A Department of Ecology Report

WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

Padden Creek
Pesticide Monitoring Program
2001 Progress Report

Abstract

Pesticide concentrations were characterized at four sites in Padden Creek in Bellingham from April to June, 2001. The pesticide monitoring was part of a larger effort by the Washington State Department of Ecology, Western Washington University, and the City of Bellingham to evaluate water quality conditions in the Padden Creek watershed and identify areas of concern, as well as educate the public and focus on other pollution control efforts.

Eighteen of 207 targeted pesticides were detected at four sample sites during four sampling events. Two sampling events occurred during rainfall and runoff conditions while streamflows were rising and/or falling, and the other two occurred during stable streamflow conditions and well after rainfall had ceased.

The seven most frequently detected pesticides were dichlobenil, diuron, diazinon, MCPP (Mecoprop), 2,4-D, trichlopyr, and pentachlorophenol. Each of these seven pesticides was found at least once at each sample site during the study. Other pesticides detected were dicamba, simazine, prometon, chlorothalonil, MCPA, lenacil, 4-nitrophenol, terbutylazine, atrazine, and 2,3,4,6-tetrachlorophenol. A breakdown product of dichlobenil, 2,6-dichlorobenzamide, was also detected. The concentrations of most detected pesticides in Padden Creek were low, being at or slightly above detection limits. Two compounds, diazinon and chlorothalonil (Daconil), exceeded criteria for the protection of aquatic life.

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by Keith Seiders
December 2001

Publication No. 01-03-045
Waterbody No. WA-01-1622

Publication Information

This report is available on the Department of Ecology home page on the World Wide Web at http://www.ecy.wa.gov/biblio/0103045.html

For additional copies of this report, contact the Department of Ecology Publications Distribution Office and refer to publication number 01-03-045
E-mail: ecypub@ecy.wa.gov
Phone: (360) 407-7472
Address: PO Box 47600, Olympia WA 98504-7600

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Acknowledgements

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

- David Laws, Stuart Magoon, Cliff Kirchmer, Dale Norton, Will Kendra, Rob Plotnikoff, and Matt Kadlec, all of Ecology, for project development and/or review of the monitoring plan. Joan Vandersypen, of Western Washington University, also reviewed the plan and provided information about other monitoring activities in the watershed.

- Manchester Environmental Laboratory staff for consultations during project planning and for processing, analysis, and reporting of sample results: Will White, Pam Covey, Kamilee Ginder, Meredith Jones, Bob Carrell, Greg Perez, Norm Olsen, and Karin Feddersen.

- Padden Creek resident Mark Roberts for volunteering his time to help collect samples, monitor stream flow, and provide information about the watershed.

- Morgan Roose, Brandee Era, and Steve Golding for their help with sample collection.

- Renee LaCroix and Peg Wendling of the City of Bellingham for rainfall data and information about the watershed.

- Joan LeTourneau for formatting and editing the final report.

Background

Recent water quality studies in the Puget Sound region have raised concern about the impact of residential use of pesticides on the aquatic environment (Bortleson and Davis, 1997; Voss et al., 1997). Residents receive little education on the use of pesticides, which leads to improper application of products and subsequent risks to aquatic life.

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 education to change the behavior of residents with regard to their use of pesticides. Several groups are cooperating 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 groups cooperate under the umbrella of the "Whatcom Watersheds Pledge" program. The program provides educational materials and technical assistance to Bellingham-area residents to help them identify and implement actions to reduce water pollution.

For part of this study, water quality monitoring was conducted to provide information about the Padden Creek watershed. Ecology's Environmental Assessment Program monitored pesticide levels, and Western Washington University (WWU) and the City of Bellingham monitored general water quality parameters and benthic macroinvertebrates.

This document reports the results of the first year's sampling effort by Ecology. The Quality Assurance Project Plan (QAPP) for this project (Seiders and Norton, 2001) describes the background, study design, and methodology of the project in more detail.

Study Objectives

The objectives of the Ecology Padden Creek pesticide monitoring component are to:

- Characterize pesticide concentrations in the Padden Creek watershed during the spring season of two consecutive years.
- Compare pesticide concentrations 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 WWU and City of Bellingham monitoring component are to:

- Evaluate water quality conditions in the Padden Creek watershed and identify areas of greatest concern.
- Educate the public and focus on other pollution control efforts.
- 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) on four occasions during April, May, and June of 2001. Table 1 describes sample site locations. A similar sampling effort is scheduled for the spring of 2002, after the public education effort is completed.

Table 1. Sample site descriptions.

Site	Location	Ecology pesticides	WWU water quality and macroinvertebrates
PC-1	Padden Creek at Marine View Park	-	X
PC-2	Padden Creek at Fairhaven Park	X	X
PC-3	Connelly Creek just upstream of confluence with Padden Creek	X	X
PC-4	Padden Creek upstream of confluence with Connelly Creek	X	X
PC-5	Padden Creek below outlet of Lake Padden	X	X
PC-6	Unnamed Creek above Lake Padden	-	X

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 sample came from each quarter-point. Sample containers for pesticide analyses were specially cleaned by the manufacturer for such use as described in the QAPP.

Water samples were analyzed for three classes of pesticides: nitrogen and organophosphorous pesticides, and chlorophenoxy herbicides (Appendix A). Samples were also analyzed for total suspended solids (TSS) and total organic carbon (TOC) to aid the interpretation of pesticide data. Measurements of flow, pH, temperature, and specific conductance were made in the field as described in the QAPP. Streams stage height gages were installed at sites PC2 and PC3 for the duration of the study. Stream stage height at PC2 and PC3 was determined multiple times during the sampling event in order to determine the nature of the hydrograph during the sampling event. Stream levels at sites PC4 and PC5 were determined by measuring down from a reference point above the stream to the water’s surface.

Sample collection was attempted during periods when pesticide transport was likely to occur through runoff processes. The criteria for sampling were three or more 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 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) for the three-month period were collected by the City of Bellingham. The city maintains several rain gages and also uses the National Weather Service data from the Bellingham Airport. Rainfall data from the city's 38th Street rain gage were used in the analyses below.

Quality Assurance

The 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 such as: holding times being met, the assessment of method performance using method blanks and surrogate recovery data, and laboratory duplicate analyses. The case narratives pronounced data useable as qualified. Field transfer blanks that were analyzed showed no contamination. Results from field duplicates were qualified as non-detects or estimates and as such were not useful to determine sampling precision. The available quality assurance information revealed no indications of problems with the sampling or analytical aspects of the 2001 sampling effort. The case narratives from the laboratory analyses are found in Appendix B.

Results

Hydrologic Conditions during Sampling Events

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).

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. Figures 1-4 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. 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. In all sample events, the cumulative rainfall met or exceeded suggested target ranges for sampling (0.15-0.35 inches) as described in the QAPP. The nature of rainfall and stage height preceding and during the sampling period helps illustrate the range of sampling conditions that occurred during the spring 2001 sampling.

