adoption of the FSQVs, Ecology uses best professional judgment on a case-by-case basis to evaluate freshwater sediment quality through the use of biological testing or comparison with available FSQVs. Several FSQVs have been used to evaluate SVOC and metals concentrations in freshwater sediments. They range from levels where biological effects always occur to levels below which biological effects sometimes occur. This list of available FSQVs can be found in Table 8.

Table 8. Available freshwater sediment quality values (FSQVs).

Chemical	LAET	LEL	FPM
SVOCs (µg/Kg dw)			
Acenaphthene	1060		1060
Acenaphthylene	470		470
Anthracene	1230	220	1200
Benzo(a)anthracene	4260	320	4260
Benzo(a)pyrene	3300	370	3300
Benzo(ghi)perylene	4020	170	4020
Bis(2-Ethylhexyl) Phthalate	2520		230
Butylbenzylphthalate	260		260
Carbazole	923		
Chrysene	5940		5940
Dimethylphthalate	311		46
Di-N-Butylphthalate	103		
Di-N-Octyl Phthalate	11		26
Fluoranthene	11100	750	11000
Fluorene	1070	190	1000
Naphthalene	529		500
Phenanthrene	6100	560	6100
Pyrene	8790	490	8800
Metals (mg/Kg dw)			
Arsenic	31.4	6	20
Copper	619	16	80
Lead	335	31	335
Mercury	0.8	0.2	0.50
Zinc	683	120	140

LAET - Lowest apparent effects threshold (SAIC and Avocet Consulting 2003)
LEL - Lowest effects level (SAIC and Avocet Consulting 2002)
FPM - Floating Percentile Method (SAIC and Avocet Consulting 2003)

Lowest apparent effects threshold (LAET) values are based on the lowest level above which biological effects have always been observed to occur. Lowest effects levels (LELs) are based on a level at which adverse biological effects are seen in 5% of benthic species. An alternative to LAETs and LELs is the Floating Percentile Method (FPM). This method has recently been recommended for adoption in Washington State because it is more reliable and provides FSQVs that are more predictive of toxicity in the available Washington State data (SAIC and Avocet 2003).

The majority of the detections and exceedances of the FSQVs were at the Meridian Street stations (CB1 and CB2). Both of these stations are located in an area with a high volume of traffic. Five of the 33 detected SVOCs were found to exceed recommended FSQVs for the protection of aquatic life. Di-n-butyl phthalate was above its LAET of 103 µg/Kg at both Meridian Street stations. Butylbenzyl phthalate was above its FPM of 260 µg/Kg at the Irongate industrial area. Bis (2-ethylhexyl) phthalate was above its FPM of 230 µg/Kg at the upper and lower Meridian Street stations and the Irongate industrial area station.

Arsenic, copper, lead, mercury, and zinc were detected in the sediment of the catch basins. Zinc was the only metal detected that exceeded its recommended FSQVs (Table 8) at two stations (CB1 and CB2) during the sampling event (Table 7). It is common to find metals present in sediments near roadways and in urban areas.

Comparison to Environmental Quality Data

Many of the pesticides detected in Squalicum Creek have been found in other urban streams in the Puget Sound basin. The Puget Sound basin extends from the Canadian border to Olympia. A comparison of concentrations of three selected pesticides from the Squalicum Creek watershed was made to other urban creeks in the Puget Sound basin. The comparison showed that the concentrations found in the Squalicum Creek watershed were similar to those found in other Puget Sound basin creeks (Table 9). Bortleson and Davis (1997) report results from seven urban streams from sampling conducted from 1987 to 1995. The most commonly detected pesticides in the study included the herbicides 2,4-D, dicamba, dichlobenil, diuron, MCPP, and the insecticide diazinon. A recently published study on Padden Creek, near Squalicum Creek, detected many of the same compounds (Seiders 2003). Squalicum Creek was similar. There were detections of the above compounds and also MCPA, pentachlorophenol, triclopyr and bromacil.

Table 9. Comparison of selected pesticides in water from the Squalicum Creek watershed and creeks in the Puget Sound basin (µg/L).

