Monitoring Workplan for the Assessment of Synthetic Pyrethroids in San Diego County Watersheds

Final Report

Prepared For:

The County of San Diego

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Final

Monitoring Workplan for the Assessment of Synthetic Pyrethroids in San Diego County Watersheds

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1.0 INTRODUCTION

In accordance with the Receiving Waters and Urban Runoff Monitoring and Reporting Program No. R9-2007-0001 permit requirements, the San Diego Municipal Copermittees (Copermittees) are submitting a monitoring program to assess the occurrence and effects of synthetic pyrethroids (pyrethroids) in San Diego County Watersheds. This pyrethroid monitoring program will focus on sediment and water column assessments to evaluate the presence and potential effects of pyrethroids in urban waterways within the San Diego region.

BACKGROUND

The United States Environmental Protection Agency (USEPA) has restricted retail sales and urban uses of the previously common organophosphate (OP) pesticides diazinon and chlorpyrifos. The ban is expected to significantly reduce current source loadings of diazinon and chlorpyrifos and the resulting aquatic toxicity associated with diazinon and chlorpyrifos. However, there is concern that pyrethroids may be used in place of diazinon and chlorpyrifos, which may also result in impairment of aquatic life uses through toxicity. The San Diego Regional Monitoring Program has demonstrated that diazinon concentrations have significantly decreased over the past five years of monitoring throughout the region (Weston Solutions, 2007). Acute and chronic toxicity towards *Ceriodaphnia dubia* has also decreased significantly in the region. However, toxicity towards *Hyalella azteca* has remained persistent or has increased in some watersheds of the county. *Hyalella azteca,* which is a sediment grazer, has been shown to be more sensitive to pyrethroids in comparison to *Ceriodaphnia dubia*, which is a filter feeder (Weston Solutions, 2007). Since pyrethroids are extremely hydrophobic compounds, the route of exposure is primarily related to sediment contact. Pyrethroid pesticide usage in urban environments has gradually increased since the restriction of diazinon and chlorpyrifos (CDPR, 2007). Although pyrethroid pesticides are applied for a variety of uses in urban areas throughout the State of California, including structural pest control and landscape maintenance, only a limited number of assessments of the occurrence and effects of pyrethroids in urban waterways are available.

A review of available monitoring programs from throughout California[1] was conducted to identify other region's program design elements that may be applicable to the San Diego Municipal Copermittees Regional Monitoring Program to fulfill the requirements of the Receiving Waters and Urban Runoff Monitoring and Reporting Program No. R9-2007-0001. The review provided information on where synthetic pyrethroids are likely occurring, and how other programs are addressing the assessment of these compounds. A number of the monitoring programs reviewed have been developed either to answer specific or general questions relating to water body issues or to assess spatial distribution of pyrethroids. Toxicity to sediment-dwelling organisms related to pyrethroids has been documented in California urban surface waters. Sediment studies have found that pyrethroid insecticides can cause adverse effects in aquatic ecosystems receiving urban runoff.

In one study conducted by the Central Valley Water Board SWAMP program, a high occurrence of sediment toxicity was identified in several urban creeks located within the suburbs of Roseville (Weston *et al*., 2004, and Weston *et al*., 2005). The findings indicated that nearly all sampled creek sediments caused toxicity to the test organism *Hyalella azteca,* and several pyrethroids were present in sediment samples at toxic concentrations. Other evaluations of sediments from urban creeks in Northern California identified pyrethroids as the cause of toxicity in sediments (Weston *et al*. 2005, Amweg *et al*. 2006). In addition, these studies have shown that synthetic pyrethroids are not typically found in the water column unless they are associated with high total suspended solids (TSS) content since they are highly hydrophobic and readily bind to sediments in aquatic environments.

1.1 Monitoring Objectives and Assessment Questions

The current Receiving Waters and Urban Runoff Monitoring and Reporting Program Permit No. R9-2007-0001 (Permit) requires in Section A7: "The Copermittees shall collaborate to develop and implement a monitoring program to measure and assess the presence of pyrethroids in receiving waters. This program shall be implemented within each watershed and shall begin no later than 2007-2008 monitoring year" (RWQCB, 2007).

In order to measure and assess the presence of pyrethroids, the following questions are asked:

Q1. Are synthetic pyrethroids detected in San Diego County Watersheds and if so, at what concentrations?