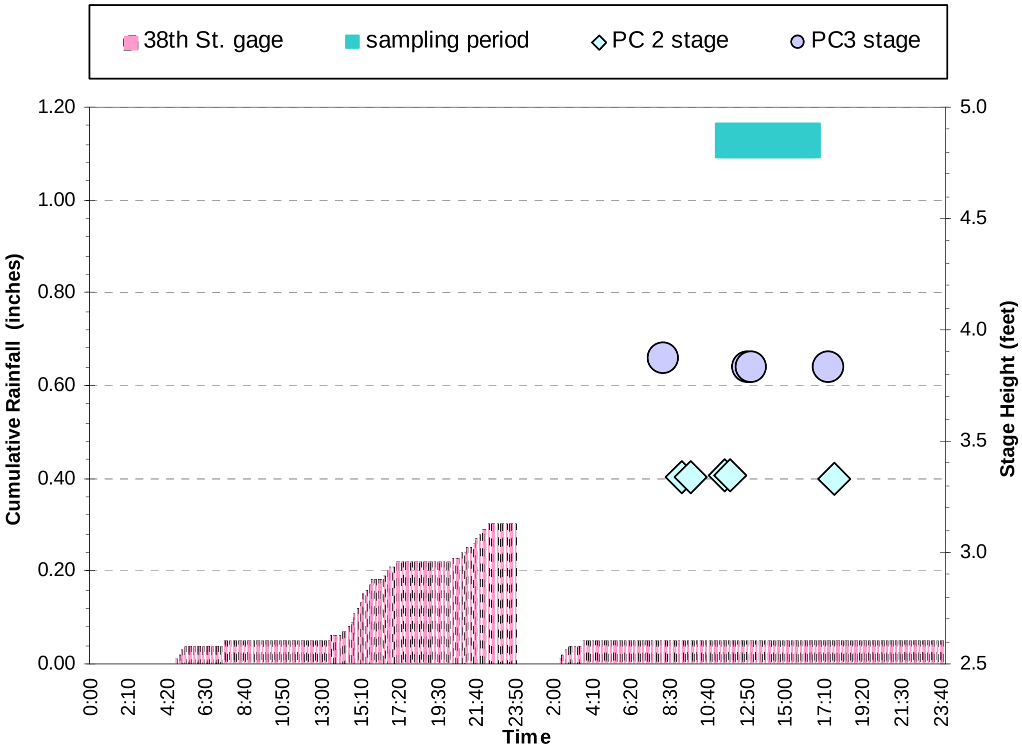

Figure 1. 38th Street gage cumulative rainfall: 4/22/01 - 4/23/01.

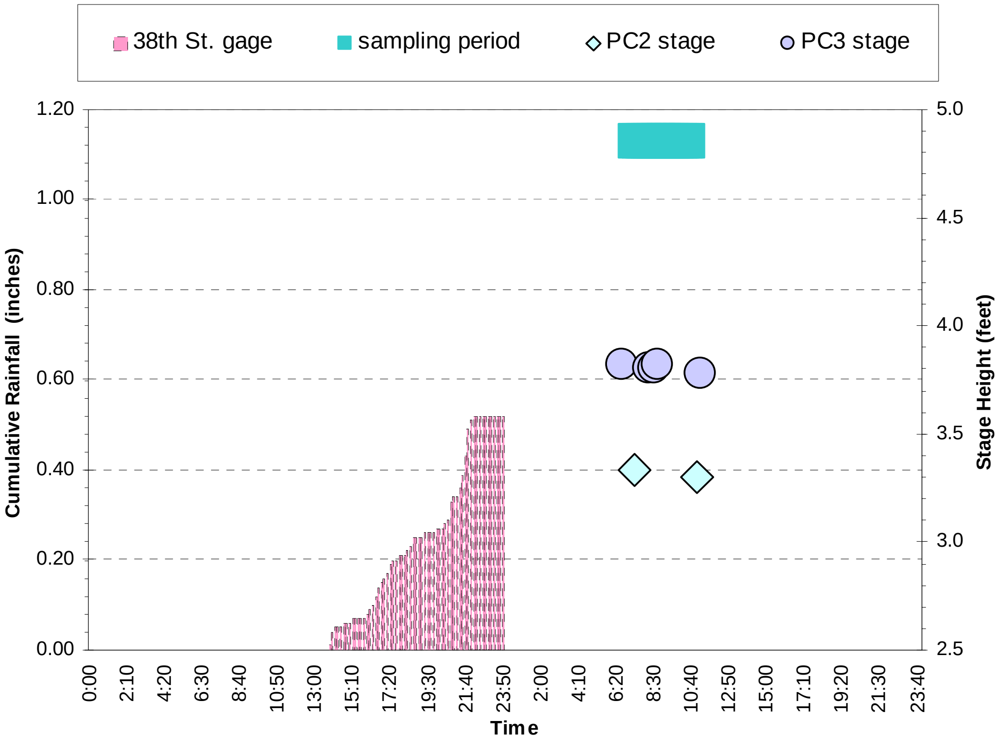

Figure 2. 38th Street gage cumulative rainfall: 5/4/01 - 5/5/01.

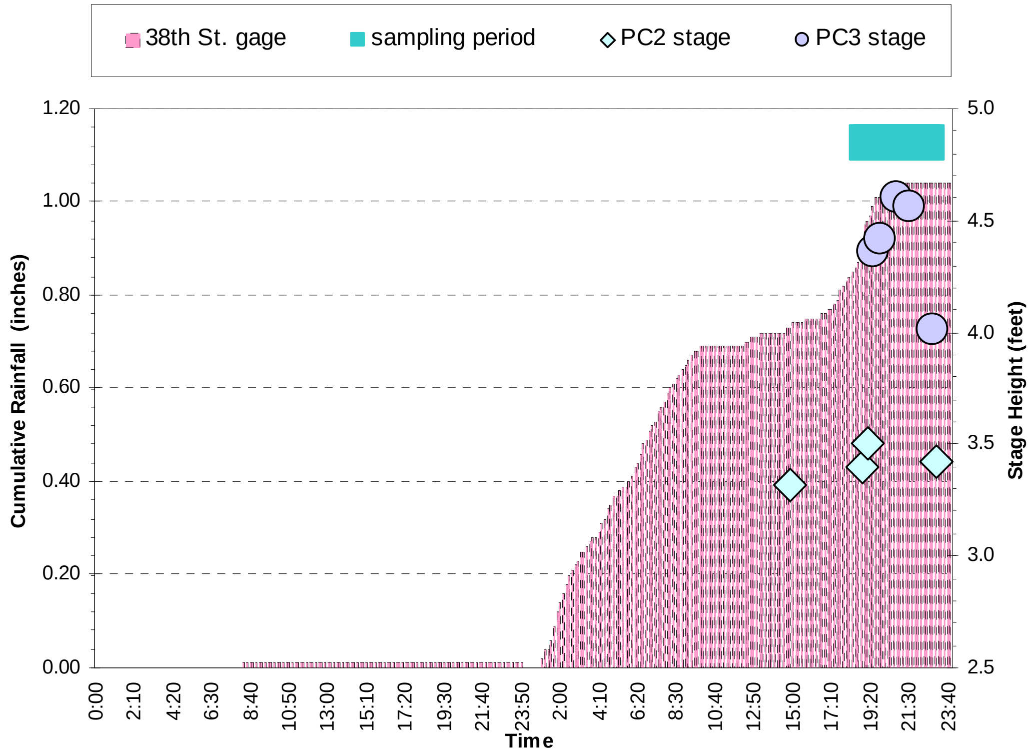

Figure 3. 38th Street gage cumulative rainfall: 5/13/01 - 5/14/01.

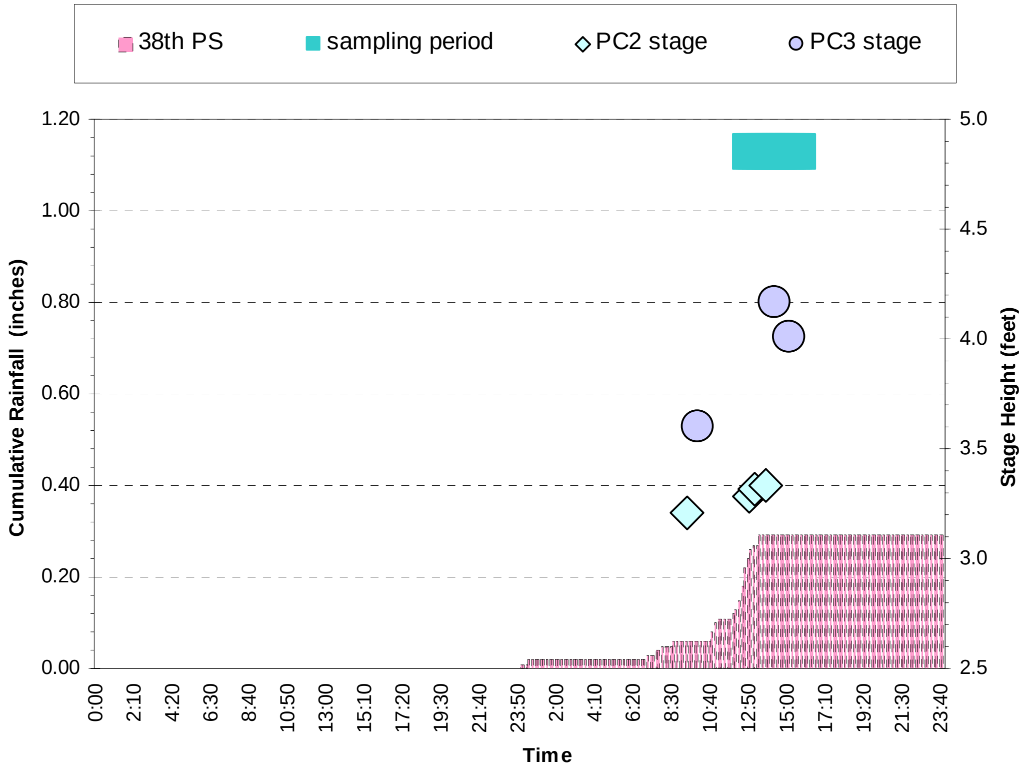

Figure 4. 38th Street gage cumulative rainfall: 6/26/01 - 6/27/01.

