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Padden Creek Pesticide Study: Final Report

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Padden Creek Pesticide Study: Final Report

by
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Abstract

Pesticide levels in water were characterized at four sites in Padden Creek from April to June in 2001 and in 2003. The pesticide monitoring was part of a larger effort by the Department of Ecology, Western Washington University, and the City of Bellingham to evaluate water quality conditions in the Padden Creek basin and to identify areas of concern. The results of this study will be used to educate the public and intensify efforts in preventing pollution from residential applications.

Nineteen of 111 pesticides were detected among four sample sites during six sampling events, four in 2001 and two in 2003. The 19 pesticides are as follows:

- Fourteen herbicides: dichlobenil, diuron, MCPP (mecoprop), 2,4-D, trichlopyr, pentachlorophenol, prometon, dicamba, simazine, MCPA, lenacil, terbuthylazine, atrazine, and bromoxynil.
- Two herbicide breakdown products: 2,3,4,6-tetrachloropheno, and 2,6-dichlorobenzamide.
- Two fungicides: chlorothalonil (daconil) and 4-nitrophenol, a breakdown product.
- One insecticide: diazinon. This was detected only during the 2001 sampling events.

Concentrations of pesticides detected in Padden Creek were low, with most being at or slightly above detection limits. Two compounds, diazinon and chlorothalonil, exceeded criteria for the protection of aquatic life during the 2001 sampling events.

Acknowledgements

Many individuals helped develop and carry out this pesticide monitoring project for Padden Creek. We are grateful to all for their contributions:

- Padden Creek resident Mark Roberts for volunteering his time to help collect samples, monitor streamflow, and provide information about the watershed.
- Renee LaCroix and Peg Wendling of the City of Bellingham for rainfall data and information about the watershed.
- Joan Vandersypen of Western Washington University for commenting on the plan and providing information about other monitoring activities in the watershed.
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    - Dale Norton, Richard Jack, and David Laws for review of the final report.
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Background

Recent water quality studies in the Puget Sound region have raised concern about the impacts residentially applied pesticides are having on the aquatic environment (Bortleson and Davis, 1997; Voss et al., 1999, Embry et al., 2000). Although homeowners use large quantities of pesticides, they receive little training or education. This can lead to improper application of products and subsequent harm to aquatic life. The general term "pesticide" includes herbicides, fungicides, algaecides, and insecticides.

The Padden Creek watershed in Bellingham, Washington was selected to study the effects of residentially-used pesticides on an urban stream and the effectiveness of targeted educational outreach in changing the behavior of residents with regard to their use of pesticides. Several groups cooperated towards the goal to minimize pollution from residential sources to urban streams in Bellingham. They include the Bellingham Field Office of the Department of Ecology, Western Washington University, City of Bellingham, and RESources, an environmental education group. These participants cooperate under the umbrella of the Whatcom Watersheds Pledge program. The program provides educational materials and technical assistance to residents living in various watersheds in Whatcom County and encourages them to make a commitment to implement specific actions to reduce water pollution.

Water quality monitoring of Padden Creek was performed to characterize water quality before and after basin residents were educated about pesticides and their alternatives. Monitoring included 111 pesticides, general water quality parameters, and benthic macroinvertebrates. Ecology's Environmental Assessment Program characterized pesticide levels in the stream. Western Washington University and the City of Bellingham monitored general water quality parameters and benthic macroinvertebrates.

This document reports only the results from Ecology's pesticide monitoring efforts in 2001 and 2003, and includes much of the information that was reported for the first year's monitoring effort (Seiders, 2001). The Quality Assurance (QA) Project Plan for this project (Seiders and Norton, 2001) describes the background, study design, and methodology of the project in more detail.

This current report does not address the characterization and evaluation of pesticide use by watershed residents, and changes from 2001 to 2003, which were coordinated by Ecology's Bellingham Field Office. General water quality and benthic macroinvertebrate monitoring results from Western Washington University and the City of Bellingham also are not addressed in this report.

Study Objectives

The objectives of the Padden Creek pesticide monitoring component were to:

- Characterize pesticide concentrations in the watershed during the spring of two years.
- Compare pesticide concentrations in Padden Creek before and after implementation of an education outreach program.
- Evaluate if differences in pesticide concentrations, if present, can be attributed to the education efforts.

The objectives of the Western Washington University and City of Bellingham monitoring component were to:

- Evaluate water quality conditions in the Padden Creek watershed and identify areas of greatest concern.
- Explore how pesticide levels affect macroinvertebrate communities.

Methods

Water samples for pesticide analysis were collected from three sites in Padden Creek and one tributary stream (Connelly Creek) four times during April, May, and June of 2001 and twice during April and June of 2003. A single grab sample was taken in May 2002 from a stormwater pipe discharging to Padden Creek near site PC5.

Figure 1 shows sample site locations in the watershed. PC2 was the site farthest downstream. PC3 was at the mouth of Connelly Creek. PC4 was in Padden Creek just upstream of the confluence with Connelly Creek. PC5, at the outlet of Padden Lake, served as an upstream baseline site.

Three points (quarter-point transects) across the stream at each site were sampled to create a composite sample for pesticide analyses. These sub-samples were collected using a hand-held glass jar that was dipped in the stream. The water depth at time of sampling was less than one foot. The sub-samples were then split into one-gallon glass sample containers so that one-third of the composite samples came from each quarter-point. Sample containers for pesticide analyses were supplied by MEL and were specially cleaned by the manufacturer for such use according to EPA (1990) specifications.

Water samples were analyzed for three classes of pesticides: nitrogen and organophosphorous compounds and chlorophenoxy herbicides (Appendix A). Samples were also analyzed for total suspended solids (TSS) and total organic carbon (TOC) to aid in the interpretation of pesticide data. Laboratory analytical methods are described in Table 1. Field determination of pH, temperature, specific conductance, and streamflow followed instrument manufacturers' procedures and are described in Ecology's protocols for field measurements (Cusimano, 1993).

Table 1. Laboratory Analytical Methods.

Parameter	Practical Quantitation Limit [1]	Analytical Method
Total Suspended Solids	1.0 mg/L	Gravimetric – EPA 160.2
Total Organic Carbon	1.0 mg/L	Combustion IR – EPA 415.1
Nitrogen Pesticides	0.01-1.0 mg/L	GC/AED – EPA 8085
Organophosphorous Pesticides	0.01-1.0 mg/L	GC/AED – EPA 8085
Chlorophenoxy Herbicides	0.01-1.0 mg/L	GC/AED – EPA 8085

[1] The PQL varies among individual target compounds and should be within the stated range.

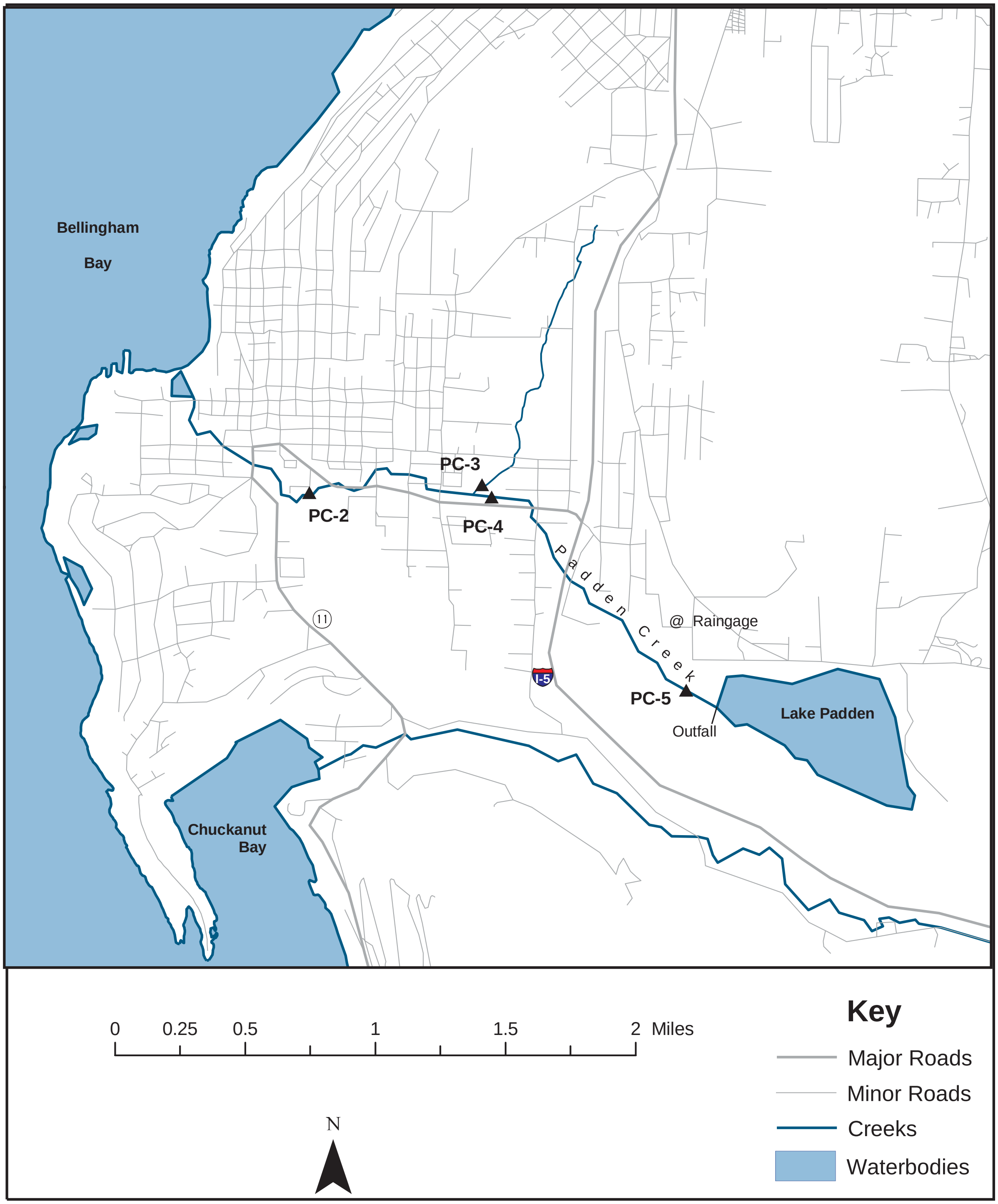

Figure 1. Padden Creek Water and Sediment Sampling Stations.