This question will be addressed by collection and analysis of sediment samples at the mass loading stations (MLS) and temporary watershed assessment stations (TWAS) one time during the monitoring season on a rotational basis. Water column samples will be collected during storm events only from the existing MLS and TWAS as part of the Regional Monitoring Program analytical constituent list. Water column analyses during storm events will provide information on the spatial distribution of pyrethroids within the watershed during storm events.

Q2. If detected, are synthetic pyrethroids in San Diego County Watersheds causing toxicity to aquatic organisms in the water column or detected at equal to or above published LC50s for Hyalella azteca in sediment?

This question will be addressed by comparing water column pyrethroid sample results collected during storm events to water column toxicity results. Water column toxicity is performed as part of the Permit monitoring requirements of the Receiving Waters and Urban Runoff Monitoring and Reporting Program No. R9-2007-0001. Detected concentrations of synthetic pyrethroids in sediment will be compared to published literature values for LC_{50}s for the test organism *Hyalella azteca.* Additionally, total organic carbon and grain size distribution data will provide relevant information for assessing sediment pyrethroid concentrations.

2.0 MONITORING DESIGN

The assessment of pyrethroids throughout the State has recently been evolving. The pyrethroid assessment programs used for the development of this workplan are presented in the References

Section. Nearly all sediment studies evaluated sediment toxicity to *Hyalella azteca* (freshwater) or *Eohaustorius estuarius* (saltwater), sediment concentrations of pyrethroids, and % organic carbon (%oc). The organic carbon content is important since increasing %oc infers lower pyrethroid toxicity since the compounds are less bioavailable as they bind to the organic carbon. While some researchers have evaluated water column samples, others have shown that synthetic pyrethroids are typically not found in the water column unless they are associated with high suspended solids (TSS) content since they are hydrophobic. Therefore, the assessment of synthetic pyrethroids in sediment and during storm event flows will provide information on where pyrethroids are being detected in San Diego County Watersheds.

Many studies have performed toxicity analyses on sediments for *Hyalella azteca* and sediment chemistry to link toxicity responses to concentrations of contaminants, therefore, this monitoring program will use published LC_{50} values for pyrethroids to evaluate the potential for sediment toxicity to *Hyalella azteca*. Analysis of the information has led to the strong relationship between published literature values for LC_{50}s for the test organism *Hyalella azteca*, which allows for a comparison of pyrethroid concentrations to assess potential for toxicity to organisms in lieu of toxicity testing. Many of the studies reviewed were early studies to understand the impact of synthetic pyrethroids in the environment to aquatic organisms, and further, these studies required the linkage of the pyrethroids presence to toxicity effects.

The monitoring design will follow the rotational monitoring schedule outlined in the Permit as outlined in Section N, Table 1 and summarized in Table 2.1 below.

2.1 Sediment Assessment

2.1.1 Sampling Locations

Sediment samples will be collected from the MLS and TWAS locations on a rotational basis as shown in Table 2-1. Sampling locations are shown by monitoring year in Appendix A-1.

2.1.2 Sampling Frequency

Sediment sampling will occur greater than 72 hours but less than two weeks following the first storm event of the season. Since the majority of pesticide applications occur during late summer to early fall, samples will be collected following the "first flush" of the wet season in order to capture the greatest effects of dry season pesticide applications. A review of the San Diego County historical monitoring data has shown that the first storms of the season typically have the highest concentrations of organophosphate pesticides which are believed to represent similar characteristics for synthetic pyrethroids (Weston Solutions, 2007). Sediment sampling will occur one time per year on a rotational basis. The northern portion of San Diego County and one station located in the southern portion (Chollas Creek) will be sampled during monitoring years 2007-2008 and 2010-2011 (Table 2-1). Sediment samples will be collected from the base of each watershed during monitoring year 2008-2009 (Bight '08) (Table 2-1). The southern portion of the County will be sampled during monitoring years 2009-2010 and 2011-2012 (Table 2-1).

A summary of sample schedule for sediment sampling and total number of samples per monitoring year is presented in Table 2-1.

Table 2-1. Sample Schedule for Collection of Sediment Samples from Mass Loading Stations.

Watershed	Permit Year 2007-2008	Permit Year 2008-2009*	Permit Year 2009-2010	Permit Year 2010-2011	Permit Year 2011-2012
Santa Margarita River	1	1		1	
San Luis Rey River	2	1		2	
Loma Alta Creek**	1	1		1	
Buena Vista Creek**	1	1		1	
Agua Hedionda Creek	2	1		2	
Escondido Creek	2	1		2	
San Dieguito River	3	1		3	
Los Peñasquitos Creek	3	1		3	
Rose Creek**		1	1		1
Tecolote Creek		1	2		2
San Diego River		1	4		4
Chollas Creek	1	1	1	1	1
Sweetwater River		1	2		2
Otay River**		1	1		1
Tijuana River		1	3		3
Total Samples	**16**	**15**	**14**	**16**	**14**

* All MLS stations will be sampled during Permit Year 2008-2009 .
**Temporary watershed assessment stations are subject to change based on watershed activities.