Location	Minimum	Maximum	Mean[2]
2,4-D			
Squalicum Creek	0.0310	0.31	0.1360
Puget Sound Basin[1]	0.0057	0.27	0.0837
MCPA			
Squalicum Creek	0.005	0.45	0.114
Puget Sound Basin[1]	0.014	1.20	0.260
MCPP (Mecoprop)			
Squalicum Creek	0.0043	1.4	0.2246
Puget Sound Basin[1]	0.0055	1.5	0.1828

[1] Data generated from Ecology's Environmental Information Management System
[2] Arithmetic mean of detections

Many of the compounds detected in sediment from catch basins near Squalicum Creek are similar to those found in urban areas. A comparison of selected chemicals from this project and other urban areas in western Washington State shows that the Squalicum Creek watershed has similar compounds. However, the mean concentrations for three of the four comparison chemicals found in the Squalicum Creek watershed are above the mean concentrations for western Washington (Table 10). A study of storm drains on Whatcom Creek and Squalicum Harbor in Bellingham also found similar compounds to the ones detected in the catch basins near Squalicum Creek (Cubbage 1994).

Table 10. Comparison of selected semi-volatile organic carbon compounds in sediment from the Squalicum Creek watershed with sediment from western Washington locations (µg/Kg dw).

Location	Minimum	Maximum	Mean[2]
bis(2-ethylhexyl) phthalate			
Squalicum Creek	4020	15100	8900
Western Washington[1]	81	16900	2100
di-n-butyl-phthalate			
Squalicum Creek	153	188	170
Western Washington[1]	33	16600	1770
fluoranthene			
Squalicum Creek	45	1390	590
Western Washington[1]	5.5	2390	530
pyrene			
Squalicum Creek	48	1470	670
Western Washington[1]	6.1	2730	500

[1] Data generated from Ecology's Environmental Information Management System
[2]Arithmetic mean of detections

Chemicals of Concern

Data generated from this project were used to produce a list of chemicals of concern for sampling locations. A chemical was placed on the list if it exceeded applicable water or FPM sediment quality values. In cases where no FPM values were available, the LAET was used. After each list of chemicals was developed, station locations were prioritized according to the number of chemicals detected above water or sediment quality values and the magnitude of the exceedences.

A priority list of nine water or sediment stations was identified (Table 11). Highest priority was assigned to CB2, and lowest priority was assigned to SQ4. CB2 had five chemicals of concern with the majority having exceedence factors greater than 2. Second on the list was CB1. Both CB1 and CB2 are located on or near Meridian Street. Third on the list was station CB4. Station CB4, located near the Irongate industrial area, had three SVOCs above FSQVs and had exceedence factors greater than 2. The remainder of the stations on the list had few chemicals above water or sediment quality values and low exceedence factors, compared to those stations higher in priority.

Based on the prioritized list (Table 11), most of the educational and source-control efforts should focus on the area around Meridian Street and the Irongate industrial area.

Table 11. Summary of compounds exceeding standards by station.

Priority	Station	Chemical	Exceedance Factor
Sediment[1]			
1	CB2	Bis (2-ethylhexyl) phthalate	66
		Di-N-Octylphthalate	41
		Zinc	2.7
		Di-N-Butylphthalate	1.8
		Dimethylphthalate	1.2
2	CB1	Dimethylphthalate	68
		Bis (2-ethylhexyl) phthalate	33
		Di-N-butylphthalate	1.5
		Zinc	1.4
3	CB4	Bis (2-ethylhexyl) phthalate	18
		Dimethylphthalate	4.3
		Butylbenzylphthalate	2.2
Water[2]			
4	SQ1	Diazinon	3.8
		MCPP (Mecoprop)	1.6
5	SQ2	Diazinon	3.3
		MCPP (Mecoprop)	2.2
6	SQ6	MCPP (Mecoprop)	4.1
		Mercury	1.2
7	SQ5	Zinc	1.8
		Mercury	1
8	SQ3	MCPP (Mecoprop)	2
9	SQ4	MCPP (Mecoprop)	1.5

[1] Floating Percentile Method - Freshwater Sediment Quality Values (SAIC and Avocet 2003)
[2] Various water quality standards (Menconi and Cox 1994, Stortelder et al. 1989, WAC 1997)
Note - No chemicals exceeded standards at CB3, CB5, and SQ7.

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Conclusions

Water was collected from seven sites in the Squalicum Creek watershed on three occasions between November 2002 and June 2003. Five metals were detected, with two (mercury and zinc) above water quality criteria for the protection of aquatic life. Twelve pesticides and two pesticide breakdown products were detected in surface water. The most frequently detected pesticides were bromacil, dichlobenil, 2,4-D, MCPP, pentachlorophenol, and triclopyr. Two of the 12 detected pesticides (MCPP and diazinon) were above water quality criteria for the protection of aquatic life; these two pesticides are commonly used for home, garden, commercial, and roadside maintenance.