Streamflow was also determined during each sample event at each site. Stream stage height gages were installed at sites PC2 and PC3 in 2001, while stream levels at PC4 and PC5 were determined by measuring down from a reference point above the stream to the water's surface. Stream stage heights at PC2 and PC3 were determined multiple times during the 2001 sampling events in order to determine the nature of the hydrograph during the sampling event. Stage height was not monitored during the 2003 sampling events.

Sample collection was attempted during periods when pesticide transport was likely to occur through runoff processes. The criteria for sampling were several days of dry weather followed by precipitation that would likely cause an increase in streamflow at the sample sites. Weather forecasts and local contacts were used to help select rainfall events to sample. A single composite water sample at each site was collected during the sampling event. Efforts were not made to sample the entire stream hydrograph because of the logistical challenges and limited resources associated with this effort.

Continuous rainfall data (10-minute interval) from the City of Bellingham's 38th Street rain gage were used for analyses in this report. The city maintains several rain gages and also uses the National Weather Service data from the Bellingham Airport. The 38th Street rain gage is located at the pumping station near Padden Lake.

Quality Assurance

Quality of data was assessed by examining several sources of information. The case narratives from the analytical laboratory described results from the laboratory's quality control practices which assessed method performance using method blanks, surrogate recovery data, matrix spikes and duplicates, laboratory control samples, and laboratory duplicate analyses. All samples were extracted and analyzed within the appropriate holding times. The case narratives pronounced data useable as qualified and discussed reasons for the qualified results.

Many of the pesticide results were qualified as estimated values. The primary reason for this was that many results occurred between an analyte's practical quantitation limit (PQL) and the method detection limit (MDL). The area between the MDL and PQL is at the limit of analytical sensitivity, so results are qualified as estimated values. A secondary reason that results were qualified as estimates was that quality control limits were exceeded for indicators of analytical performance, such as surrogate recoveries, laboratory control samples, and matrix spikes.

All results, except one from field duplicate samples for pesticides, were qualified as non-detects or estimates and as such were not useful to determine sampling precision. The exception was a dichlobenil detection at PC2 on 4/1/03. Results for the sample and duplicate sample (0.23 and 0.21 ug/L) indicated good precision with a relative percent difference (RPD) of 4.5%. Field transfer blanks showed no detectable levels of pesticides.

Pesticide quantitation limits varied over one to three orders of magnitude yet remained within the expected target range of 0.01 – 1.0 ug/L. Variation in quantitation limits throughout the study period is due to various factors such as matrix interferences, instrument performance, and the analysts' levels of experience.

Results from field duplicate samples and duplicate field measurements also demonstrated good precision. Duplicate field measurements of pH, temperature, conductivity, and flow had RPDs of less than 2%. Precision was also good for duplicate samples of TSS (RPDs 0-15%) and TOC (0-11%).

The available quality assurance information indicated no significant problems with the sampling or analytical aspects of the 2001 and 2003 sampling efforts. The case narratives from the laboratory analyses are on file at Ecology's Manchester Environmental Laboratory.

Results

Hydrologic Conditions

The transport of pesticides to streams in this study area is believed to be primarily through runoff during and after rain events. The timing of sample collection in relation to pesticide applications, rainfall intensity, and runoff are large determinants of the presence and concentration of pesticides at the sample sites. Pesticide transport and presence in streams is generally highest during periods of peak rainfall and runoff, and the logistics of sampling these periods can be challenging (EPA, 1992). Criteria for sample collection in this study was at least several days of dry weather followed by precipitation that results in an increase in streamflow at the sample sites. The target range for cumulative rainfall was determined to be 0.15-0.35 inches as described in the QA Project Plan. Figure 2 shows daily precipitation in the study area and reveals the variability in precipitation patterns through each spring sampling season. Streamflow at the time of sample collection is shown in Figure 3.

Hydrologic conditions during sampling events were examined by plotting the variables of rainfall, flow, and stage height during sampling events. For 2001, Figures 3-6 depict cumulative rainfall, stream stage height at sites PC2 and PC3, and the time period over which samples were collected in relation to rainfall and stage height. For 2003, Figures 7 and 8 show cumulative rainfall and the sample collection period. Cumulative rainfall is calculated on a 24-hour period beginning at midnight. The flat (horizontal) part of the cumulative rainfall represents times of no rainfall while the sharply rising parts of the chart represent times of intense rainfall.

2001 Hydrologic Conditions

On sample dates 4/23/01 and 5/5/01 (Figures 4 and 5), sampling began 6-12 hours after the rain event had ceased. The stage height record for PC2 and PC3 show little or no change in the stream stage height during the sampling event. On 4/23/01, the stage height at each site appeared to remain level while the 5/5/01 stage height dropped slightly during the sampling period. The 4/23/01 rain event of about 0.35 inch may have generated runoff during peak rainfall intensity, yet it appears that the sampling event occurred after the streamflow had stabilized. The 5/5/01 event, with a cumulative rainfall of just over 0.5 inch, appears to have captured decreasing flows which had likely peaked during the time period of greatest rainfall intensity (around 2200 hours on 5/4/01).

The sampling on 5/14/01 and 6/27/01 (Figures 6 and 7) occurred during and just after periods of peak rainfall. The 5/14/01 event was the largest of the four events sampled, with a cumulative rainfall just over one inch. The sampling period occurred during a time when streamflow rose, peaked, and then decreased. The stage height at PC3 (Connelly Creek) changed by at least 0.6 feet during the sampling period, reflecting the flashy nature of this smaller and more heavily developed basin. The 6/27/01 event had the smallest cumulative rainfall (about 0.3 inch) of the four events, yet sampling occurred during and after peak rainfall intensity. The stage height record of PC2 shows an increasing flow during the sampling period while PC3 exhibits a rising, peaking, and falling flow.

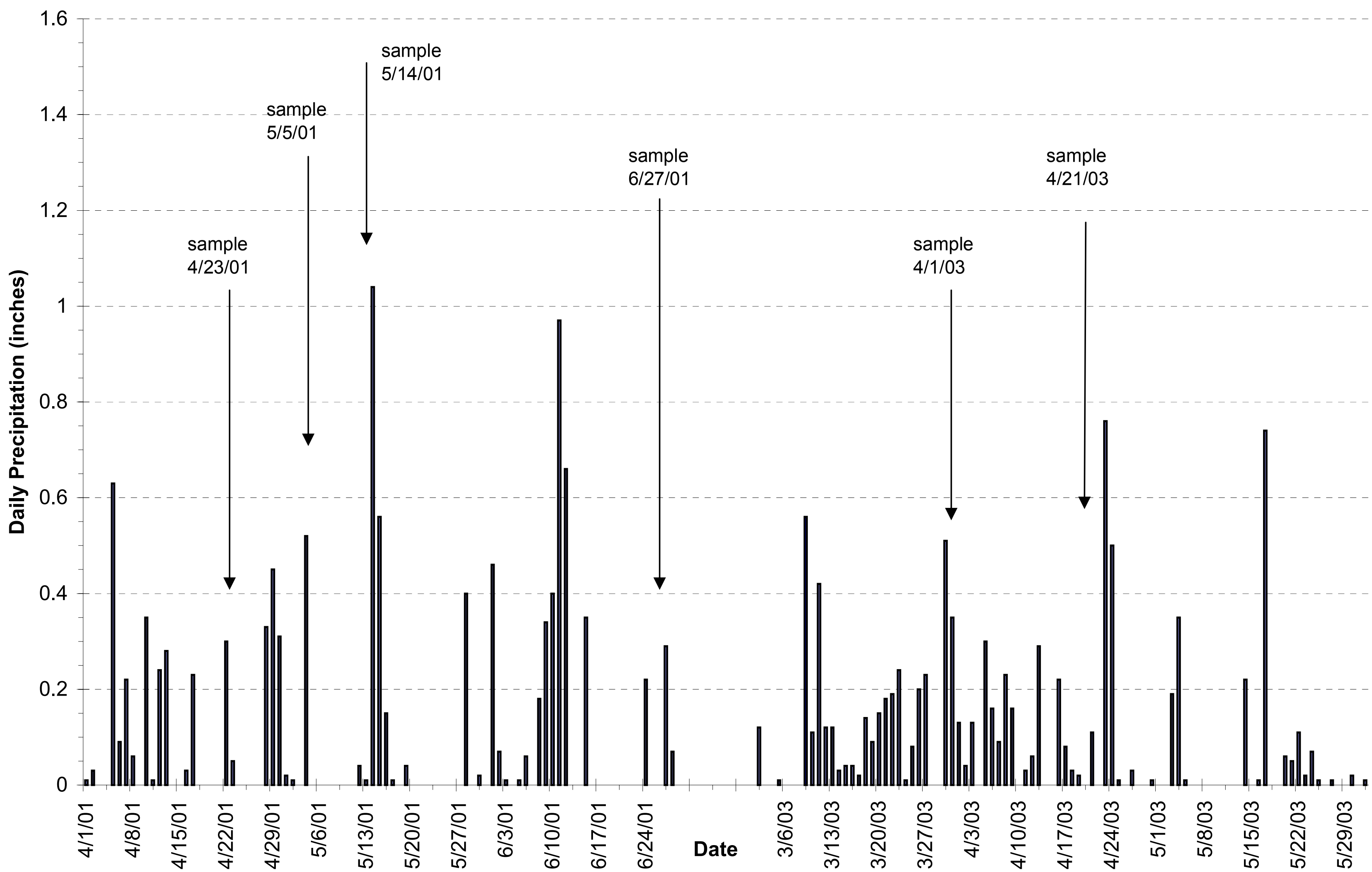

Figure 2. Daily Precipitation in Padden Creek Basin During Spring Sampling in 2001 and 2003