2.1.3 Sample Collection

Sediment samples will be collected from the top two centimeters of the sediment using a piston core (or similar device) to capture the most recently deposited sediments associated with runoff. Three transects will be chosen at each site and five equidistant locations within each transect will be selected for sampling. One sample from each location within each transect will be sampled for a total of five samples per transect. Fifteen total samples will be collected from each site and equal mass sub-samples will be composited into a single sample for analysis.

The top two centimeters of sediment at each location will be scooped into a stainless steel mixing bowl using stainless steel spoons. The sediment from each site will then be homogenized and placed into an 8 oz. laboratory-certified, sterile glass jar. Samples will be stored on ice immediately following collection for transfer to the analytical laboratory.

Field measurements for pH, conductivity, temperature and turbidity will be collected at each location. Field measurements for pH, conductivity and temperature will be made using an Oakton CON10 pH/temperature/conductivity meter and all field measurements for turbidity will be made using a Hach 2100P Turbidity meter.

A field data log will be completed at each location (Attachment 1). The field data log will include empirical observations of the site and sediment and water quality characteristics. Observations include parameters such as meteorological conditions at time of sampling, and odor and color of the sediment and water.

2.1.4 Sample Analyses

Analysis of synthetic pyrethroids will be performed by CRG Marine Laboratories of Torrance, California. Sediment samples will be analyzed using gas chromatography/mass spectrometry in negative chemical ionization mode (NCI) following EPA Method 8270 guidelines. The synergist piperonyl butoxide will be analyzed using electron impact (EI) mode of detection. Total organic carbon (TOC) will also be analyzed to provide a comparison of bioavailability. Studies have shown that as the percentage of TOC increases, toxicity associated with synthetic pyrethroids decreases (Maund *et al*., 2002). Grain size distribution will also be performed to determine the relationship between sediment pyrethroid concentrations and grain size. A summary of analytical methods and detection limits are presented in Table 2-2.

Table 2-2. Analytical Constituent List and Detection Limits for Sediment Samples.

Group	Analyte	Method	Fraction	Units	MDL	RL
Synthetic Pyrethroids	Allethrin	EPA 8270 NCI-GCMS	Total	ng/g	5	10
Synthetic Pyrethroids	Bifenthrin	EPA 8270 NCI-GCMS	Total	ng/g	5	25
Synthetic Pyrethroids	Cyfluthrin	EPA 8270 NCI-GCMS	Total	ng/g	5	25
Synthetic Pyrethroids	Cypermethrin	EPA 8270 NCI-GCMS	Total	ng/g	5	25
Synthetic Pyrethroids	Danitol	EPA 8270 NCI-GCMS	Total	ng/g	5	25
Synthetic Pyrethroids	Deltamethrin	EPA 8270 NCI-GCMS	Total	ng/g	5	25
Synthetic Pyrethroids	L-Cyhalothrin	EPA 8270 NCI-GCMS	Total	ng/g	5	25
Synthetic Pyrethroids	Permethrin	EPA 8270 NCI-GCMS	Total	ng/g	5	25
Synthetic Pyrethroids	Prallethrin	EPA 8270 NCI-GCMS	Total	ng/g	5	25
Synthetic Pyrethroids	Piperonyl Butoxide	EPA 8270C EI-GCMS	Total	ng/g	5	25
Conventionals	Total Organic Carbon	ASTM D-2567	Total	%	0.5	1
Conventionals	Grain Size Distribution	Plumb, 1981	N/A	%	N/A	N/A

2.2 Water Quality Assessment

2.2.1 Sampling Locations

Water quality samples will be collected during storm events only from the existing mass loading stations (MLS) and temporary watershed assessment stations (TWAS) as part of the Regional Monitoring Program analytical constituent list. Pyrethroids are not typically found in the water column unless associated with suspended particulates. Non-storm event flow conditions are typically low in velocity and it is not suspected that pyrethroids would be associated with these ambient dry weather conditions. For this reason, only storm event monitoring will be performed as part of the water quality assessment. Water quality sample locations by monitoring year are shown in Appendix A-1. Water quality samples will be collected from the MLS and TWAS (during storm events only) in order to compare pyrethroid analyses with chemistry and toxicity analyses that are currently being performed to evaluate the effects of current pesticide use within each watershed.

