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# **TECHNICAL MEMORANDUM**

# Analysis of Bay Area Urban Creeks Monitoring, 2004-05

Prepared by:

Armand Ruby Armand Ruby Consulting

Prepared for:

**Clean Estuary Partnership** 

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# Introduction

The Clean Estuary Partnership (CEP) provided funding during 2004-05 for monitoring of urban creeks, to supplement monitoring already planned by local agencies in the Bay Area. The purpose of the monitoring was to support the development and implementation of the *Diazinon and Pesticide-Related Toxicity in Bay Area Urban Creeks Water Quality Attainment Strategy and Total Maximum Daily Load* ("the WQAS"; Johnson, 2005). This technical memorandum summarizes the analysis of the monitoring data and assimilation of other relevant scientific information, and includes recommendations for monitoring and program management in 2005-06 and beyond.

The CEP-sponsored urban creeks monitoring is a component of the *CEP Urban Creeks Monitoring Plan* (Ruby, 2004), and was performed in accordance with that plan. The preparation of the monitoring plan and implementation of the monitoring program was guided by the Diazinon/Toxicity Work Group of the CEP's Technical Committee. The focus of the monitoring effort was on storm-event-based monitoring of creek flows for pesticides and aquatic toxicity during winter/spring of the 2004-05 wet season. The CEP covered the costs of chemical analysis for selected pesticides, as well as toxicity testing for water samples from selected urban creeks. Local agencies were responsible for storm tracking, sample collection, and delivery of samples to a central laboratory.

This technical memorandum provides the results of the CEP-sponsored monitoring of urban creeks, along with summaries of the results of similar monitoring performed by local and state agencies in Bay Area creeks during 2004-05. The memorandum contains an analysis of the 2004-05 monitoring data, including assessments of spatial and temporal variation of the data, and comparisons of the data to the proposed TMDL targets for diazinon and toxicity.

The memorandum also summarizes the results of relevant scientific research and studies related to pesticide use in urban watersheds within the Bay Area, chemical concentrations of pesticides in urban creek waters and sediments, and effects of pesticides on water and sediment quality and aquatic life, relying principally upon information generated by the Urban Pesticide Pollution Prevention (UP3) Project.

The 2004-05 monitoring data serve as indicators of levels of diazinon and related toxicity in Bay Area urban creeks as the federal phase-out of diazinon uses is implemented. It is recognized that the use of "replacement pesticides" as substitutes for diazinon may result in changes in patterns of pesticide occurrence and related water quality impacts in urban creeks. The CEP Urban Creeks Monitoring Plan is intended to be adaptable to changing conditions; the results of the 2004-05 monitoring and related research will be used to help direct future monitoring efforts for Bay Area urban creeks.

This memorandum includes recommendations for monitoring during 2005-06 in selected, representative urban creeks, including consideration of the monitoring requirements and management questions specified in the latest version of the WQAS, preventative and preemptive monitoring alternatives, and program management needs.

# Background

In past monitoring, Bay Area urban creek water has been found to contain elevated concentrations of diazinon, and to be toxic to aquatic test organisms, particularly *Ceriodaphnia dubia*, a common water flea (see summary in Johnson, 2005). Pesticides— and diazinon in particular—were identified through toxicity identification evaluations (TIEs) and other studies in the 1990's as the principal causative agents in such cases of urban creek toxicity. Once among the most commonly-used pesticides, diazinon use has declined sharply in response to U.S. Environmental Protection Agency regulatory actions to limit allowable uses, deemed necessary to mitigate potential impacts on human health (especially for children in residential settings and agricultural workers), and ecological impacts on birds and other wildlife.

Because concern exists that insecticide substitutes for diazinon may have toxic effects in ambient waters (TDC Environmental, 2003), the Bay Area urban creeks WQAS targets diazinon specifically, while concurrently addressing the potential for other pesticide-related toxicity in urban creeks.

The WQAS Implementation Plan, as described in the Water Board's Final Project Report (Johnson, 2005), includes the following proposed monitoring requirements (see Section 11, Monitoring and Adaptive Implementation):

- *Program Design*: Urban runoff management agencies in the Bay Area must design and implement a monitoring program and describe it in a monitoring plan.
- *Watershed Characterization*: The monitoring plan must include characterization of the Bay Area's urban creek watersheds and selection of representative creeks for monitoring. The selected creeks must represent the various regions of the Bay Area and allow the Water Board to extrapolate the monitoring results to urban creeks not selected for monitoring.
- *Site Selection and Sample Collection*: Sampling sites must be identified for the selected creeks; these sites must represent the essential range of creek conditions, including conditions near storm drain outfalls. Sampling must be conducted during storms that produce substantial runoff, and during the dry season.
- *Analytical Tests*: The chemical analysis and toxicity tests to be performed must be specified in the monitoring plan; these tests must include measurement of diazinon concentrations in water, general water quality parameters, water column toxicity, and other tests as necessary and feasible.