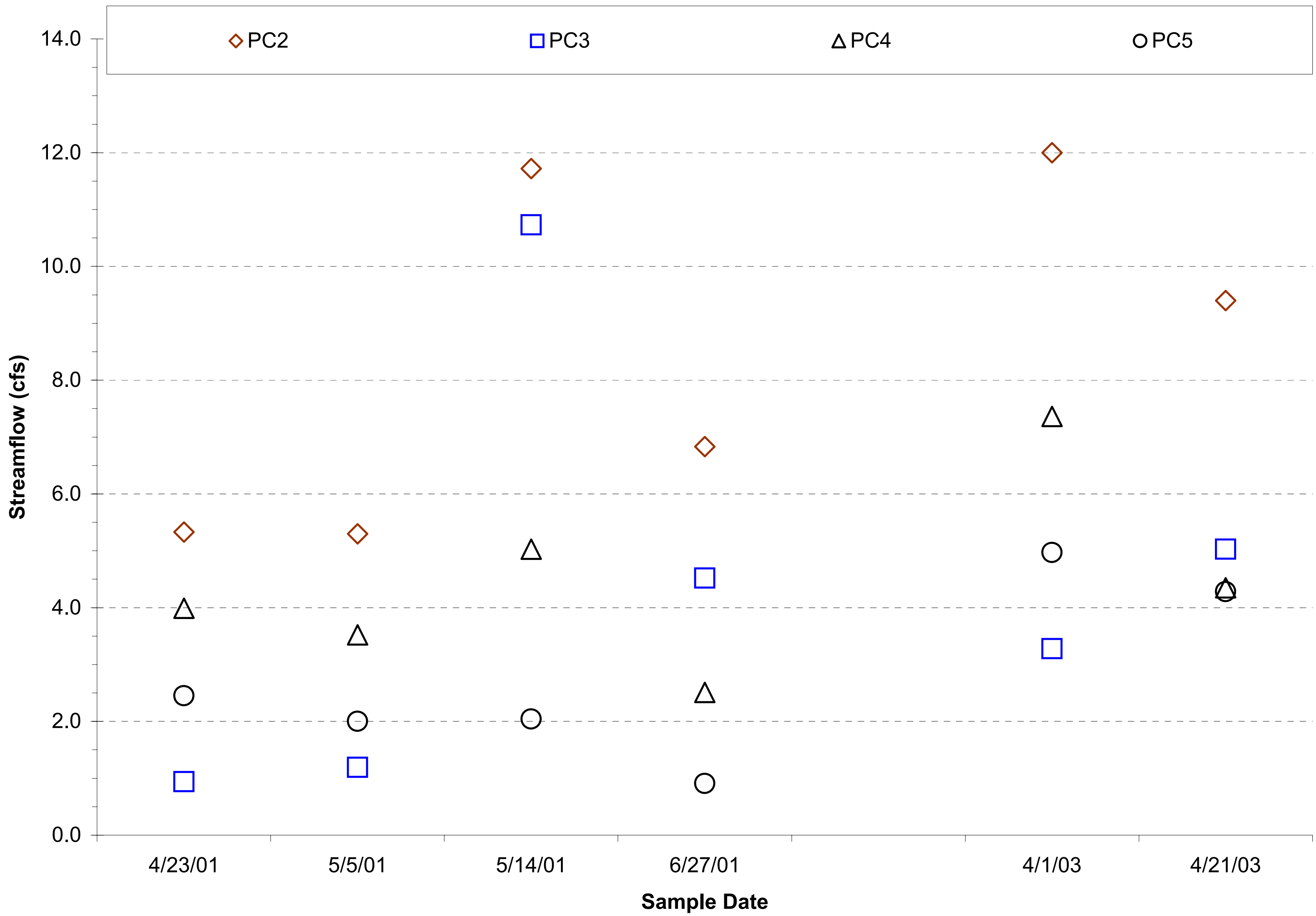

Figure 3. Streamflow During Sampling Events for the Padden Creek Pesticide Study.

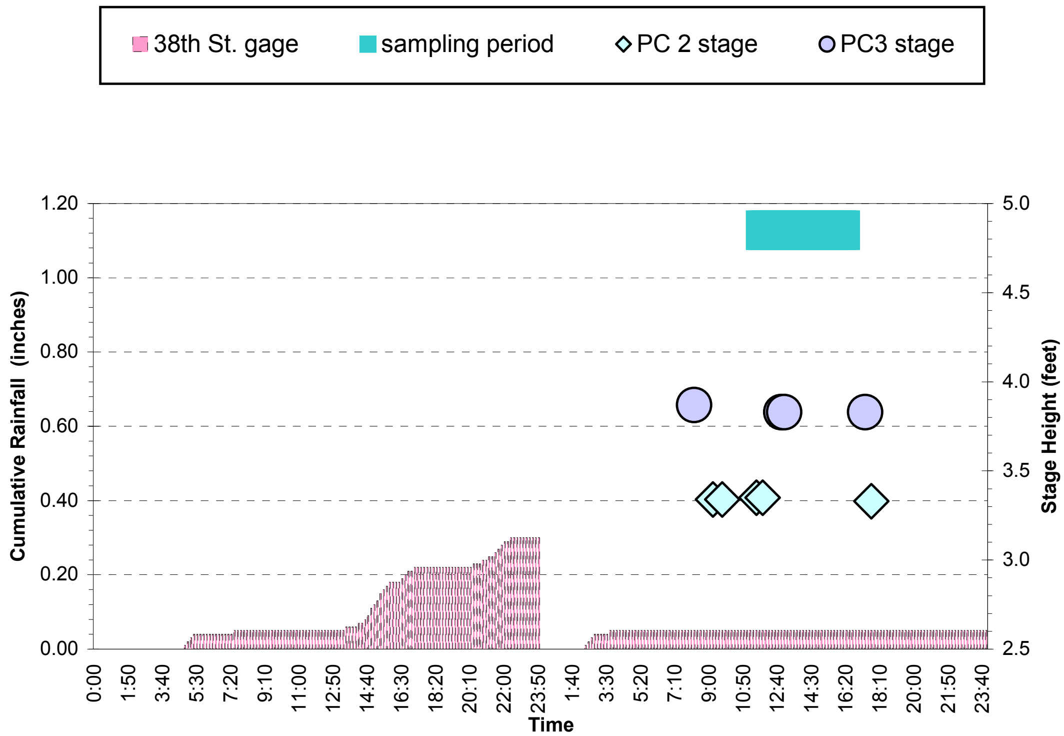

Figure 4. 38th Street gage cumulative rainfall: 4/22/01 - 4/23/01.

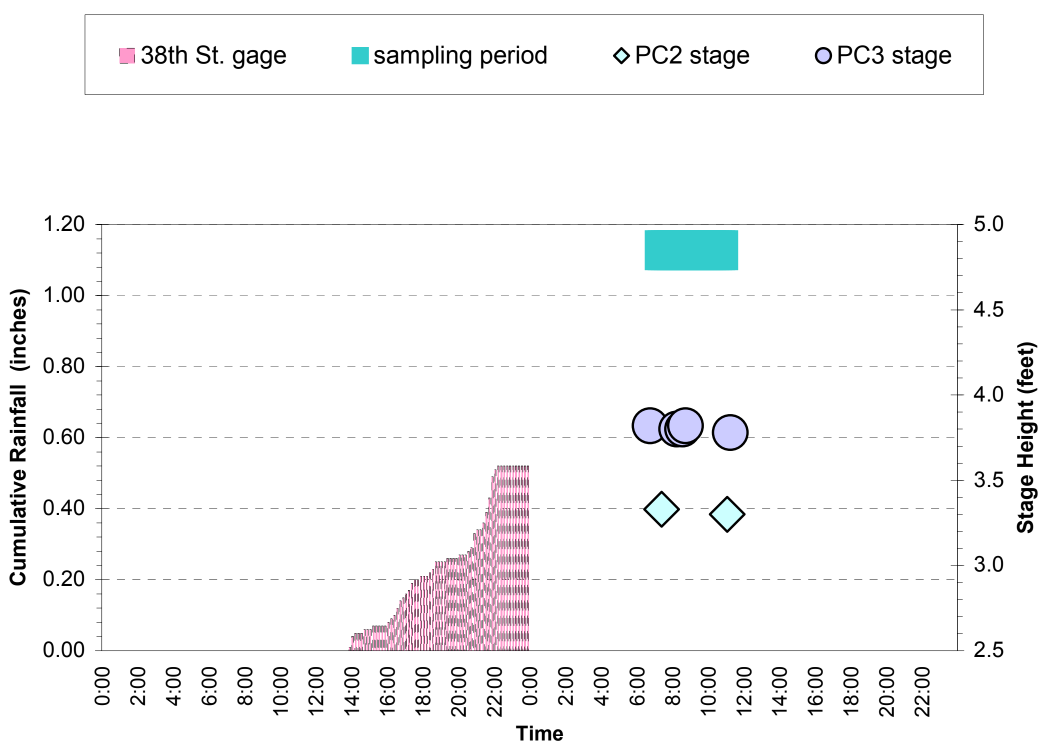

Figure 5. 38th Street gage cumulative rainfall: 5/4/01 - 5/5/01.