2.2.2 Sampling Frequency

Water quality samples will be collected during storm events only. Sampling will occur two times per year on a rotational basis as part of the Regional Monitoring Program. Sampling in the northern watersheds will occur during monitoring years 2007-2008 and 2010-2011 (Table 2-3). Water quality samples will be collected one time from all MLS during Bight ’08 monitoring year 2008-2009 (Table 2-3). Sampling in the southern watersheds will occur during monitoring years 2009-2010 and 2011-2012 (Table 2-3). Table 2-3 presents a summary of sample frequency for the collection of water quality samples.

Table 2-3. Sample Frequency for Collection of Water Quality Samples from Mass Loading Stations and Temporary Watershed Assessment Stations.

Watershed	Permit Year 2007-2008		Permit Year 2008-2009*		Permit Year 2009-2010		Permit Year 2010-2011		Permit Year 2011-2012	
	MLS	TWAS	MLS	TWAS	MLS	TWAS	MLS	TWAS	MLS	TWAS
Santa Margarita River	2		1				2			
San Luis Rey River	2	2	1				2	2		
Loma Alta Creek**		2						2		
Buena Vista Creek**		2						2		
Agua Hedionda Creek	2	2	1				2	2		
Escondido Creek	2	2	1				2	2		
San Dieguito River	2	4	1				2	4		
Los Peñasquitos Creek	2	4	1				2	4		
Rose Creek**						2				2
Tecolote Creek			1		2	2			2	2
San Diego River			1		2	6			2	6
Chollas Creek	2		1		2		2		2	
Sweetwater River			1		2	2			2	2
Otay River**						2				2
Tijuana River			1		2	4			2	4
Total Samples per Monitoring Year	**32**		**11**		**28**		**32**		**28**	

* All MLS will be sampled during Permit Year 2008-2009.
**These sites are temporary watershed assessment stations and are subject to change based on watershed activities.

2.2.3 Sample Collection

Sample collection will occur as part of the Regional Monitoring Program during storm events only. Automated sampling equipment will be used to collect flow-weighted composite water quality samples during storm events. American Sigma flow meters will be installed to measure velocity and stage height. American Sigma automated samplers will be used to collect sample grabs at a rate dependent on flow. The automated sampler collects grab samples via a peristaltic pumping mechanism. Water samples are pumped through a Teflon intake device and Teflon tubing into a 20-liter laboratory-certified, contaminant-free borosilicate glass sample bottle. Sample bottles will be kept on ice during the storm event and during transfer to the analytical laboratory.

Field measurements for pH, conductivity, and temperature will be collected at each location. Field measurements for pH, conductivity and temperature will be made using an Oakton CON10 pH/temperature/conductivity meter.

A field data log will be completed at each location (Attachment 2). The field data log will include empirical observations of the site and sediment and water quality characteristics.

Observations include parameters such as meteorological conditions at time of sampling, and odor and color of the sediment and water.

2.2.4 Sample Analyses

Analysis of synthetic pyrethroids will be performed by CRG Marine Laboratories of Torrance, California. Water quality samples will be analyzed using gas chromatography/mass spectrometry in negative chemical ionization mode (NCI) following EPA Method 625 guidelines. The synergist piperonyl butoxide will be analyzed using electron impact (EI) mode of detection. A summary of the analytical method for synthetic pyrethroids and detection limits are presented in Table 2-4.

Table 2-4. Synthetic Pyrethroid Constituent List for Water Samples

Group	Analyte	Method	Fraction	Units	MDL	RL
Synthetic Pyrethroids	Allethrin	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	Bifenthrin	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	Cyfluthrin	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	Cypermethrin	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	Danitol	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	Deltamethrin	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	L-Cyhalothrin	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	Permethrin	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	Prallethrin	EPA 625 NCI-GCMS	Total	ng/l	2	5
Synthetic Pyrethroids	Piperonyl Butoxide	EPA 625 EI-GCMS	Total	ng/l	2	5

2.3 Sample Handling

All samples collected will be stored in the appropriate container type for the analytical method to be performed. Sediment and water quality samples will be labeled with the following information:

- project name
- sample identification number
- site location
- date and time collected
- analyses to be performed
- sample preservation

Samples will then be stored on ice (4 °C) for transfer to the proper analytical laboratory. The sample containers used will be certified as clean and sterile by the laboratory performing the analyses. Samples will be delivered to the appropriate laboratory and analyses initiated within specified holding times. Sample storage and holding times are summarized in Table 2-5.