On April 23 and May 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 April 23 the stage height at each site appeared to remain level while the May 5 stage height dropped slightly during the sampling period. The April 23 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 May 5 event, with a cumulative rainfall of just over 0.5 inch, appears to have captured decreasing flows which had likely peaked during the period of greatest rainfall intensity (around 2200 hours on May 4).

The sampling on May 14 and June 27 occurred during and just after periods of peak rainfall. The May 14 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 site 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 June 27 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.

The criteria for sampling were adequate for sampling runoff events: several days of dry weather followed by precipitation (about 0.3 inch) that would likely cause an increase in streamflow. A challenge in sampling was the collection of samples during optimal conditions of rainfall and runoff. While two sample outings captured runoff events, two did not. Improvements in the timing of sample collection could be gained by increasing the ability to monitor conditions and sample on short notice. Several potential runoff events were not sampled due to lack of information about local runoff conditions and/or availability of sampling personnel at all times (i.e., 24 hours a day for the three-month sampling season).

Streamflows measured during the spring of 2001 suggest that flows were adequately characterized at the four sites. The summed flow of PC3 and PC4 was within 11% of the flow measured at PC2 for three of the four sample dates (Table 2). For the May 14 sampling 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.

Table 2. Padden Creek Pesticide Study: Field Measurements and General Chemistry Results.

Date	Time	Site	pH (SU)	Temp (Celsius)	Cond (umhos/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
4/23/01	1355	PC4	7.8	11.3	86.8	6	4.2		3.99		4.89
4/23/01	1315	PC3	8.1	10.9	184.2	2	4.3		0.94	3.83	4.64
4/23/01	1215	PC2	8.1	10.1	109.3	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
5/5/01	920	PC4	7.5	9.8	89.1	4	4.2		3.52		5.06
5/5/01	825	PC3	7.6	9.0	177.0	2	5.1		1.19	3.80	
5/5/01	740	PC2	7.8	9.4	116.2	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
5/14/01	2020	PC4	7.4	11.7	97.8	56	5.8		5.03		4.98
5/14/01	1955	PC3	7.4	12.1	98.4	68	9.1	J	10.73	4.60	
5/14/01	1920	PC2	7.0	12.0	102.3	72	9.8	J	11.72	0.60	
6/27/01	1440	PC5	6.3	18.2	101.0	3	6.7	J	0.91		2.69
6/27/01	1525	PC4	6.0	15.5	110.0	16	5.8	J	2.51		5.08
6/27/01	1426	PC3	6.0	16.4	105.0	44	11.1	J	4.52	4.17	
6/27/01	1315	PC2	7.4	15.7	108.0	73	11.8	J	6.83	0.52	

Water Quality Results

Results from field measurements and general chemistry analyses are summarized in Table 2. Several observations about these data are noteworthy. Stream temperature at PC5 is consistently higher, and TSS lower, than at other sites and is due to this site being the outlet channel for Lake Padden. Total suspended solids and TOC values for the sampling events of May 14 and June 27 are noticeably higher than those for the April 23 and May 5 events and are likely due to the higher rainfall and runoff conditions on those dates. TOC and TSS also appear to have increased from upstream to downstream sites during these rain events. The higher rainfall and runoff conditions allow greater transport of organic and inorganic materials from the land to the stream.

Eighteen of approximately 107 target analytes were detected among the four sample sites during the spring 2001 sampling. Table 3 contains the analytical results for the pesticides that were detected and is organized by pesticide names, sample dates, and sample sites. The shaded values are results where the analyte was detected, and the bold values are results that had no qualifiers associated with them. Outlined values exceeded water quality criteria for the protection of aquatic life. Of the results for the 18 pesticide, 33% were qualified as estimates (values were at or near the method detection limit), 9% had no qualifier (reflecting a greater confidence in the result being accurate), and the remaining 58% were qualified as non-detects.

Table 3. Padden Creek Study: Pesticides Detected in Water.

All values in ug/L. Detected values shaded; unqualified values in bold; values exceeding aquatic life criteria outlined.

Sample Date --->	4/23/01				5/5/01				5/14/01				6/27/01			
Sample Site --->	PC2	PC3	PC4	PC5	PC2	PC3	PC4	PC5	PC2	PC3	PC4	PC5	PC2	PC3	PC4	PC5
Nitrogen pesticides																
Dichlobenil	0.014 J	0.0094 J	0.042 U	0.005 J	0.045 J	0.044 J	0.0645 J	0.0087 J	**0.25**	**0.7**	0.056 J	0.040 U	**0.066**	**0.077**	0.039 U	0.0075 UJ
Simazine	0.012 J	0.020 U	0.021 U	0.021 U	0.005 J	0.008 J	0.020 U	0.005 J	0.020 U	0.020 U	0.021 U	0.013 J	0.020 U	0.020 U	0.020 U	0.020 U
Diuron	0.087 NJ	0.067 J	0.075 NJ	0.12 NJ	0.021 NJ	**0.234**	0.021 J	0.13 U	0.06 NJ	0.1 J	0.15 NJ	**0.12**	0.048 UJ	0.12 U	0.027 NJ	0.04 NJ
Atrazine	0.020 U	0.020 U	0.021 U	0.021 U	0.020 U	0.017 J	0.020 U	0.021 U	0.020 U	0.020 U	0.021 U	0.020 U	0.020 U	0.020 U	0.020 U	0.020 U
Prometon (Pramitol 5P)	0.020 U	0.020 U	0.021 U	0.021 U	0.024 U	0.043 J	0.005 J	0.021 U	0.026 UJ	0.020 UJ	0.066 UJ	0.020 U	0.045 J	0.037 J	0.020 U	0.020 U
Chlorothalonil (Daconil)	0.048 U	0.048 U	0.050 U	0.050 U	0.049 U	0.050 U	0.049 U	0.050 U	**0.14**^{e}	**0.35**^{e}	**0.21**^{e}	0.048 U	0.048 U	0.047 U	0.047 U	0.048 U
Lenacil	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	**0.05**	**0.062**	n/a	n/a	n/a	n/a	n/a	n/a
Benzamide, 2,6-dichloro-	n/a	n/a	n/a	n/a	0.003 J	0.007 J	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Terbutylazine	0.012 J	n/a	n/a	n/a	n/a	0.027 J	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Organophoshorus pesticides																
Diazinon	0.013^a J	0.013^a J	0.0042 J	0.0046 J	0.08^b J	0.204^c J	0.007 J	0.017^d U	0.012^a J	0.065^b J	0.18^c J	0.019^a J	0.016^d U	0.030^a J	0.016^d U	0.016^d U
Chlorophenoxy herbicides																
MCPP (Mecoprop)	0.063 NJ	0.14 J	0.33 U	0.33 U	0.085 J	0.15 J	0.026 J	0.032 J	0.18 J	**0.58**	0.042 J	**0.68**	0.2 J	**0.52**	0.0043 J	0.18 J
2,4-D	0.063 NJ	0.15 J	0.17 U	0.17 U	0.059 J	0.11 J	0.036 J	0.038 J	0.52 J	**0.69**	**1.9**	**0.5**	**0.19**	**0.69**	0.083 J	0.39
Trichlopyr	0.027 NJ	0.073 J	0.14 U	0.14 U	0.062 J	0.13 J	0.0098 J	0.13 U	0.098 J	0.13 J	0.26 J	0.13 J	0.12 J	**0.3**	**0.14**	0.033 J
Pentachlorophenol	0.043 NJ	0.15 J	0.084 U	0.084 U	0.036 J	**0.1**	0.0098 J	0.080 U	0.032 J	**0.19**	0.077 J	0.026 J	**0.12**	**0.11**	0.067 J	0.012 J
Dicamba I	0.17 U	0.17 U	0.17 U	0.17 U	0.16 NJ	0.17 NJ	0.16 U	0.16 U	**0.16**	0.033 J	1.6 U	0.16 U	0.17 U	0.16 U	0.006 J	0.033 J
MCPA	0.33 U	0.33 U	0.33 U	0.33 U	0.033 J	0.33 U	0.33 U	0.32 U	0.014 NJ	0.036 J	3.2 U	0.32 U	0.33 U	0.33 U	0.33 U	0.33 U
4-Nitrophenol	0.29 U	0.29 U	0.29 U	0.29 U	0.29 U	0.29 U	0.29 U	0.28 U	0.27 U	0.28 U	2.8 U	0.28 U	0.29 U	0.28 U	0.049 J	0.051 J
2,3,4,6 Tetrachlorophenol	0.092 U	0.091 U	0.092 U	0.092 U	0.090 U	0.091 U	0.090 U	0.088 U	0.086 U	0.088 U	0.88 U	0.088 U	0.092 U	0.090 U	0.0043 J	0.092 U
Other																
Caffeine	0.019 J	n/a	0.007 NJ	n/a	0.014 J	0.021 J	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.21	n/a	n/a
Acetaminophen	n/a	n/a	0.08 NJ	n/a	0.12 J	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