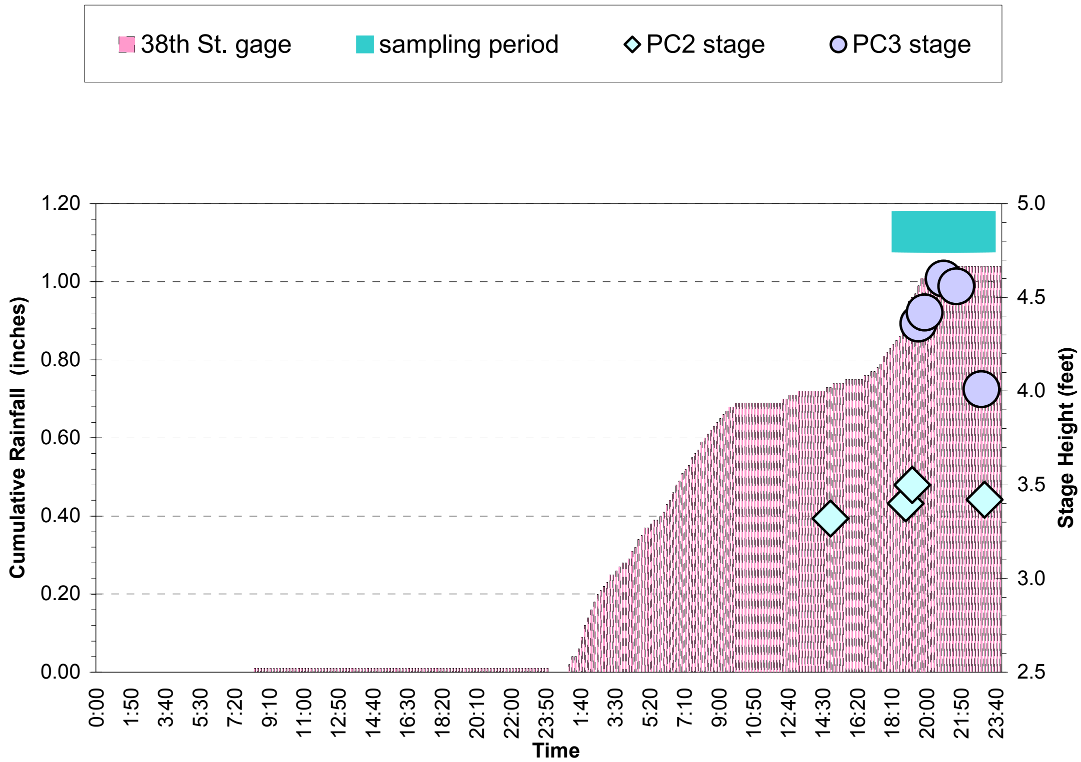

Figure 6. 38th Street gage cumulative rainfall: 5/13/01 - 5/14/01.

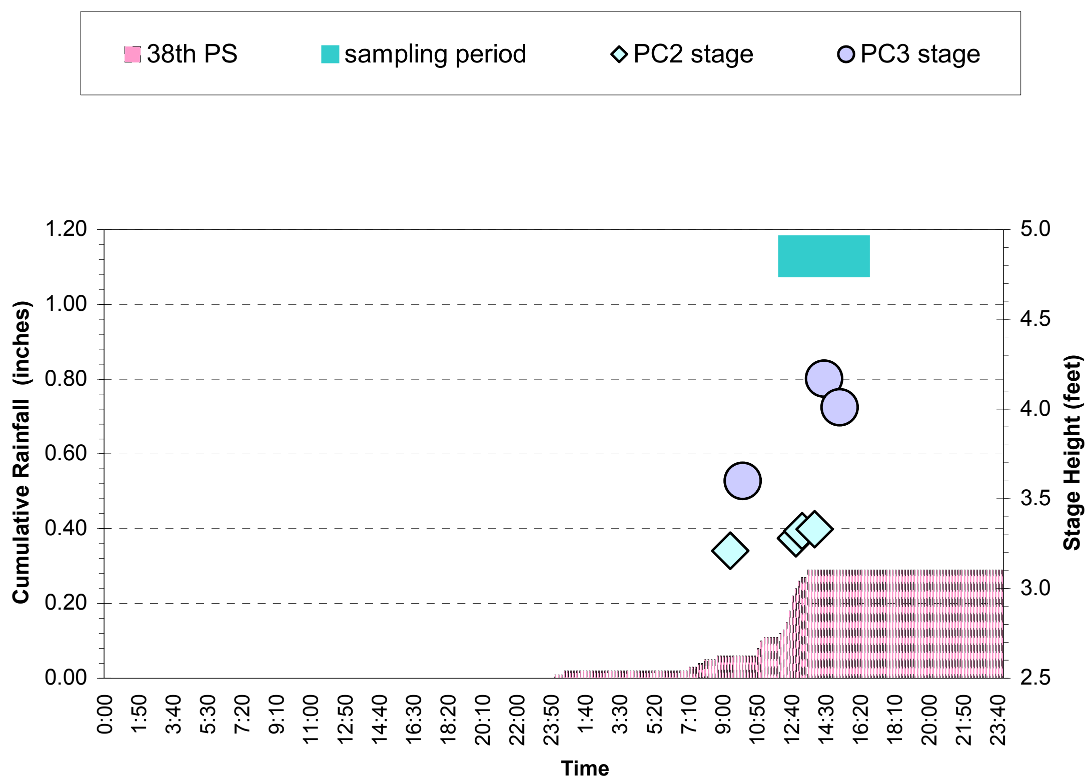

Figure 7. 38th Street gage cumulative rainfall: 6/26/01 - 6/27/01.

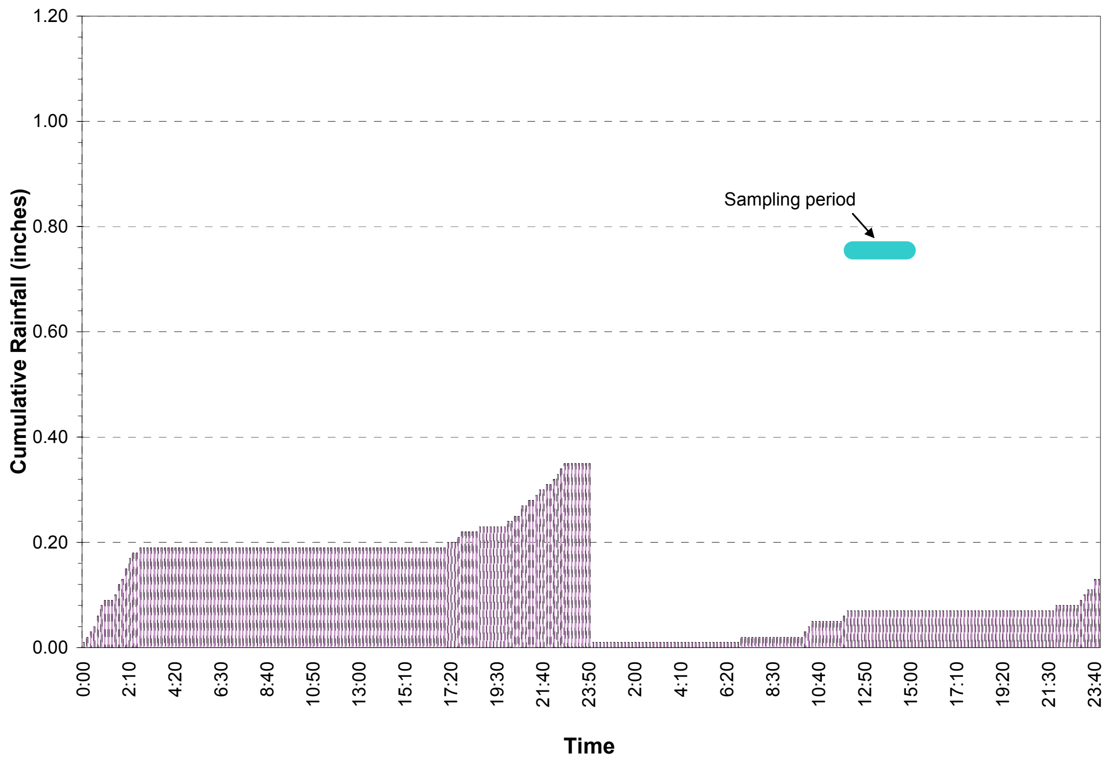

Figure 8. 38th Street gage cumulative rainfall: 3/31/03 - 4/1/03

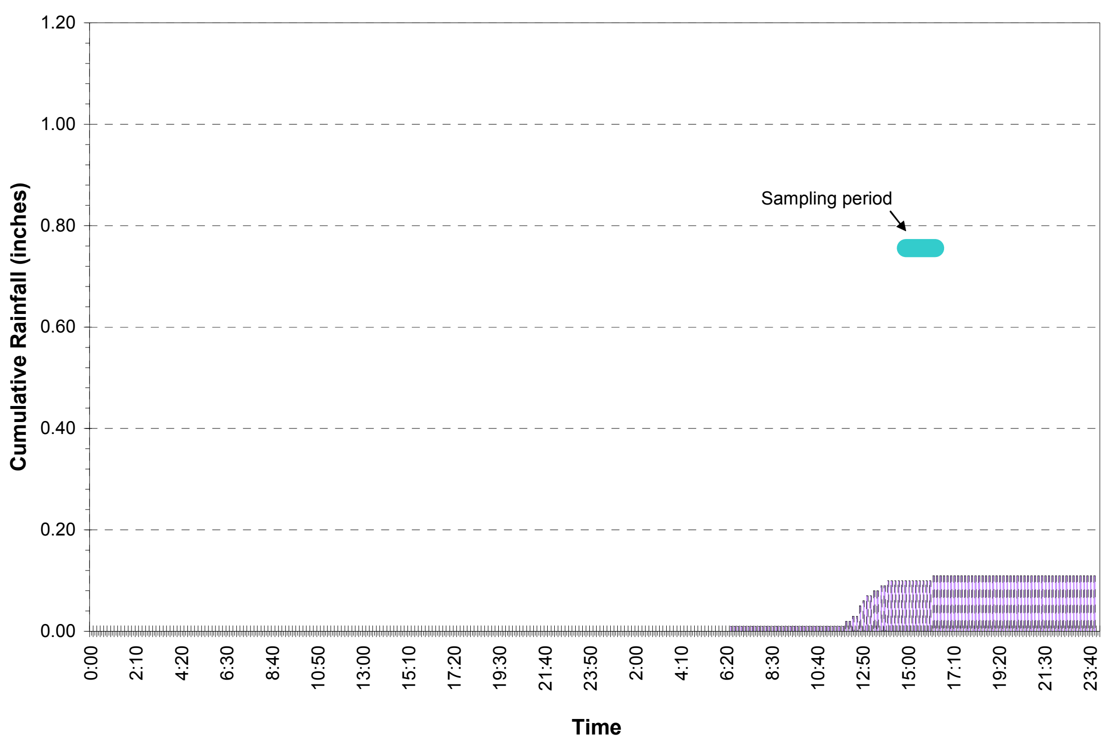

Figure 9. 38th Street gage cumulative rainfall: 4/20/03 - 4/21/03.