Table 2-5. Sample Containers and Storage Times for Synthetic Pyrethroids and Related Analyses.

Analysis	Method	Matrix	Container	Recommended Holding Time	Storage
Synthetic Pyrethroids	EPA 8270 NCI-GCMS	Sediment	50 g Glass Jar	40 Days	4°C
Synthetic Pyrethroids	EPA 625 NCI-GCMS	Water	2L Amber Glass	7/40 Days*	4°C
Total Organic Carbon	ASTM D-2567	Sediment	50 g Glass Jar	14 Days	4°C
Grain Size Distribution	Plumb, 1981	Sediment	50 g Glass Jar	NA	NA

*7 days holding for extraction and 40 days after extraction.

2.4 Chain of Custody

Chain-of-custody (COC) forms will be completed for each sample and accompany the samples to the appropriate laboratories. An example COC is provided (Attachment 3).

Samples will be considered to be in custody if they are:

(1) in the custodian's possession or view,
(2) retained in a secured place (under lock) with restricted access, or
(3) placed in a container and secured with an official seal such that the sample could not be reached without breaking the seal.

COC procedures will be used for all samples throughout the collection, transport, and analytical process. COC procedures will be initiated during sample collection. A COC record will be provided with each sample or group of samples. Each person who will have custody of the samples will sign the form and ensure the samples will not be left unattended unless properly secured.

Documentation of sample handling and custody includes the following:

- Sample identifier
- Sample collection date and time
- Any special notations on sample characteristics or analysis
- Initials of the person collecting the sample
- Date the sample was sent to the analytical laboratory
- Shipping company and waybill information.

Completed COC forms will be placed in a plastic envelope and kept inside the container containing the samples. Once delivered to the analytical laboratory, the COC form will be signed by the person receiving the samples. The condition of the samples will be noted and recorded by the receiver. COC records will be included in the final reports prepared by the analytical laboratories and are considered an integral part of the report.

2.5 Quality Assurance/Quality Control

Quality assurance and quality control (QA/QC) for sampling processes will include proper collection of the samples in order to minimize the possibility of contamination. All samples will be collected in laboratory supplied, laboratory-certified, contaminant-free sample bottles. The sediment samples will first be collected using stainless steel spoons and mixing bowls and then transferred to laboratory-certified, contaminant-free glass jars. All sampling equipment will be thoroughly washed with alconox, rinsed, and followed by three final rinses with deionized water. The water quality composite samples will first be collected in laboratory-certified, contaminant-free borosilicate glass bottles and subsequently transferred into laboratory-certified, contaminant-free sample bottles once composited.

Field measurements for pH, conductivity and temperature will be made using an Oakton CON10 pH/temperature/conductivity meter according to manufacturer's specifications. All field measurements for turbidity will be made using a Hach 2100P Turbidity meter. Calibration of the instruments will be conducted prior to each sampling event following the manufacturer's specifications.

Evaluation of sample variability will be performed by collecting one sample duplicate per monitoring event. The relative percent difference between sample duplicates will be compared to SWAMP guidelines for pesticide analyses (there currently are no SWAMP guidelines for pyrethroids).

Evaluation of laboratory variability will be performed by submitting one split sample to an alternate laboratory for comparison of sample results between laboratories. Analytical detection limits and methods must be sensitive enough for comparability between laboratories.

An equipment rinse blank will be collected during the sediment sampling events and analyzed for pyrethroids. Equipment rinse blanks are check samples that assess contamination originating from the collection, transport, or storage of environmental samples. The equipment rinse blank will consist of pouring analyte free water through the sample collection equipment and collecting this water for chemistry analyses. The equipment rinse blank will be collected to verify that field cleansing procedures were adequate and sampling handling and transportation did not introduce any analytes of interest.

The chemistry analyses of the samples will be performed under the guidelines of the quality assurance and quality control programs established by CRG Marine Laboratories.

3.0 ASSESSMENT AND REPORTING

3.1 Synthetic Pyrethroid Assessment

In order to assess pyrethroids, the following questions are asked with the basis for the monitoring design:

Q1. Where are Synthetic Pyrethroids being detected in San Diego County Watersheds?

This question will be answered by presenting concentrations on maps and providing data in tables on where pyrethroids are detected in sediment and water column samples. Water column analyses will provide information on the spatial distribution of pyrethroids during storm events. Additionally, the frequency of detection over the Permit term will be assessed using bar graphs, maps and data in tables.