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 a target analyte

a - Exceeds the Recommended Maximum Concentration (0.009 ug/L) of NAS/NAE, 1973
b - Exceeds chronic criteria (0.04 ug/L) of Menconi and Cox (1994).
c - Exceeds acute criteria (0.16 ug/L) of Menconi and Cox (1994).
d - Potentially exceeds the Recommended Maximum Concentration (0.009 ug/L) of NAS/NAE, 1973
e - Exceeds chronic criteria (0.1 ug/L) of Norris and Dost (1992).

The location, time, and frequency of pesticide detection were examined. The greatest number of pesticide detections occurred at sites PC2 and PC3 (Figure 5). 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. The greatest number of detections occurred during the second and third sampling events. The third and fourth sampling events contained the largest number of pesticide results that had no data qualifiers associated with them (Table 3).

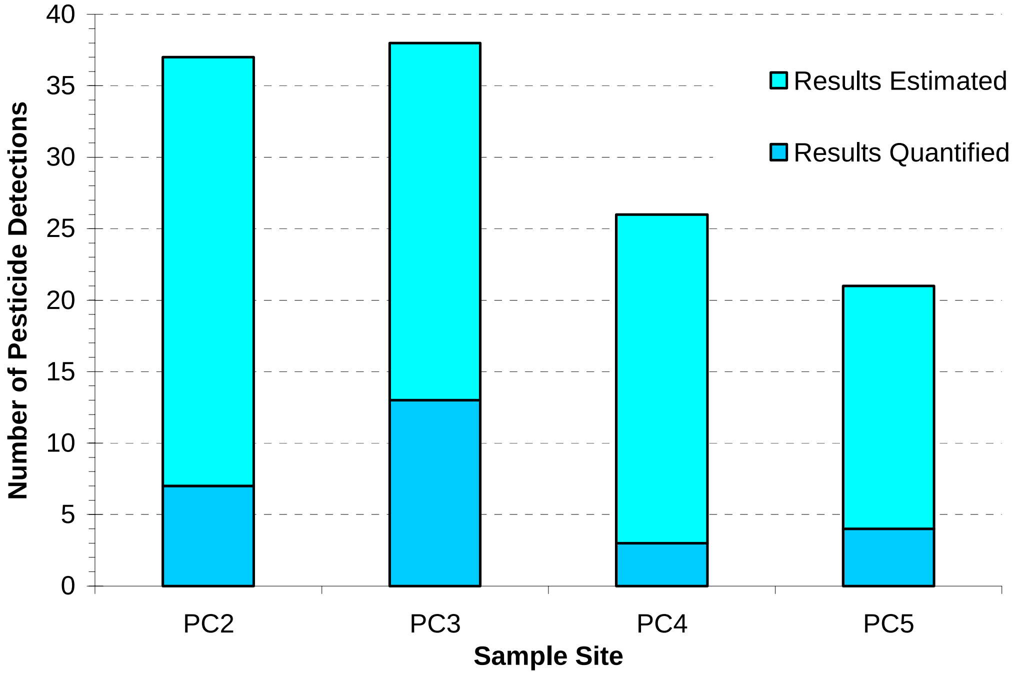

Figure 5. Number of Pesticide Detections per Site: Padden Creek 2001

Seven pesticides were detected at least once during each sampling event: dichlobenil, diuron, diazinon, MCPP (Mecoprop), 2,4-D, trichlopyr, and pentachlorophenol. These same seven pesticides were the most frequently detected as seen in Figure 6. 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; 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 and dicamba, and the insecticide diazinon. Dichlobenil, diuron, and MCPP were also commonly found.

Most pesticides were found at low concentrations, and few 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 7). The herbicide chlorothalonil (Daconil) exceeded the chronic criteria of Norris and Dost (1992) on three occasions (Figure 8).