Streamflows measured during the 2001 sample events suggest that flows were adequately characterized at the different sites. Flow information can also provide some insight into the flow regime of the stream during the sampling period. For 2001, the summed flow of PC3 and PC4 was within 11% of the flow measured at PC2 for three of the four sample dates. For the 5/14/01sampling event, the summed flow of PC3 and PC4 was about 34% higher than the flow at PC2. This discrepancy was likely due to the time that flows were measured in relation to increases in streamflow during the rainfall and runoff event: the PC2 flow was measured 30 - 60 minutes before flows were measured at PC3 and PC4 and before a noticeable increase in rainfall and runoff intensity.

Collection of water quality samples during optimal conditions of rainfall and runoff is challenging with limited resources. Of the four sample events during the spring of 2001, the first two missed the period of rainfall and runoff while the latter two captured the desired hydrologic conditions. In all 2001 sample events, the cumulative rainfall met or exceeded suggested target ranges for sampling (0.15-0.35 inches) as described in the QA Project Plan.

2003 Hydrologic Conditions

The 2003 sample events on 4/1/03 and 4/21/03 (Figures 8 and 9) each occurred at the end of a period of light rainfall. For 4/1/03, rainfall of 0.07 inches accumulated over a five-hour period just prior to sampling. This rainfall followed two previous days of rainfall: 0.35 inches on 3/31/03 and 0.51 inches on 3/30/03. The 4/1/03 sample event occurred after several days of rainfall, and optimal runoff conditions had likely passed.

The 4/21/03 sampling event occurred after several days of dry weather, yet the rainfall of 0.10 inches in the previous three hours did not amount to the desired range for sampling (0.15-0.35 inches). The previous three days had little or no rainfall: 0.03 inches on 4/18//03, 0.01 inches on 4/19/03, and no rainfall on 4/20/03.

Flow measurements from different sites provide some clues to streamflow behavior during the sample events. For the 4/1/03 sample event, the summed flow of PC3 and PC4 was about 89% of the flow measured at PC2, suggesting that additional flow, perhaps groundwater, entered the stream between PC2 and the confluence of PC3 and PC4. The 4/21/03 flow measurement at PC5 equaled the sum of flows measured at PC3 and PC4, suggesting little or no additional flow or runoff between these locations.

Water Quality Results

General Chemistry

Results from the 2001 and 2003 field measurements and general chemistry analyses are summarized in Table 2. Several observations about the 2001 data are noteworthy. Stream temperature at PC5 is consistently higher, and TSS lower, than at other sites and is likely due to this site being the outlet channel for Lake Padden. TSS and TOC values for the sampling events of 5/14/01 and 6/27/01 are noticeably higher than those for the 4/23/01 and 5/5/01 events and are likely due to the higher rainfall and runoff conditions on those dates. Levels of TOC and TSS also appear to have increased from upstream to downstream sites during these rain events.

Table 2. Field Measurements and General Chemistry Results.

Date	Time	Site	pH (SU)	Temp (Celsius)	Cond (umho/cm)	TSS (mg/L)	TOC (mg/L)		Flow (cfs)	Gage (feet)	Tape-down (feet)
4/23/01	1525	PC5	7.8	11.9	80.3	3	4.3		2.45	-	2.59
	1355	PC4	7.8	11.3	86.8	6	4.2		3.99	-	4.89
	1315	PC3	8.1	10.9	184	2	4.3		0.94	3.83	4.64
	1215	PC2	8.1	10.1	109	3	4.4		5.33	0.55	3.63
5/5/01	1010	PC5	7.7	12.0	82.8	1	4.2		2.00	-	2.63
	920	PC4	7.5	9.8	89.1	4	4.2		3.52	-	5.06
	825	PC3	7.6	9.0	177	2	5.1		1.19	3.80	-
	740	PC2	7.8	9.4	116	6	4.7		5.30	0.53	-
5/14/01	2220	PC5	7.7	12.8	84.2	7	4.8		2.04	-	2.65
	2020	PC4	7.4	11.7	97.8	56	5.8		5.03	-	4.98
	1955	PC3	7.4	12.1	98.4	68	9.1	J	10.7	4.60	-
	1920	PC2	7.0	12.0	102	72	9.8	J	11.7	0.60	-
6/27/01	1440	PC5	6.3	18.2	101	3	6.7	J	0.91	-	2.69
	1525	PC4	6.0	15.5	110	16	5.8	J	2.51	-	5.08
	1426	PC3	6.0	16.4	105	44	11.1	J	4.52	4.17	-
	1315	PC2	7.4	15.7	108	73	11.8	J	6.83	0.52	-
4/1/03	12:00	PC5	8.0	9.5	101	3	4.4		4.97	-	-
	13:30	PC4	8.1	9.4	112	12	4.3		7.36	-	-
	14:00	PC3	7.9	9.2	199	5	5.5		3.28	-	-
	14:30	PC2	8.1	9.8	151	6	5.1		12.0	-	-
4/21/03	16:00	PC5	7.5	10.7	92	4	4.2		4.28	-	-
	15:45	PC4	7.7	11.0	150	25	8.7		4.35	-	-
	15:00	PC3	8.0	10.8	100	6	4.1		5.03	-	-
	14:30	PC2	7.9	10.8	120	21	5.9		9.40	-	-

J = The analyte was positively identified. The associated numerical result in an estimate.

High rainfall and runoff conditions generally allow greater transport of organic and inorganic materials from the land to the stream. Flow by itself is not necessarily a good predictor of TSS and TOC because other factors are involved, such as the type and amount of material available for transport during runoff events. Relationships between flow and TSS were examined with scatterplots for each site and showed no relationships with the few data points used (n=6 for each site). Runoff was not quantified for each sample event so it could not be related to levels of TSS and TOC.

In 2003, stream temperatures were more consistent among the sample sites than they were in 2001, and conductivity was generally higher in 2001 except for the early 2001 PC3 sample events. Values for TSS at PC5 in 2003 were, like 2001 values, among the lowest of the sites. No field measurements or general chemistry samples were taken when the outfall near PC5 was sampled on 5/14/02.

Pesticides

Nineteen of 111 target analytes were detected among four sample sites during the 2001 and 2003 sampling. Four herbicides were detected in the sample taken from the outfall near PC5 on 5/14/02. Appendix B contains the analytical results for the pesticides detected.

Fourteen of the 19 detected pesticides were herbicides: dichlobenil, diuron, MCPP (mecoprop), 2,4-D, trichlopyr, pentachlorophenol, prometon, dicamba, simazine, MCPA, lenacil, terbuthylazine, atrazine, and bromoxynil. Two were herbicide breakdown products: 2,3,4,6-tetrachlorophenol and 2,6-dichlorobenzamide. Two were fungicides: chlorothalonil and 4-nitrophenol, a breakdown product. One insecticide, diazinon, was detected only during the 2001 sampling events.

The concentrations of most detected pesticides were low, being at or slightly above detection limits, making comparisons between stations and years difficult. Most of these pesticides were also detected infrequently. Of the results for the 18 pesticides detected in 2001, 33% were qualified as estimates (values were at or near the method detection limit), 9% had no qualifier (reflecting greater accuracy), and the remaining 58% were qualified as non-detects. Of the 11 pesticides detected in 2003, 26% were qualified as estimates, 3% had no qualifier, and the remaining 70% were qualified as non-detects.

The location, time, and frequency of pesticide detections in 2001 and 2003 were examined to better understand their presence. The greatest number of pesticide detections occurred at PC2 and PC3. These sites are at the lower end of the Padden and Connelly creek basins and drain the highest density areas of development in the watershed. For 2001, the greatest number of detections occurred during the second and third sampling events, while the third and fourth sampling events contained a large number of pesticide results without data qualifiers (Appendix B). For 2003, the location, time, and frequency of pesticide detections were similar between the two sample events. The greatest number of detections occurred at sites PC2, PC3, and PC4.

Figure 10 depicts the frequency of pesticide detections across all sites and sample events for the 19 pesticides detected during 2001 and 2003. Frequency is expressed as the number of detections divided by the number of possible detections, expressed as a percentage. The number of possible detections is the number of sites times the number of sample events for a given sample year.