Q2. If detected, are synthetic pyrethroids in San Diego County Watersheds causing toxicity to aquatic organisms in the water column or detected at equal to or above published LC50s for Hyalella azteca in sediment?

This question will be answered by comparing water column pyrethroid samples collected during storm events to water column toxicity results. Water column toxicity is part of the standard Permit monitoring requirements. Concentrations of synthetic pyrethroids detected in sediment will be compared to published literature values for sediment LC_{50}s for *Hyalella azteca*. Reported LC_{50}s for *Hyalella azteca* for sediment and water are provided in Table 3-1.

Table 3-1. Reported Synthetic Pyrethroid LC_{50} Values for *Hyalella Azteca*

Test Chemical	Exposure Period	LC_{50} (µg/L water)	LC_{50} (µg/kg sediment)	LC_{50} (µg/g Organic Carbon) or <u>% OC</u>	Reference
Bifenthrin	10 days	-	3.0 - 8.2	0.52	Amweg et al. 2005
Bifenthrin	96 hr	0.0093	-	NA	Anderson et al. in press
Bifenthrin	96 hr	0.013	-	NA	Weston Solutions, 2006
Bifenthrin	96 hr	-	-	0.52	Amweg et al. 2005
Cyfluthrin	10 days	-	12.5 - 14.9	1.08	Amweg et al. 2005
Deltamethrin	10 days	-	9.8 - 10.0	0.79	Amweg et al. 2005
Esfenvalerate	10 days	-	10.4 - 48.3	1.54	Amweg et al. 2005
Lambda-Cyhalothrin	10 days	-	5.2 - 6.0	0.45	Amweg et al. 2005
Cypermethrin	10 days	-	-	0.38	Amweg et al. 2005
Cypermethrin	10 days	-	3.6	<u>*1%*</u>	Maund et al. 2002
Cypermethrin	10 days	-	18	<u>*3%*</u>	Maund et al. 2002
Cypermethrin	10 days	-	23	<u>*13%*</u>	Maund et al. 2002
Permethrin	10 days	-	57 - 112	10.83	Amweg et al. 2005
Permethrin	96 hr	0.039 - 0.047	-	NA	Wheelock et al. 2005
Permethrin	96 hr	0.021	-	NA	Anderson et al. in press

The concentrations detected in each watershed will be assessed annually for those watersheds monitored and at the end of the five year period the data will be combined and assessed. Concentrations of pyrethroids from both sediment and storm water monitoring will be presented in data tables and graphically displayed on maps showing sampling locations. Comparison to published literature values for LC_{50}s will be presented in data tables and bar graphs. Water column sample results will be presented in data tables and graphs and compared to toxicity results for each watershed. The water column sample results will be included as a part of the triad assessment matrix regarding the chemistry, toxicity, and biology weight-of-evidence assessment for each watershed.

3.2 Reporting

Reporting of synthetic pyrethroid sediment and water quality monitoring assessments will be included in the San Diego County Municipal Copermittees Urban Runoff Monitoring Annual Report. Pyrethroid data will be included as part of each Watershed Management Area Assessment and assessed as above.

4.0 REFERENCES

1. Monitoring Program Review References:
    - San Francisco Bay, Clean Estuary Partnership, Ruby. A, 2006, CEP Urban Creeks Monitoring Plan, 2005-06
    - Newport Bay and San Diego Creek Watershed, Gan, J., et al., 2005, Survey of Synthetic Pyrethroids in San Diego Creek and Newport Bay.
    - Chollas Creek PRISM, City of San Diego (2006), Water and Sediment Quality Monitoring for Chollas Creek
    - San Francisco Estuary Program (2004), PRISM Grant, Investigations of Sources and Effects of Pyrethroid Pesticides in Watersheds of the San Francisco Bay Estuary.
    - Department of Pesticide Regulation, Study #214 (2003), Protocol for Monitoring the Occurrence and Concentration of Esfenvalerate and Permethrin Pyrethroids.
    - Department of Pesticide Regulation, Study #229 (2005), Continuing Assessment of Pyrethroid Contamination of Surface Waters and Bed Sediments in High Pyrethroid-Use Regions of California.
    - Surface Water Ambient Monitoring Program (SWRCB Region 5, 2006-07), Incidence and Biological Effects of Pyrethroid Pesticides in the Urban Creeks of California.