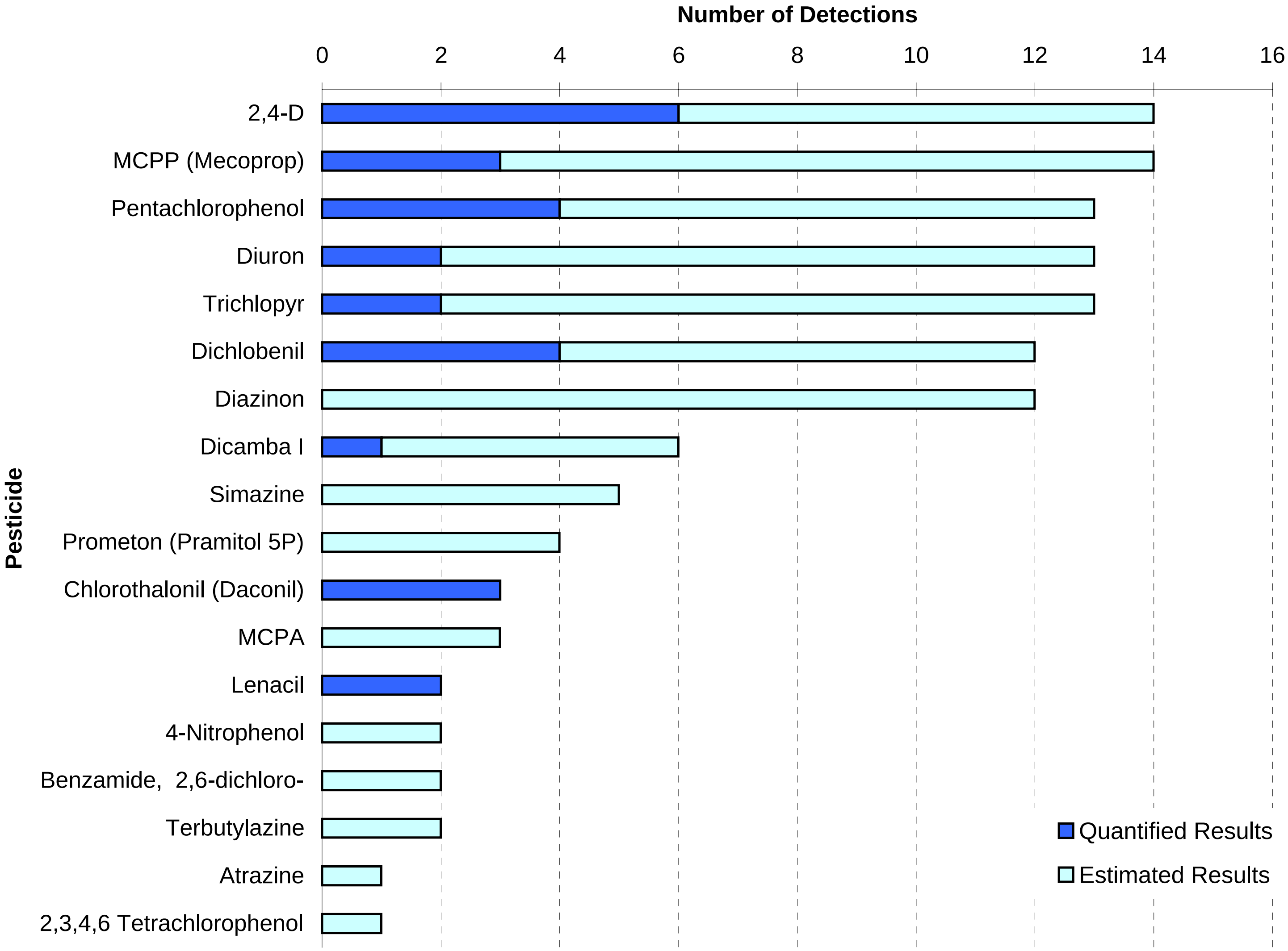

Figure 6. Frequency of Pesticide Detection: Padden Creek 2001

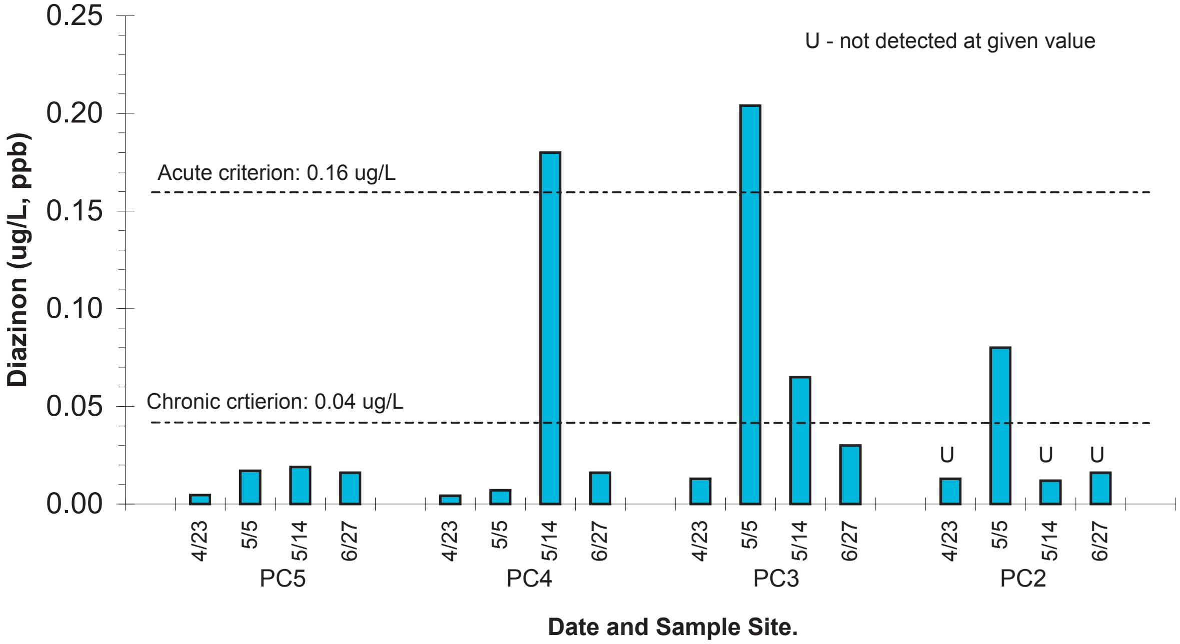

Figure 7. Diazinon Concentrations in Padden Creek, Spring 2001.

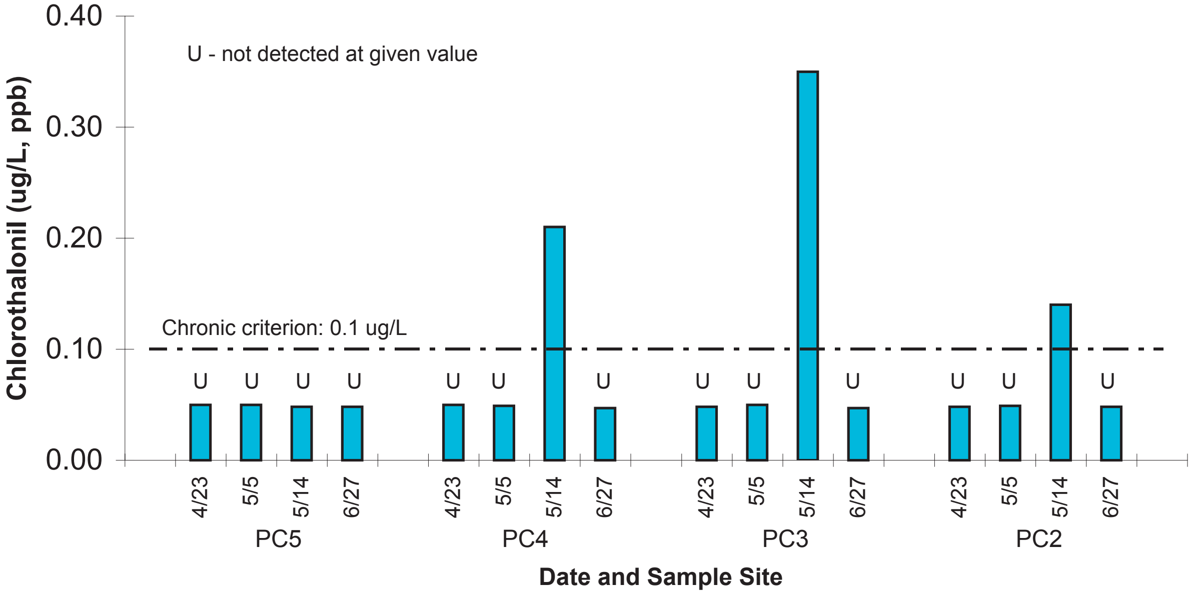

Figure 8. Chlorothalonil Concentrations in Padden Creek, Spring 2001.

Summary

Four sampling events in the Padden Creek watershed during the spring of 2001 detected 18 of 207 targeted pesticides at four sample sites. Of the four sampling events, two occurred during or immediately after rainfall and runoff conditions while streamflows were rising and/or falling, and two occurred during stable streamflow conditions and well after rainfall had ceased. The strategy to sample during rainfall and runoff conditions was partly successful, and encountered the typical challenges associated with storm-event sampling.

Pesticides were detected for each of the four sampling events. The seven most frequently detected pesticides were dichlobenil, diuron, diazinon, MCPP (Mecoprop), 2,4-D, trichlopyr, and pentachlorophenol. Each of these seven pesticides was found at least once at each sample site during the study. Concentrations of most detected pesticides in Padden Creek were low, being at or slightly above detection limits. Two compounds, diazinon and chlorothalonil (Daconil), exceeded criteria for the protection of aquatic life.

The results from the four monitoring events provided adequate information about pesticides in Padden Creek during different hydrologic conditions for the purpose of educating the public. The presence, time, and frequency of pesticide detections may help residents recognize that pesticides are transported to the streams and can affect water quality, even in the absence of active rainfall and runoff conditions.

Recommendations

Recommendations for future monitoring are:

- Discontinue efforts to monitor pesticides for the purpose of evaluating the effectiveness of the public education program. The low concentrations, small sample size, and high variability of pesticide results from the 2001 monitoring will likely negate the ability to attribute any observed changes in pesticide levels to the educational effort.

- Due to the expense of pesticide monitoring, shift resources currently dedicated to pesticide monitoring to public education. The education effort may affect greater changes in pesticide use than would collection of more pesticide data.

- Consider additional pesticide monitoring after evaluating the education efforts and the results from general chemistry and benthic invertebrate monitoring. If pesticide monitoring is desired in 2003 or later, the methods used during this 2001 monitoring should be adequate. Improvements in the timing of sample collection as related to rainfall and runoff events could be gained by increasing the ability to monitor conditions and conduct sampling on short notice.