Sediment was collected from five sites in the Squalicum Creek watershed on one occasion in December 2002. This sampling event detected 33 semi-volatile organic carbon compounds (SVOCs), of which five were above recommended freshwater sediment quality values (FSQVs) for the protection of aquatic life. Two of the five compounds exceeding FSQVs – Bis(2-ethylhexl) phthalate and Di-N-Octyl phthalate – were found to be 18 to 66 times higher than their Floating Percentile Method (FPM). The majority of the detected compounds and exceedances were found at the Meridian Street stations (CB1 and CB2), located on a street with high traffic volume. Five metals were detected, with zinc exceeding its FPM at two sampling stations.

Results from the water sampling events document concentrations of toxic contaminants present in the water of Squalicum Creek during wet weather conditions. The presence, time, and frequency of pesticide detections may help residents, businesses, and applicators recognize that pesticides are transported to the streams and can affect water quality. Results from the sediment sampling event also provide useful information about concentrations of toxic contaminants in sediment; these contaminants have a potential to enter Squalicum Creek during heavy rainfall and runoff conditions.

A list of chemicals of concern was developed for each station. These chemicals were prioritized by the number of exceedences of water or sediment quality values and chemical specific exceedence factors. Based on the information on this list, the lower part of the watershed (i.e., the area near Meridian Street) should be the focus for educational and source-control efforts.

In addition to the information on toxic contaminants present in Squalicum Creek, land use areas of highest concern for educational and source-control efforts were identified by number of detections and exceedences of quality values (Figure 1). Land use areas in the lower part of the watershed (regions 1 through 3) are of highest concern, and areas in the upper part of the watershed (region 4) are of lowest concern. Regions 5 and 6 could not be ranked due to the lack of data.

Recommendations

Based on the data collected and analyzed, the following recommendations are made:

- The Whatcom Watersheds Pledge program should focus its educational and source-control efforts in the urbanized areas (stations SQ3, SQ4, CB1, CB2, CB4) in the lower portion of the Squalicum Creek watershed, using the chemicals of concern list in Table 11. Additional educational efforts should be directed at residential and commercial areas where yard products, particularly MCPP (mecoprop), are applied.

- Bioassays or similar biological tests should be conducted to assess the toxicity of sediments at the Meridian Street catch basin sampling sites (CB1, CB2) and at the Irongate industrial area catch basin site (CB4).

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Appendix. Water and Sediment Locations

Table A1. Water sampling locations and descriptions for Squalicum Creek.

Station	Latitude	Longitude	Description
SQ1	48˚ 46' 01.0"	122˚ 29' 47.0"	Mouth of Squalicum Creek at Squalicum Parkway above intertidal influence
SQ2	48˚ 46' 30.4"	122˚ 29' 24.2"	Mouth of Baker Creek before the confluence of Squalicum Creek at Squalicum Parkway
SQ3	48˚ 46' 29.7"	122˚ 29' 18.0"	Squalicum Creek before the confluence of Baker Creek at Squalicum Parkway
SQ4	48˚ 47' 0.86"	122˚ 28' 54.5"	Baker Creek at McLeod Road near the intersection with Telegraph Road
SQ5	48˚ 46' 32.3"	122˚ 27' 46.4"	Squalicum Creek upstream of I-5 and downstream of Sunset Pond outlet
SQ6	48˚ 47' 47.8"	122˚ 25' 26.5"	Toad Lake Drainage at Dewey Road
SQ7	48˚ 48' 01.3"	122˚ 24' 07.4"	Squalicum Creek off of Mt Baker Highway

Positions listed in degrees/minutes/seconds.
Datum = NAD 83

Table A2. Catch basin sediment sampling locations and descriptions for Squalicum Creek.

Station	Latitude	Longitude	Description
CB1	48˚ 46' 37.14"	122˚ 29' 4.38"	Meridian Street by Cornwall Park
CB2	48˚ 46' 57.58"	122˚ 29' 5.05"	Meridian Street underneath Interstate Highway 5
CB3	48˚ 46' 34.09"	122˚ 27' 35.41"	Sunset Pond
CB4	48˚ 46' 56.96"	122˚ 27' 8.21"	SW corner of Irongate facility
CB5	48˚ 47' 52.60"	122˚ 20' 55.44"	Squalicum Lake

Positions listed in degrees/minutes/seconds.
Datum = NAD 83