Amweg, E.L., D.P. Weston, and N.M. Ureda. 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, California, U.S.A. *Environmental Toxicology and Chemistry* 24: 966-972 (with correction in *Environmental Toxicology and Chemistry* 2005, 24: 1300-13-1).

Amweg, E.L., D.P. Weston, J. You, and M.J. Lydy. 2006. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. *Environmental Science & Technology* 40(5): 1700-1706.

Anderson B.S., B.M. Phillips, J.W. Hunt, S.A. Huntley, K. Worcester, N. Richard, and R.S. Tjeerdema. *In Press*. Evidence of pesticide impacts in the Santa Maria River watershed (California, USA). *Environmental Toxicology and Chemistry.*

California Department of Pesticide Regulation (CDPR). 2007. Pesticide Usage Report (PUR) database. Available on-line. http://www.cdpr.ca.gov/docs/pur/pur05rep/05_pur.htm

Maund, S.J., M.J. Hamer, et al. 2002. "Partitioning, Bioavailability, and Toxicity of the Pyrethroid Insecticide Cypermethrin in Sediments". *Environmental Toxicology and Chemistry* (21)1: 9-15.

Plumb, R.H., Jr. 1981. Procedures for Handling and Chemical Analysis of Sediment and Water Samples. Technical Report EPA/CE-81-1. U.S. Environmental Protection Agency/U.S. Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material. U.S. Army Waterways Experiment Station, Vicksburg, MS. 471 pp.

Regional Water Quality Control Board. 2006. San Diego Municipal Copermittees Responses to Comments, *Receiving Waters and Urban Runoff Monitoring and Reporting Program No. R9-2007-0001*. August 2006.

Regional Water Quality Control Board. 2007. California Regional Water Quality Control Board San Diego Region, Order No. R9-2007-0001, NPDES No. CAS0108758, Waste Discharge Requirements For Discharges of Urban Runoff from the Municipal Separate Storm Sewer Systems (MS4s) Draining the Watersheds of the County of San Diego, the Incorporated Cities of San Diego County, The San Diego Unified Port District, and the San Diego County Regional Airport Authority. January 2007.

Weston, D.P., J. You, and M.J. Lydy. 2004. "Distribution and Toxicity of Sediment-Associated Pesticides in Agriculture-Dominated Water Bodies California's Central Valley." *Environmental Science and Technology* 38(10): 2752-2759.

Weston, D.P., R.W. Holmes, J. You, and M.J. Lydy. 2005. Aquatic toxicity due to residential use of pyrethroid insecticides. *Environmental Science & Technology* 39(24): 9778-9784.

Weston Solutions, Inc. 2006. Aquatic Bioassay Laboratory Data Developed for the Evaluation of Technical Grade Bifenthrin for Toxicity Identification Evaluations.

Weston Solutions, Inc. 2007. *San Diego County Municipal Copermittees 2005-2006 Urban Runoff Monitoring*. Prepared for the County of San Diego. January 2007.

ATTACHMENT 1

Sediment Field Log

SEDIMENT FIELD DATA LOG

PROJECT/SURVEY NAME	DATE	PROJECT MANAGER	RECORDER
STATION NAME	NAV DATUM	LATITUDE	LONGITUDE
SAMPLE IDENTIFICATION	TIME STARTED (AT SITE)	TIME FINISHED (AT SITE)	SAMPLE TIME
FIELD TEAM			

SAMPLE INFORMATION

SAMPLE TYPE	☐ GRAB	☐ COMPOSITE	**COLLECTION METHOD**	☐ MANUAL (S.S. SPOON)	☐ OTHER	______
IF COMPOSITE, NUMBER OF COMPOSITED GRAB SAMPLES				______		
ALIGNMENT OF COMPOSITE SAMPLE SITES			☐ ACROSS CHANNEL		☐ ALONG CHANNEL	
DEPTH OF SURFACE SEDIMENT GRAB			______			
QA/QC SAMPLES	☐ FIELD DUP.	☐ LAB SPLIT	☐ MS/MSD	☐ EQUIPMENT BLANK	☐ FIELD BLANK	

VISUAL OBSERVATIONS

ODOR	☐ PETROLEUM	☐ SOLVENTS	☐ SEWAGE	☐ ORGANIC (ROTTEN EGGS)	☐ NONE	☐ OTHER ______
COLOR	☐ BLACK	☐ BROWN	☐ GREEN	☐ TAN		☐ OTHER ______
CONSISTENCY	☐ SANDY	☐ SILTY	☐ GRANULAR	☐ CLAYEY		☐ OTHER ______