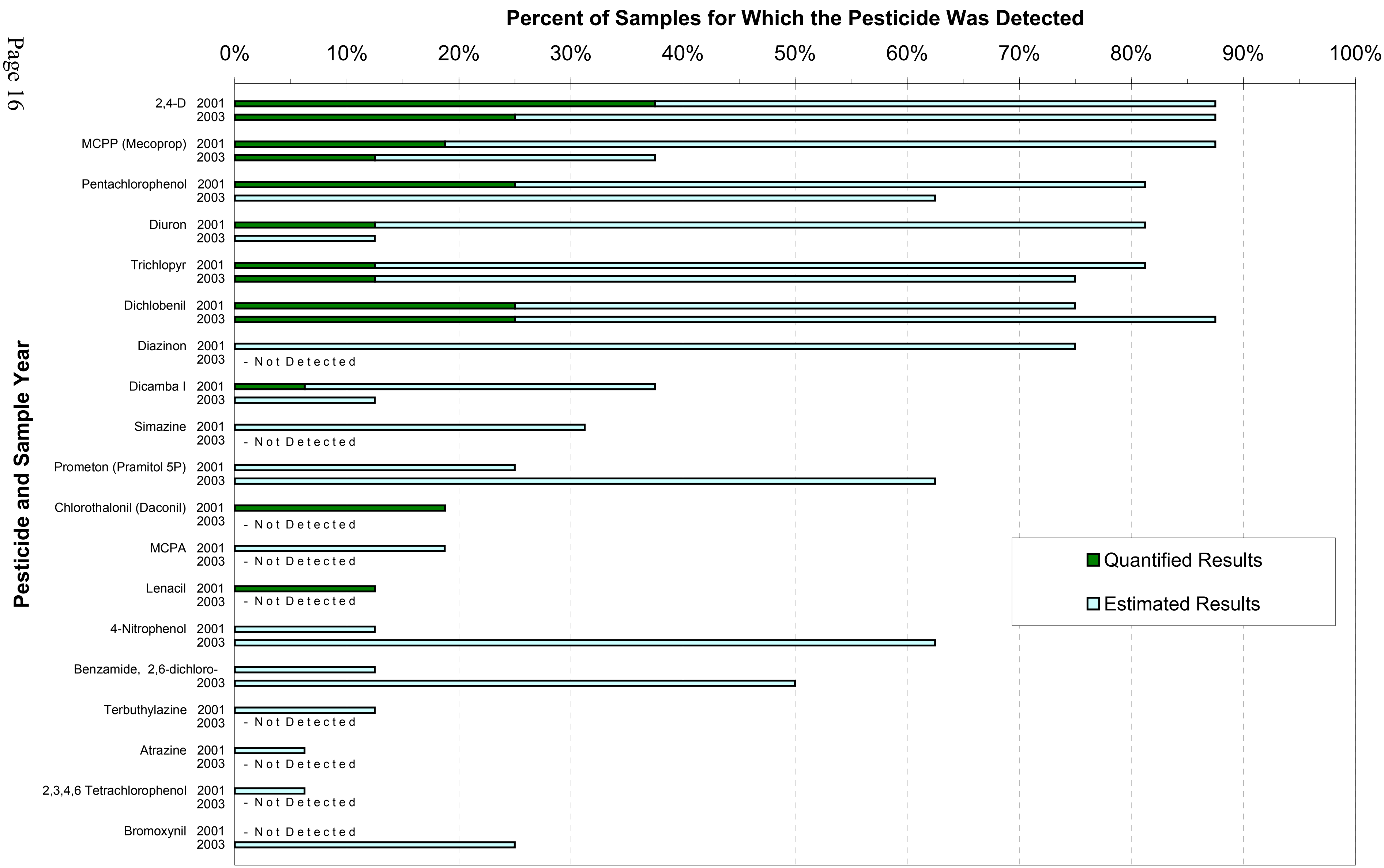

Figure 10. Frequency of Pesticide Detections in Padden Creek, 2001 and 2003.

The five most frequently detected and quantified compounds were the herbicides 2,4-D, dichlobenil, MCPP (mecoprop), trichlopyr, and pentachlorophenol. The herbicides 2,4-D, dichlobenil, trichlopyr, and pentachlorophenol were detected at similar frequencies in 2001 and 2003. Several herbicide products were detected at a higher frequency in 2003 than in 2001: prometon, bromoxynil, and the breakdown products 4-nitrophenol and 2,6-dichlorobenzamide. Detection frequencies for MCPP, diuron, and the remaining pesticides were higher in 2001 than in 2003.

Streamflow and rainfall were examined to see whether they correlated with the number of pesticide detections during any one sampling event. Linear regressions of flow and the number of pesticide detections at sample sites showed no relationship between the two. Linear regression using the number of pesticide detections at PC3 and PC4, and the 24-hour antecedent precipitation, showed a moderate correlation between the two yielding an R^2 value of 0.62. The number of pesticide detections increased as the 24-hour antecedent precipitation increased. Antecedent precipitation was used as it is likely the major pesticide transport mechanism in the study area.

Many of the pesticides detected in Padden Creek have been detected in other urban streams in Puget Sound. The urban environment includes residential, commercial, public, and industrial land uses, and pesticides used in these settings have the potential to be transported to streams. Bortleson and Davis (1997) report results from seven urban streams from sampling conducted from 1987 to 1995. The most commonly detected pesticides in that study included the herbicides 2,4-D, dicamba, dichlobenil, diuron, MCPP, and the insecticide diazinon.

Table 3 compares the range of values for the most frequently detected pesticides from this study to the range of values found in 14 streams around Puget Sound during studies from 1987 to 1998 (Bortleson and Davis, 1997, Embry et al., 2000). The range of values for most pesticides in Padden Creek were similar to those from other studies. Several exceptions include the herbicides MCPP, diuron, and simazine. The largest values detected for these three herbicides in previous studies were greater than ten times the highest values found for these herbicides during the current study.

Two pesticides exceeded criteria for the protection of aquatic life. The insecticide diazinon exceeded chronic and acute criteria of Menconi and Cox (1994) on several occasions (Figure 11). The herbicide chlorothalonil (daconil) exceeded the chronic criteria of Norris and Dost (1992) on three occasions (Figure 12). The detection limits for these two pesticides in 2003 were sometimes higher than the respective criteria, so in these cases the criteria were potentially exceeded. Fifty percent of the diazinon results in 2003 were flagged as non-detects, while about 38% of the chlorothalonil results were flagged as non-detects. Other pesticides were found at low concentrations and were well below criteria for the protection of aquatic life.

In December 2000, EPA announced plans to phase out diazinon for indoor uses beginning in March 2001, and for all lawn, garden, and turf uses by December 2003. EPA took this action under the Food Quality Protection Act of 1996. This law requires the review of older organophosphorus pesticides because they pose the greatest potential risk to children (EPA, 2000).

Table 3. Concentration Range (in ug/L) of Most Frequently
Detected Pesticides in Padden Creek and 14 Streams in Puget Sound.

Pesticide	Padden Creek (2001 - 2003)	14 Streams (1987-1998) [a, b]
2,4-D	0.036 -1.9	0.008 - 1.0
MCPP (mecoprop)	0.0043 - 0.15	0.009 - 1.7
Pentachlorophenol	0.0098 - 0.0648	0.007 - 0.075
Diuron	0.019 - 0.234	0.02 - 3.1
Trichlopyr	0.0098 - 0.3	0.006 - 0.21
Dichlobenil	0.0015 - 0.7	0.006 - 0.20
Diazinon	0.0042 - 0.204	0.003 - 0.501
Simazine	0.005 - 0.013	0.003 - 0.7
Prometon	0.0044 - 0.15	0.008 - 0.2
Chlorothalonil	0.14 - 0.35	-

a - Bortleson and Davis, 1997.
b - Embry et al., 2000.
Most values in each of the studies were below the practical quantitation limit (PQL).

Diazinon was recently the most widely used pesticide ingredient for application around the home, on lawns, and in gardens. Its wide use resulted in it being one of the leading causes of acute insecticide poisoning for humans and wildlife. This pesticide is highly toxic to birds, mammals, honey bees, and other beneficial insects. It is also very highly toxic to freshwater fish and invertebrates following acute exposure. Diazinon is one of the most commonly found pesticides in air, rain, and drinking and surface water.

Diazinon is the latest organophosphorous pesticide to be phased out. In August of 1999, EPA announced action against methyl parathion and azinphos methyl to protect children from pesticide residues in food. In December of 2000, manufacture of chlorpyrifos (dursban) for nearly all residential uses was discontinued (EPA, 2000).

Chlorothalonil is a broad-spectrum organochlorine fungicide used to control fungi that threaten vegetables, trees, small fruits, turf, ornamentals, and other agricultural crops. Chlorothalonil and its metabolites are highly toxic to fish, aquatic invertebrates, and marine organisms (Extoxnet, 1996).

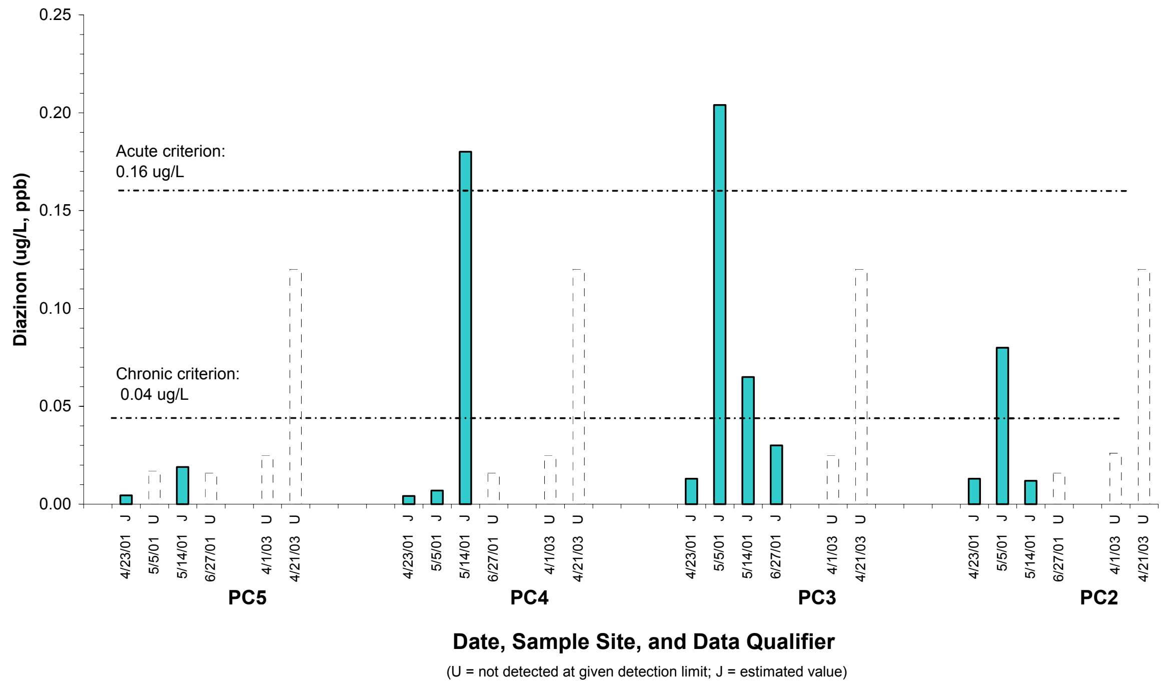

Figure 11. Diazinon in Padden Creek, 2001 and 2003.