References

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Appendix A

Target Pesticides for the Padden Creek Water Quality Study

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

Nitrogen Compounds

Alachlor
Ametryn
Atraton
Atrazine
Benefin
Bromacil
Butachlor
Butylate
Carboxin
Chlorothalonil (Daconil)
Chlorpropham
Cyanazine
Cycloate
Di-allate (Avadex)
Diphenamid
Dichlobenil
Eptam
Ethalfluralin (Sonalan)
Fenarimol
Fluridone
Hexazinone
Metalaxyl
Metolachlor
Metribuzin
MGK264
Molinate
Napropamide
Norflurazon
Oxyfluorfen
Pebulate
Pendimethalin
Profluaralin
Prometon (Pramitol 5p)
Prometryn
Pronamide (Kerb)
Propachlor (Ramrod)
Propazine
Simazine
Tebuthiuron
Terbacil
Terbutryn (Igran)
Treflan (Trifluralin)
Triadimefon
Triallate
Vernolate

Surrogate

1,3-Dimethyl-2-nitrobenzene

Organophosphorus Compounds

Abate (Temephos)
Azinphos (Guthion)
Bolstar (Sulprofos)
Carbophenothion
Chlorpyrifos
Coumaphos
Demeton-O
Demeton-S
Diazinon
Dichlorvos (DDVP)
Dimethoate
Dioxathion
Disulfoton (Di-Syston)
EPN
Ethion
Ethoprop
Azinphos Ethyl (Ethyl Guthion)
Fenamiphos
Fenitrothion
Fensulfothion
Fenthion
Fonofos
Imidan
Malathion
Merphos (1 & 2)
Methyl Chlorpyrifos
Methyl Paraoxon
Methyl Parathion
Mevinphos
Parathion
Phorate
Phosphamidan
Propetamphos
Ronnel
Sulfotepp
Tribufos (DEF)
Tetrachlorvinphos (Gardona)

Surrogate

Triphenyl Phosphate

Chlorophenoxy Herbicides

Acifluorfen (Blazer)
Bentazon
Bromoxynil
2,4-D
Dacthal (DCPA)
2,4-DB
Dicamba I
3,5-Dichlorobenzoic Acid
Dichlorprop
Diclofop-Methyl
Dinoseb
Ioxynil
MCPA
MCPP (Mecoprop)
4-Nitrophenol
Pentachlorophenol
Picloram
2,4,5-T
2,4,5-TB
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
2,4,5-TP (Silvex)
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Trichlopyr

Surrogate

2,4,6-Tribromophenol

Appendix B

Laboratory Case Narratives

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Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard Washington 98366

May 15, 2001

TO: Keith Seiders

FROM: Meredith Jones, Chemist

SUBJECT: General Chemistry Quality Assurance Memo for Padden Creek Pesticides week 17

SUMMARY

The data generated by the analysis of these samples can be used without qualification. All analyses requested were evaluated by established regulatory quality assurance guidelines.

SAMPLE INFORMATION

Samples for Padden Creek Pesticides week 17 project were received by Manchester Environmental Laboratory on 04/24/01 in good condition.

HOLDING TIMES

All analyses were performed within established EPA holding times.

ANALYSIS PERFORMANCE

Instrument Calibration

Instrument calibration was checked by initial calibration verification standards and blanks. All initial and continuing calibration verification standards were within control limits. A correlation coefficient of 0.995 or greater was met. Balances are professionally calibrated yearly and calibrated in-house daily. Oven temperature is recorded before and after each analysis batch.

Procedural Blanks

The procedural blanks associated with these samples showed no significant analytical levels of analytes.

Spiked Sample Analysis

Spiked sample analyses were performed where applicable with all spike recoveries within acceptance limits of ± 25%. Spiked sample analysis is performed at a frequency of at least 5%.

Precision Data

Spiked sample results and duplicate sample results were used to evaluate precision on this sample set. Relative Percent Differences (RPD) for general chemistry parameters were within acceptance limits of ± 20% for duplicate analysis. Laboratory duplication is performed at a frequency of at least 10%. Precision and accuracy specifications are based on sample concentrations greater than four times the reporting limit. For results near the reporting limit, the criteria are not guaranteed to be better than +/- the method detection limit.

Laboratory Control Sample (LCS) Analyses

LCS analyses were within the windows established for each parameter.

Other Quality Assurance Measures and Issues

The “U” qualification indicates that the analyte was not detected at or above the reporting limit.

Please call Jim Ross at (360) 871-8808 or Meredith Jones at (360) 871-8833 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

May 15, 2001

TO: Keith Seiders

FROM: Meredith Jones, Chemist

SUBJECT: General Chemistry Quality Assurance Memo for Padden Creek Pesticides week 18

SUMMARY

The data generated by the analysis of these samples can be used without qualification. All analyses requested were evaluated by established regulatory quality assurance guidelines.

SAMPLE INFORMATION

Samples for Padden Creek Pesticides week 18 project were received by Manchester Environmental Laboratory on 05/07/01 in good condition.

HOLDING TIMES

All analyses were performed within established EPA holding times.

ANALYSIS PERFORMANCE

Instrument Calibration

Instrument calibration was checked by initial calibration verification standards and blanks. All initial and continuing calibration verification standards were within control limits. A correlation coefficient of 0.995 or greater was met. Balances are professionally calibrated yearly and calibrated in-house daily. Oven temperature is recorded before and after each analysis batch.

Procedural Blanks

The procedural blanks associated with these samples showed no significant analytical levels of analytes.

Spiked Sample Analysis

Spiked sample analyses were performed where applicable with all spike recoveries within acceptance limits of ± 25%. Spiked sample analysis is performed at a frequency of at least 5%.

Precision Data

Spiked sample results and duplicate sample results were used to evaluate precision on this sample set. Relative Percent Differences (RPD) for general chemistry parameters were within acceptance limits of ± 20% for duplicate analysis. Laboratory duplication is performed at a frequency of at least 10%. Precision and accuracy specifications are based on sample concentrations greater than four times the reporting limit. For results near the reporting limit, the criteria are not guaranteed to be better than +/- the method detection limit.

Laboratory Control Sample (LCS) Analyses

LCS analyses were within the windows established for each parameter.

Please call Jim Ross at (360) 871-8808 or Meredith Jones at (360) 871-8833 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

June 6, 2001

TO: Keith Seiders

FROM: Kamilee Ginder, Chemist

SUBJECT: General Chemistry Quality Assurance Memo for Padden Creek Pesticides-20

SUMMARY

The data generated by the analysis of these samples can be used noting the qualifications discussed in this memo. Total Organic Carbon samples 01208105 and 01208106 are qualified as estimates due to them not meeting the instrument precision requirements for multiple injections although they did meet the <20 Relative Percent Difference requirements for duplicates. Possible causes for the variation are the black specks found in sample 01208105 and microorganism activity. These samples were analyzed in duplicate for quality assurance purposes. Total Organic Carbon sample 01208110 was under the 1.0ppm detection limit and was therefore qualified. All analyses requested were evaluated by established regulatory quality assurance guidelines.

SAMPLE INFORMATION

Samples for Padden Creek Pesticides-20 project were received by Manchester Environmental Laboratory on 05/15/01 in good condition.

HOLDING TIMES

All analyses were performed within established EPA holding times.

ANALYSIS PERFORMANCE

Instrument Calibration

Instrument calibration was checked by initial calibration verification standards and blanks. All initial and continuing calibration verification standards were within control limits. A correlation coefficient of 0.995 or greater was met. Balances are professionally calibrated yearly and calibrated in-house daily. Oven temperature is recorded before and after each analysis batch.

Procedural Blanks

The procedural blanks associated with these samples showed no significant analytical levels of analytes.

Spiked Sample Analysis

Spiked sample analyses were performed where applicable with all spike recoveries within acceptance limits of ± 25%. Spiked sample analysis is performed at a frequency of at least 5%.

Precision Data

Spiked sample results and duplicate sample results were used to evaluate precision on this sample set. Relative Percent Differences (RPD) for general chemistry parameters were within acceptance limits of ± 20% for duplicate analysis. Laboratory duplication is performed at a frequency of at least 10%. Precision and accuracy specifications are based on sample concentrations greater than four times the reporting limit. For results near the reporting limit, the criteria are not guaranteed to be better than +/- the method detection limit.