NOTES ON VISUAL OBSERVATIONS ______

______

PHOTOS

PHOTOS TAKEN	☐ YES	☐ NO	**PHOTO NUMBER(S)**	______

NOTES ON PHOTOS ______

______

______

ATTACHMENT 2

Water Quality Field Log

WATER QUALITY FIELD DATA LOG

PROJECT/SURVEY NAME	DATE	PROJECT MANAGER	RECORDER
STATION NAME	NAV DATUM	LATITUDE	LONGITUDE
SAMPLE IDENTIFICATION	TIME STARTED (AT SITE)	TIME FINISHED (AT SITE)	GRAB SAMPLE TIME
FIELD TEAM			

METEOROLOGICAL CHARACTERISTICS (DESCRIBE RAINFALL, WIND, TEMPERATURE, ETC.)

WATER QUALITY APPEARANCE

ODOR	☐ HYDROGEN SULFIDE	☐ MUSTY	☐ SEWAGE	☐ AMMONIA	☐ GASOLINE	☐ OTHER ______
	☐ SOAP	☐ CHLORINE	☐ NONE			
COLOR	☐ YELLOW	☐ GREEN	☐ BLUE	☐ BROWN	☐ BLACK	☐ OTHER ______
	☐ GRAY	☐ WHITE	☐ COLORLESS			
FLOATING MATERIALS	☐ TRASH OR DEBRIS	☐ OIL AND GREASE	☐ ORGANIC MATERIAL	☐ SCUM	☐ SUDS	☐ OTHER ______
	☐ OBJECTS (DESCRIBE)					
TURBIDITY	☐ HEAVY CLOUDINESS, OPAQUE		☐ CLOUDY	☐ SOME CLOUDINESS	☐ NONE	

WATER QUALITY APPEARANCE COMMENTS:

EROSION AND VEGETATION (DESCRIBE ANY VISUAL SIGNS OF SLIDE SLOPE EROSION AND/OR CHANGE IN VEGETATION CONDITION)

FIELD MEASUREMENTS: pH ______ TEMPERATURE (°c) ______ CONDUCTIVITY (µS/cm) ______ DO ______

FLOW WEIGHTED COMPOSITE SAMPLE INFORMATION (ENTER TIME OF BOTTLE CHANGES)

BOTTLE #1 ______ BOTTLE #2 ______ BOTTLE #3 ______

BOTTLE #4 ______ BOTTLE #5 ______ BOTTLE #6 ______

SAMPLING ACTIVITIES (DESCRIBE ALL ACTIONS TAKEN AT EACH SITE VISIT AND PROVIDE ADDITIONAL COMMENTS AS NECESSARY)

TEAM LEADER'S SIGNATURE ______________________

ATTACHMENT 3

Chain of Custody Form

WESTON SOLUTIONS

☐ 2433 Impala Drive • Carlsbad, CA 92008 • (760) 931-8081, FAX 931-1580
☐ 98 Main St., Ste. #428 • Tiburon, CA 94920 • (415) 435-1847, FAX 435-0479
☐ 1440 Broadway, Ste. 908 • Oakland, CA 94612 • (510) 808-0302, FAX 891-9710
☐ 152 Sunset View Lane • Sequim, WA 98382 • (360) 582-1758, FAX 582-1679
☐ 4729 NE View Drive • Port Gamble, WA 98364 • (360) 297-6903, FAX 297-6905

CHAIN OF CUSTODY

No. 10150

DATE______________ PAGE_____ OF_____

PROJECT NAME / SURVEY / PROJECT NUMBER

PROJECT MANAGER

COMPANY

ADDRESS

PHONE/FAX

SAMPLE I.D.	DATE	TIME	MATRIX	INITIALS	NUMBER &TYPE OF CONTAINERS	ANALYSIS/TEST REQUESTED					PRESERVED HOW/ COMMENTS	FOR WESTON USE ONLY: SAMPLE TEMP. UPON RECEIPT	WESTON LAB ID

SPECIAL INSTRUCTIONS/COMMENTS:

SHIPPING:

Shipping VIA: Airbill No:

SAMPLE CONDITION UPON RECEIPT (FOR WESTON USE ONLY):

RELINQUISHED BY	RECEIVED BY	RELINQUISHED BY	RECEIVED BY	RELINQUISHED BY	RECEIVED BY
Signature	Signature	Signature	Signature	Signature	Signature
Firm	Firm	Firm	Firm	Firm	Firm
Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time

WHITE – return to originator • YELLOW – lab • PINK – retained by originator