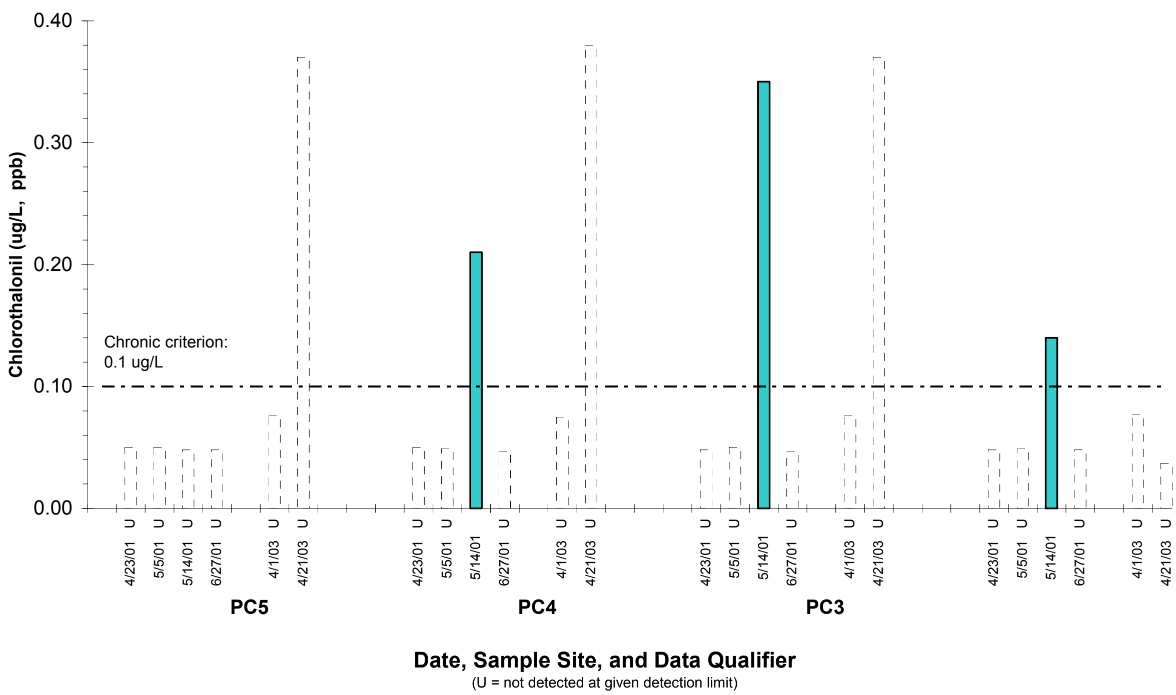

Figure 12. Chlorothalonil in Padden Creek, 2001 and 2003.

Comparison Between 2001 and 2003

Determining the effectiveness of nonpoint source control projects requires a substantial investment in implementing controls and monitoring water quality. Spooner and Line (1993) describe two challenges that a project's monitoring design and data analysis plans must overcome in order to determine effectiveness of nonpoint source pollution control projects: (1) detection of significant changes in water quality and in nonpoint source pollution control actions; and (2) associating changes in water quality to changes in pollution controls. Meeting these challenges is difficult because of the need to account for so many variables that affect the generation, transport, and detection of target pollutants (EPA, 1997).

The detection of significant changes in pesticide concentrations from one year to the next in this study was confounded by factors that influence the variability of the data, such as pesticide application (amounts, timing, and location), hydrologic conditions affecting pesticide transport, and the methods of sampling and laboratory analysis.

Analytical reporting limits frequently varied over one to two orders of magnitude for some analytes, resulting in non-detect values that were much higher than detected values on different dates (e.g., the fungicide chlorothalonil and the herbicides diuron and trichlopyr). These instances preclude making appropriate comparisons between pesticide concentrations.

The hydrologic conditions at the time of sample collection also confounds evaluation of differences between the two sample seasons. Hydrologic conditions were most similar during the 4/23/01 and 4/1/03 events. In each case, little rain (<= 0.1 inches) fell on the day of sampling with most of this falling in the several hours prior to sampling. Even though the hydrologic profiles for 6/27/01 and 4/21/03 events appear similar, the cumulative rainfall for the 4/21/03 event was 0.1 inches, only a third of the 0.3 inches recorded for the 6/27/01 sample event.

While the project plan called for testing differences between pesticide concentrations from 2001 and 2003 using parametric or nonparametric statistical tests, no tests were performed because of the small number of samples, the even smaller number of pesticide quantifications that could be used in such tests, and the presence of many censored values (non-detects and estimated values).

Even if differences in pesticide concentrations from 2001 and 2003 had been found, determining the reasons for those differences would be challenging due to factors described above. Ideally, all factors would have been held constant except the one that was being evaluated, which in this case was pesticide application by watershed residents. To attribute any changes in pesticide levels in streams to the public education program would need substantial documentation of pesticide use behaviors by watershed residents and commercial/government applicators for periods before and after the public education program.

Conclusions

Four sampling events in the Padden Creek basin in 2001 and two events in 2003 detected 19 of 111 target pesticides. Two sampling events in 2001 occurred during desired conditions, i.e., during or immediately after rainfall and runoff conditions while streamflows were rising and/or falling. Two sampling events in 2001 occurred during stable streamflow conditions and well after rainfall had ceased. The two sampling events in 2003 also appear to have occurred during stable streamflow conditions following light rainfall.

Pesticides were detected on each of the six sampling events which occurred between April and June in 2001 and in 2003. The most frequently detected pesticides were dichlobenil, diuron, diazinon, MCPP (mecoprop), 2,4-D, trichlopyr, pentachlorophenol, and prometon. Each of these seven pesticides was found at least once at each sample site during the study. Concentrations of pesticides detected in Padden Creek were low, being at or slightly above detection limits. In 2001, diazinon and chlorothalonil (daconil) exceeded criteria for the protection of aquatic life several times.

The results from the six monitoring events provide useful information about pesticides in Padden Creek during different hydrologic conditions. The presence, time, and frequency of pesticide detections may help residents and applicators recognize that pesticides are transported to the streams and can affect water quality, even in the absence of active rainfall and runoff conditions.

The objectives to determine differences in pesticide concentrations between 2001 and 2003, and characterize those differences as a result of a public education campaign, were not realized. Reasons these objectives were not met include small samples sizes, variability in hydrologic conditions during sampling (pesticide transport), and variability in analytical sensitivity among samples, with most detections being at or slightly above analytical reporting limits.

Recommendations

- Future pesticide monitoring should use analytical methods that provide more consistency in detection limits in order to compare levels among years and produce lower detection limits for selected pesticides (e.g., diazinon and chlorothalonil), so adequate comparison to criteria can be made. The use of larger sample volumes for extraction and analyses may help attain lower detection limits. Laboratory staff should be consulted to explore other procedures that could yield more consistency in quantitation limits.

- Future pesticide monitoring in Padden Creek should use sample sites PC2 and PC3 and focus on pesticides most likely to impact aquatic life (e.g., diazinon and chlorothalonil). Focused effort in these areas may reduce monitoring costs.

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Appendix A. Target Pesticides for the Padden Creek Water Quality Study.

Nitrogen Compounds	Organophosphorus Compounds	Chlorophenoxy Herbicides
Alachlor	Abate (Temephos)	Acifluorfen (Blazer)
Ametryn	Azinphos (Guthion)	Bentazon
Atraton	Bolstar (Sulprofos)	Bromoxynil
Atrazine	Carbophenothion	2,4-D
Benefin	Chlorpyrifos	Dacthal (DCPA)
Bromacil	Coumaphos	2,4-DB
Butachlor	Demeton-O	Dicamba I
Butylate	Demeton-S	3,5-Dichlorobenzoic Acid
Carboxin	Diazinon	Dichlorprop
Chlorothalonil (Daconil)	Dichlorvos (DDVP)	Diclofop-Methyl
Chlorpropham	Dimethoate	Dinoseb
Cyanazine	Dioxathion	Ioxynil
Cycloate	Disulfoton (Di-Syston)	MCPA
Di-allate (Avadex)	EPN	MCPP (Mecoprop)
Diphenamid	Ethion	4-Nitrophenol
Dichlobenil	Ethoprop	Pentachlorophenol
Eptam	Azinphos Ethyl (Ethyl Guthion)	Picloram
Ethalfluralin (Sonalan)	Fenamiphos	2,4,5-T
Fenarimol	Fenitrothion	2,4,5-TB
Fluridone	Fensulfothion	2,3,4,5-Tetrachlorophenol
Hexazinone	Fenthion	2,3,4,6-Tetrachlorophenol
Metalaxyl	Fonofos	2,4,5-TP (Silvex)
Metolachlor	Imidan	2,4,5-Trichlorophenol
Metribuzin	Malathion	2,4,6-Trichlorophenol
MGK264	Merphos (1 & 2)	Trichlopyr
Molinate	Methyl Chlorpyrifos	
Napropamide	Methyl Paraoxon	
Norflurazon	Methyl Parathion	
Oxyfluorfen	Mevinphos	
Pebulate	Parathion	
Pendimethalin	Phorate	
Profluaralin	Phosphamidan	
Prometon (Pramitol 5p)	Propetamphos	
Prometryn	Ronnel	
Pronamide (Kerb)	Sulfotepp	
Propachlor (Ramrod)	Tribufos (DEF)	
Propazine	Tetrachlorvinphos (Gardona)	
Simazine		
Tebuthiuron		
Terbacil		
Terbutryn (Igran)		
Treflan (Trifluralin)		
Triadimefon		
Triallate		
Vernolate		
Bromoxynil*		
Lenacil*		
Terbuthylazine*		
2,6-Dichlorobenzamide*		

*These were not original target analytes – yet were detected during the study.

Appendix B. Pesticide Results from Four Sites in Padden Creek in 2001 and 2003.

All values in ug/L.