Laboratory Control Sample (LCS) Analyses

LCS analyses were within the windows established for each parameter.

Other Quality Assurance Measures and Issues

The “U” qualification indicates that the analyte was not detected at or above the reporting limit.

The “J” qualification signifies the result is an estimate (see SUMMARY).

Please call Jim Ross at (360) 871-8808 or Kamilee Ginder at (360) 871-8826 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard Washington 98366

August 8, 2001

TO: Keith Seiders

FROM: Kamilee Ginder, Chemist

SUBJECT: General Chemistry Quality Assurance Memo for Padden Creek Pesticides-26

SUMMARY

The data generated by the analysis of these samples can be used noting the qualifications discussed in this memo. The Total Organic Carbon (TOC) samples are qualified as estimates due to high matrix spike recovery of samples associated with the Padden samples during analysis. TOC samples were analyzed twice utilizing different calibration curves with Relative Percent Differences within the acceptance limits of ± 20% for duplicates. The second TOC analysis of most samples was done one day after the holding date. In that case original results were reported. All analyses requested were evaluated by established regulatory quality assurance guidelines.

SAMPLE INFORMATION

Samples for Padden Creek Pesticides-26 project were received by Manchester Environmental Laboratory on 06/28/01 in good condition.

HOLDING TIMES

All analyses were performed within established EPA holding times except for the second analysis of most TOC samples. Those results were not reported but used as a test for replicating results.

ANALYSIS PERFORMANCE

Instrument Calibration

Instrument calibration was checked by initial calibration verification standards and blanks. All initial and continuing calibration verification standards were within control limits. A correlation coefficient of 0.995 or greater was met. Balances are professionally calibrated yearly and calibrated in-house daily. Oven temperature is recorded before and after each analysis batch.

Procedural Blanks

The procedural blanks associated with these samples showed no significant analytical levels of analytes.

Spiked Sample Analysis

Spiked sample analyses were performed where applicable. Sample 01268106 was spiked. The first time analyzed, the spike recoveries for it and most of the other spiked samples from another project, were higher than the acceptance limits of ± 25%. The spike concentration was too low for the calibration curve used in analysis the first time. The second time the spike for sample 01268106 was within the acceptance limits so no matrix affect is thought to be interfering for the Padden samples. Spiked sample analysis is performed at a frequency of at least 5%.

Precision Data

Duplicate sample results were used to evaluate precision on this sample set. Relative Percent Differences (RPD) for general chemistry parameters were within acceptance limits of ± 20% for duplicate analysis. Laboratory duplication is performed at a frequency of at least 10%. Precision and accuracy specifications are based on sample concentrations greater than four times the reporting limit. For results near the reporting limit, the criteria are not guaranteed to be better than +/- the method detection limit.

Laboratory Control Sample (LCS) Analyses

LCS analyses were within the windows established for each parameter.

Other Quality Assurance Measures and Issues

The “U” qualification indicates that the analyte was not detected at or above the reporting limit.

The “J” qualification signifies the result is an estimate (see SUMMARY).

Please call Jim Ross at (360) 871-8808 or Kamilee Ginder at (360) 871-8826 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

June 5, 2001

Subject: Padden Creek Week 17 Project

Sample(s): 01178105-10

Officer(s): Keith Seiders

By: Bob Carrell
Organics Analysis Unit

ACID HERBICIDE ANALYSIS

ANALYTICAL METHOD(S): (Draft EPA Method 8085)

The water samples for acid herbicides were extracted following Manchester Laboratory's standard operating procedure for the extraction of herbicides. The herbicide samples were hydrolyzed at pH > 12, extracted with methylene chloride at pH < 2, solvent exchanged and derivatized along with two method blanks. These extracts were analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of herbicides is performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of hetero-atoms to empirical formulas.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration (SPC) of the target analyte being quantitated.

All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier.

HOLDING TIMES

The sample was extracted and analyzed within the method holding times.

BLANKS

No target compounds were detected in the laboratory blank at or above the practical quantitation limits (PQL's) thus demonstrating that the system was free from contamination.

SURROGATES

The 2,4-dichlorophenylacetic acid surrogate and 2,4,6-tribromophenol surrogate recoveries were acceptable.

MATRIX SPIKING

None requested.

COMMENTS

The target analytes picloram and dinoseb received the ‘UJ’ qualifier because we traditionally experience highly variable recoveries for these compounds.

The data is useable as qualified.

DATA QUALIFIER CODES

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.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

NC - Not Calculated

E - This qualifier is used when the concentration of the associated value exceeds the known calibration range.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

June 5, 2001

Subject: Padden Creek Week 18 Project

Sample(s): 01188105-09

Officer(s): Keith Seiders

By: Bob Carrell
Organics Analysis Unit

ACID HERBICIDE ANALYSIS

ANALYTICAL METHOD(S): (Draft EPA Method 8085)

The water samples for acid herbicides were extracted following Manchester Laboratory's standard operating procedure for the extraction of herbicides. The herbicide samples were hydrolyzed at pH > 12, extracted with methylene chloride at pH < 2, solvent exchanged and derivatized along with two method blanks. These extracts were analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of herbicides is performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of hetero-atoms to empirical formulas.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration (SPC) of the target analyte being quantitated.

All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier.

HOLDING TIMES

The sample was extracted and analyzed within the method holding times.

BLANKS

No target compounds were detected in the laboratory blank at or above the practical quantitation limits (PQL’s) thus demonstrating that the system was free from contamination.

SURROGATES

The 2,4-dichlorophenylacetic acid surrogate and 2,4,6-tribromophenol surrogate recoveries were acceptable.

MATRIX SPIKING

The recoveries of the matrix spike analytes were acceptable for all compounds except for picloram in 01188106 LMX2. The relative percent differences (RPD) between the two matrix spike samples, 01188106 LMX1 and LMX2 were acceptable for all analytes except for dinoseb (see comment below). No qualifiers were added due to RPD’s.

COMMENTS

The target analytes picloram and dinoseb received the ‘UJ’ qualifier because we traditionally experience highly variable recoveries for these compounds.

The data is useable as qualified.

DATA QUALIFIER CODES

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.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

NC - Not Calculated

E - This qualifier is used when the concentration of the associated value exceeds the known calibration range.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

June 7, 2001

Subject: Padden Creek Pesticides - 20 Project

Sample(s): 01208105-10

Officer(s): Keith Seiders

By: Bob Carrell
Organics Analysis Unit

ACID HERBICIDE ANALYSIS

ANALYTICAL METHOD(S): (Draft EPA Method 8085)

The water samples for acid herbicides were extracted following Manchester Laboratory's standard operating procedure for the extraction of herbicides. The herbicide samples were hydrolyzed at pH > 12, extracted with methylene chloride at pH < 2, solvent exchanged and derivatized along with two method blanks. These extracts were analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of herbicides is performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of hetero-atoms to empirical formulas.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration (SPC) of the target analyte being quantitated.

All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier.

HOLDING TIMES

The sample was extracted and analyzed within the method holding times.

BLANKS

No target compounds were detected in the laboratory blank at or above the practical quantitation limits (PQL's) thus demonstrating that the system was free from contamination.

SURROGATES

The 2,4-dichlorophenylacetic acid surrogate and 2,4,6-tribromophenol surrogate recoveries were acceptable.

MATRIX SPIKING

N/A

COMMENTS

The target analytes picloram and dinoseb received the ‘UJ’ qualifier because we traditionally experience highly variable recoveries for these compounds.

The data is useable as qualified.

DATA QUALIFIER CODES

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.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

NC - Not Calculated

E - This qualifier is used when the concentration of the associated value exceeds the known calibration range.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

July 25, 2001

Subject: Padden Creek Pesticides -26 Project

Sample(s): 01268105 - 01268110

Officer(s): Keith Seiders

By: Bob Carrell
Organics Analysis Unit

ACID HERBICIDE ANALYSIS

ANALYTICAL METHOD(S): (Draft EPA Method 8085)

The water samples for acid herbicides were extracted following Manchester Laboratory's standard operating procedure for the extraction of herbicides. The herbicide samples were hydrolyzed at pH > 12, extracted with methylene chloride at pH < 2, solvent exchanged and derivatized along with two method blanks. These extracts were analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of herbicides is performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of hetero-atoms to empirical formulas.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration (SPC) of the target analyte being quantitated.