Sample Station	Sample Date	MCPP (Mecoprop) (CH)	Diuron (N)	Trichlopyr (CH)	Dichlobenil (N)	Pentachlorophenol (CH)	2,4-D (CH)	Diazinon (OP)	Dicamba I (CH)	Simazine (N)
PC2	4/23/01	0.063 NJ	0.087 NJ	0.027 NJ	0.014 J	0.043 NJ	0.063 NJ	0.013 J	0.17 U	0.012 J
PC2	5/5/01	0.085 J	0.021 NJ	0.062 J	0.045 J	0.036 J	0.059 J	0.08 [a] J	0.16 NJ	0.005 J
PC2	5/14/01	0.18 J	0.06 NJ	0.098 J	0.25	0.032 J	0.52 J	0.012 J	0.16	0.020 U
PC2	6/27/01	0.20 J	0.048 UJ	0.12 J	0.066	0.12	0.19	0.016 U	0.17 U	0.020 U
PC2	4/1/03	0.02 J	0.194 U	0.042 J	**0.023**	0.084 U	0.061 J	0.026 U	0.17 U	0.032 U
PC2	4/21/03	0.29 U	0.092 U	0.033 J	0.0023 J	0.029 J	**0.18**	0.12 [a] U	0.15 U	0.015 U
PC3	4/23/01	0.14 J	0.067 J	0.073 J	0.0094 J	0.15 J	0.15 J	0.013 J	0.17 U	0.020 U
PC3	5/5/01	0.15 J	**0.234**	0.13 J	0.044 J	**0.10**	0.11 J	0.204 [b] J	0.17 NJ	0.008 J
PC3	5/14/01	**0.58**	0.10 J	0.13 J	**0.70**	**0.19**	**0.69**	0.065 [a] J	0.033 J	0.020 U
PC3	6/27/01	**0.52**	0.12 U	**0.30**	**0.077**	**0.11**	**0.69**	0.030 J	0.16 U	0.020 U
PC3	4/1/03	0.11 J	0.189 U	0.074 J	**0.043**	0.082 J	0.14 J	0.025 U	0.16 U	0.031 U
PC3	4/21/03	0.29 U	0.019 J	0.12 U	0.0015 J	0.015 J	0.11 J	0.12 [a] U	0.15 U	0.15 U
PC4	4/23/01	0.33 U	0.075 NJ	0.14 U	0.042 U	0.084 U	0.17 U	0.0042 J	0.17 U	0.021 U
PC4	5/5/01	0.026 J	0.021 J	0.0098 J	0.0645 J	0.0098 J	0.036 J	0.007 J	0.16 U	0.020 U
PC4	5/14/01	0.042 J	0.15 NJ	0.26 J	0.056 J	0.077 J	**1.9**	0.18 [b] J	1.6 U	0.021 U
PC4	6/27/01	0.0043 J	0.027 NJ	**0.14**	0.039 U	0.067 J	0.083 J	0.016 U	0.0060 J	0.020 U
PC4	4/1/03	0.32 U	0.188 U	0.029 J	0.003 J	0.080 U	0.069 U	0.025 U	0.16 U	0.031 U
PC4	4/21/03	**0.71**	0.94 U	0.12	0.033 J	0.05 J	**0.84**	0.13 [a] U	0.072 J	0.16 U
PC5	4/23/01	0.33 U	0.12 NJ	0.14 U	0.0050 J	0.084 U	0.17 U	0.0046 J	0.17 U	0.021 U
PC5	5/5/01	0.032 J	0.13 U	0.13 U	0.0087 J	0.080 U	0.038 J	0.017 U	0.16 U	0.0050 J
PC5	5/14/01	**0.68**	**0.12**	0.13 J	0.040 U	0.026 J	**0.5**	0.019 J	0.16 U	0.013 J
PC5	6/27/01	0.18 J	0.04 NJ	0.033 J	0.0075 UJ	0.012 J	**0.39**	0.016 U	0.033 J	0.020 U
PC5	4/1/03	0.32 U	0.190 U	0.030 J	0.063 U	0.080 U	0.066 J	0.025 U	0.16 U	0.032 U
PC5	4/21/03	0.29 U	0.92 U	0.12 U	0.0040 J	0.017 J	0.12 J	0.12 [a] U	0.14 U	0.15 U
Outfall	5/14/02	0.10 J	0.13 U	0.014 NJ	0.0420 U	0.081 U	0.12 J	0.017 U	0.16 U	0.021 U

Shaded values are results where the analyte was detected
Bold values are results that had no qualifiers associated with them.
Outlined values exceeded or potentially exceeded water quality criteria for the protection of aquatic life.

(N) = nitrogen compound, (OP) = organophosphorus compound, (CH) = chlorophenoxy herbicide
U - The analyte was not detected at or above the reported result.
J - The analyte was positively identified. The associated numerical result is an estimate.
UJ - The analyte was not detected at or above the reported estimated result.
NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.
n/a - not listed as a target analyte for that analysis

a - Exceeds or potentially exceeds chronic criteria (0.04 ug/L) of Menconi and Cox (1994).
b - Exceeds acute criteria (0.16 ug/L) of Menconi and Cox (1994).
c - Exceeds or potentially exceeds chronic criteria (0.1 ug/L) of Norris and Dost (1992).

Appendix B. Pesticide Results from Four Sites in Padden Creek in 2001 and 2003.
All values in ug/L.

Sample Station	Sample Date	Prometon (Pramitol 5P) (N)	MCPA (CH)	Chlorothalonil (Daconil) (N)	Benzamide, 2,6-dichloro- (N)	Terbuthylazine (N)	4-Nitrophenol (CH)	Lenacil (N)	Atrazine (N)	2,3,4,6 Tetrachlorophenol (CH)	Bromoxynil (CH)
PC2	4/23/01	0.020 U	0.33 U	0.048 U	n/a	0.012 J	0.29 U	n/a	0.020 U	0.092 U	n/a
PC2	5/5/01	0.024 U	0.033 J	0.049 U	0.003 J	n/a	0.29 U	n/a	0.020 U	0.090 U	n/a
PC2	5/14/01	0.026 UJ	0.014 NJ	**0.14** [c]	n/a	n/a	0.27 U	**0.05**	0.020 U	0.086 U	n/a
PC2	6/27/01	0.045 J	0.33 U	0.048 U	n/a	n/a	0.29 U	n/a	0.020 U	0.092 U	n/a
PC2	4/1/03	0.032 U	0.33 U	0.077 U	0.045 J	n/a	0.039 J	n/a	0.032 U	0.092 U	0.17 U
PC2	4/21/03	0.0044 J	0.29 U	0.037 U	n/a	n/a	0.066 J	n/a	0.015 U	0.082 U	0.036 NJ
PC3	4/23/01	0.020 U	0.33 U	0.048 U	n/a	n/a	0.29 U	n/a	0.020 U	0.091 U	n/a
PC3	5/5/01	0.043 J	0.33 U	0.050 U	0.007 J	0.027 J	0.29 U	n/a	0.017 J	0.091 U	n/a
PC3	5/14/01	0.020 UJ	0.036 J	**0.35** [c]	n/a	n/a	0.28 U	**0.062**	0.020 U	0.088 U	n/a
PC3	6/27/01	0.037 J	0.33 U	0.047 U	n/a	n/a	0.28 U	n/a	0.020 U	0.090 U	n/a
PC3	4/1/03	0.031 U	0.33 U	0.076 U	0.087 J	n/a	0.037 J	n/a	0.031 U	0.090 U	0.16 U
PC3	4/21/03	0.069 J	0.29 U	0.37 [c] U	n/a	n/a	0.012 NJ	n/a	0.15 U	0.082 U	0.15 U
PC4	4/23/01	0.021 U	0.33 U	0.050 U	n/a	n/a	0.29 U	n/a	0.021 U	0.092 U	n/a
PC4	5/5/01	0.005 J	0.33 U	0.049 U	n/a	n/a	0.29 U	n/a	0.020 U	0.090 U	n/a
PC4	5/14/01	0.066 UJ	3.2 U	**0.21** [c]	n/a	n/a	2.8 U	n/a	0.021 U	0.88 U	n/a
PC4	6/27/01	0.020 U	0.33 U	0.047 U	n/a	n/a	0.049 J	n/a	0.020 U	0.0043 J	n/a
PC4	4/1/03	0.029 J	0.32 U	0.075 U	0.016 J	n/a	0.28 U	n/a	0.031 U	0.088 U	0.16 U
PC4	4/21/03	0.16 U	0.29 U	0.38 [c] U	n/a	n/a	0.18 J	n/a	0.16 U	0.080 U	0.018 NJ
PC5	4/23/01	0.021 U	0.33 U	0.050 U	n/a	n/a	0.29 U	n/a	0.021 U	0.092 U	n/a
PC5	5/5/01	0.021 U	0.32 U	0.050 U	n/a	n/a	0.28 U	n/a	0.021 U	0.088 U	n/a
PC5	5/14/01	0.020 U	0.32 U	0.048 U	n/a	n/a	0.28 U	n/a	0.020 U	0.088 U	n/a
PC5	6/27/01	0.020 U	0.33 U	0.048 U	n/a	n/a	0.051 J	n/a	0.020 U	0.092 U	n/a
PC5	4/1/03	0.033 J	0.32 U	0.076 U	0.012 J	n/a	0.28 U	n/a	0.032 U	0.088 U	0.16 U
PC5	4/21/03	0.15 J	0.29 U	0.37 [c] U	n/a	n/a	0.28 U	n/a	0.15 U	0.080 U	0.15 U
Outfall	5/14/02	0.075 J	0.32 U	0.05 U	n/a	n/a	0.28 U	n/a	0.021 U	0.089 U	0.16 U

Shaded values are results where the analyte was detected
Bold values are results that had no qualifiers associated with them.
Outlined values exceeded or potentially exceeded water quality criteria for the protection of aquatic life.

(N) = nitrogen compound, (OP) = organophosphorus compound, (CH) = chlorophenoxy herbicide
U - The analyte was not detected at or above the reported result.
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UJ - The analyte was not detected at or above the reported estimated result.
NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.
n/a - not listed as a target analyte for that analysis

a - Exceeds or potentially exceeds chronic criteria (0.04 ug/L) of Menconi and Cox (1994).
b - Exceeds acute criteria (0.16 ug/L) of Menconi and Cox (1994).
c - Exceeds or potentially exceeds chronic criteria (0.1 ug/L) of Norris and Dost (1992).