All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier.

HOLDING TIMES

The sample was extracted and analyzed within the method holding times.

BLANKS

No target compounds were detected in the laboratory blank at or above the practical quantitation limits (PQL's) thus demonstrating that the system was free from contamination.

SURROGATES

The 2,4-dichlorophenylacetic acid surrogate and 2,4,6-tribromophenol surrogate recoveries were acceptable.

MATRIX SPIKING

The recoveries of the spiked target compounds were acceptable as were the relative percent differences (RPD's) between LMX1 and LMX2 recoveries.

COMMENTS

The target analytes picloram and dinoseb received the 'UJ' qualifier because we traditionally experience highly variable recoveries for these compounds.

The data is useable as qualified.

DATA QUALIFIER CODES

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.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

NC - Not Calculated

E - This qualifier is used when the concentration of the associated value exceeds the known calibration range.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

May 21, 2001

Subject: Padden Creek Pesticides

Sample(s): 01178105-110

Officer(s): Keith Seiders

By: Greg Perez
Organics Analysis Unit

NEUTRAL PESTICIDES ANALYSIS

ANALYTICAL METHOD(S)

The water samples for nitrogen containing, and organophosphorous pesticide analyses were extracted following Manchester Laboratory's standard operating procedure for the extraction of pesticides. The samples were extracted with methylene chloride using a stirbar apparatus then solvent exchanged to hexane. The extracts were analyzed by capillary Gas Chromatography with Atomic Emission Detection (GC/AED) following **EPA SW-846 Method 8085.** Confirmation of detected pesticides was performed by Gas Chromatography with Mass Spectrometry (GC/MS), comparisons of elemental ratios of heteroatoms to empirical formulas or dual dissimilar column comparison.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration of the target analyte being quantitated.

Target analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate,' J' qualifier.

BLANKS

No target compounds were detected in the laboratory blanks.

HOLDING TIMES

All samples were extracted and analyzed within the method holding times.

SURROGATE(S)

Dimethylnitrobenzene (DNM), Decachlorobiphenyl (DCB) and triphenylphosphate (TPP) recoveries
from the samples and the blank were within the acceptable limits.

DN4NB recoveries are generally expected to be lower than the other surrogate compounds due to its relative volatility. DMNB is more volatile than the target analytes and thus gives an indication of maximum losses during the concentration steps of the sample preparation procedure.

MATRIX SPIKING

No matrix spikes were analyzed.

COMMENTS

One herbicide not on the target list was confirmed in one sample. Trebuthylazine (trade name Valiant) was detected in sample 01178105.

The data is useable as qualified.

DATA QUALIFIER CODES

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.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

NC - Not Calculated

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

July 19,2001

Subject: Padden Creek Pesticides

Sample(s): 01188105-109

Officer(s): Keith Seiders

By: Greg Perez
Organics Analysis Unit

NEUTRAL PESTICIDES ANALYSIS

ANALYTICAL METHOD(S)

The water samples for nitrogen containing, and organophosphorous pesticide analyses were extracted following Manchester Laboratory's standard operating procedure for the extraction of pesticides. The samples were extracted with methylene chloride using a stirbar apparatus then solvent exchanged to hexane. The extracts were analyzed by capillary Gas Chromatography with Atomic Emission Detection (GC/AED) following **EPA SW-846 Method 8085.** Confirmation of detected pesticides was perfon-ned by Gas Chromatography with Mass Spectrometry (GC/MS), comparisons of elemental ratios of heteroatoms to empirical formulas or dual dissimilar column comparison.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration of the target analyte being quantitated.

Target analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate,' Y qualifier.

BLANKS

No target compounds were detected in the laboratory blanks.

HOLDING TIMES

All samples were extracted and analyzed within the method holding times.

SURROGATE(S)

Dimethylnitrobenzene (DNMB), Decachlorobiphenyl (DCB) and triphenylphosphate (TPP) recoveries from the samples and the blank were within the acceptable limits.

DN4NB recoveries are generally expected to be lower than the other surrogate compounds due to its relative volatility. DNMB is more volatile than the target analytes and thus gives an indication of maximum losses during the concentration steps of the sample preparation procedure.

MATRIX SPIKING

No matrix spikes were analyzed.

COMMENTS

One herbicide not on the target list was confirmed in one sample. Trebuthylazine (trade name Valiant) was detected in sample 01188106. 2,6-Dichlorobenzamide, which is a breakdown product of Diclobenil was found in 118105 and 106. Linuron and Diuron are only detected as a breakdown product. It has been reported as Diuron and flagged as NJ since it is impossible to tell which was the originating compound.

The data is useable as qualified.

DATA QUALIFIER CODES

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.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

NC - Not Calculated

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

August 2, 2001

Subject: Padden Creek Pesticides

Sarnple(s): 01208105 - 110

Officer(s): Keith Seiders

By: Greg Perez
Organics Analysis Unit

NEUTRAL PESTICIDES ANALYSIS

ANALYTICAL METHOD(S)

The water samples for nitrogen containing, and organophosphorous pesticide analyses were extracted following Manchester Laboratory's standard operating procedure for the extraction of pesticides. The samples were extracted with methylene chloride using a stirbar apparatus then solvent exchanged to hexane. The extracts were analyzed by capillary Gas Chromatography with Atomic Emission Detection (GC/AED) following **EPA SW-846 Method 8085.** Confirmation of detected pesticides was performed by Gas Chromatography with Mass Spectrometry (GC/N4S), comparisons of elemental ratios of heteroatoms to empirical formulas or dual dissimilar column comparison.

The method utilizes compound independent calibration (CIC) for quantitation of detected compounds. A calibration validation is performed each time CIC is used for target compounds. This is done by comparison of CIC to a single point calibration of the target analyte being quantitated.

Target analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection limit (MDL). If a target analyte is detected and its identification is unambiguously confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate,' J' qualifier.

BLANKS

No target compounds were detected in the laboratory blanks.

HOLDING TIMES

All samples were extracted and analyzed within the method holding times.

SURROGATE(S)

Dimethylnitrobenzene (DMNB), Decachlorobiphenyl (DCB) and triphenylphosphate (TPP) recoveries from the samples and the blank were within the acceptable limits.

DMNB recoveries are generally expected to be lower than the other surrogate compounds due to its relative volatility. DMNB is more volatile than the target analytes and thus gives an indication of maximum losses during the concentration steps of the sample preparation procedure.

MATRIX SPIKING

No matrix spikes were analyzed.

COMMENTS

Lenacil was detected in samples 01208105 and 106. 2,6-Dichlorobenzamide, which is a breakdown product of Diclobenil, was found in some samples. Linuron and Diuron are only detected as a breakdown product. It has been reported as Diuron and flagged as NJ since it is impossible to tell which was the originating compound.

The data is useable as qualified.

DATA QUALIFIER CODES

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.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

NC - Not Calculated

Manchester Environmental Laboratory

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CASE NARRATIVE

September 4,2001

Subject: Padden Creek Pesticides

Sample(s): 01268105 - 110

Officer(s): Keith Seiders

By: Greg Perez
Organics Analysis Unit

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DMNB recoveries are generally expected to be lower than the other surrogate compounds due to its relative volatility. DMNB is more volatile than the target analytes and thus gives an indication of maximum losses during the concentration steps of the sample preparation procedure.

MATRIX SPIKING

Sample 268106 was spiked with a subset of target compounds. Tribufos was not recovered and has been qualified as REJ for the spiked sample. Certain other compounds, which demonstrated low recoveries have been J qualified.

COMMENTS

Linuron and Diuron are only detected as a breakdown product. It has been reported as Diuron and flagged as NJ since it is impossible to tell which was the originating compound.

The data is useable as qualified.

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UJ The analyte was not detected at or above the reported estimated result.

REJ - The data are unusable for all purposes.

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