The CEP's Diazinon/Toxicity Work Group began to address the proposed requirements of the WQAS through development and implementation of a monitoring plan for urban creeks in 2004-05. The results of the implementation of the monitoring plan, including characterization of Bay Area urban watersheds and selection of representative monitoring sites, are reported in this memorandum.

While some Bay Area urban runoff management agencies, the Surface Water Ambient Monitoring Program (SWAMP), and other agencies/researchers planned monitoring of

Bay Area creeks during the 2004-05 monitoring year, this monitoring was not coordinated nor performed according to shared protocols. Coordination of the various monitoring efforts is desirable to the extent possible to gain consistency in sample collection, quality control, laboratory analytical methods and reporting limits. Such coordination is an important goal of the CEP Urban Creeks Monitoring Plan. The funding provided by the CEP for chemical analysis and toxicity testing during 2004-05 promoted the use of consistent sampling and analytical protocols. Also, by supplementing the monitoring previously planned by local agencies, the CEP funding was effectively leveraged, as substantial portions of the costs of monitoring were covered by local agencies.

Water Board staff are currently engaged in development of region-wide NPDES permit monitoring requirements for Bay Area urban runoff management agencies. The ongoing development and implementation of the CEP Urban Creeks Monitoring Plan will be coordinated with the development of these new permit requirements.

#### Monitoring Program Questions

The WQAS includes the following questions for Bay Area urban creeks monitoring:

- A. Is the diazinon concentration target being met?
- B. Are the toxicity targets being met?
- C. Is toxicity observed in urban creeks caused by a pesticide?
- D. Is urban runoff the source of any observed toxicity in urban creeks?
- E. How does observed pesticide-related toxicity in urban creeks (or pesticide concentrations contributing to such toxicity) vary in time and magnitude across urban creek watersheds?

The WQAS includes additional questions if toxicity is found: "What types of pest control practices contribute to such toxicity? Are actions already being taken to reduce pesticide discharges sufficient to meet the targets, and if not, what should be done differently?" To adequately address these questions, integrated analysis and interpretation of region-wide monitoring data will be necessary.

The CEP Urban Creeks Monitoring Plan establishes a process through which monitoring data can be used effectively in adaptive implementation of the WQAS, as the monitoring is designed to directly address the monitoring questions delineated in the WQAS. The WQAS monitoring questions are sequential in nature, with one question leading to another. Modifications to the Urban Creeks Monitoring Plan likely will be necessary to develop answers to the questions in a logical, stepwise fashion. This approach provides for efficient use of monitoring resources, as the monitoring effort is adaptively focused on specific management questions.

The ongoing Surface Water Ambient Monitoring Program also undertakes monitoring annually that includes Bay Area urban creeks. PRISM grants and other research projects also involve creek monitoring. Some Bay Area municipal urban runoff management agencies also conduct creek monitoring. The available results of these monitoring activities are incorporated with the analysis of the CEP-sponsored monitoring to address the proposed WQAS management questions.

# Objectives

The following objectives were established in the 2004-05 CEP Urban Creeks Monitoring Plan to address the proposed WQAS management questions described above:

For proposed management question "A" – *Is the diazinon concentration target being met*?:

- Coordinate and supplement monitoring of Bay Area urban creeks during the 2004-05 wet season to provide screening-level data on the concentrations of diazinon in creek waters.
- Analyze the monitoring data to determine whether the proposed diazinon targets are being exceeded, and if so with what frequency and over what geographic distribution.

For proposed management question "B"- Are the toxicity targets being met?:

- Coordinate and supplement monitoring of Bay Area urban creeks during the 2004-05 wet season to provide for acute and chronic toxicity testing of creek waters using standard aquatic bioassays.
- Analyze the monitoring data to determine whether the proposed toxicity targets are exceeded, and if so with what frequency and over what geographic distribution.

For proposed management question "C" - *Is toxicity observed in urban creeks caused by a pesticide*?:

- Correlate diazinon and toxicity data from 2004-05 monitoring to determine whether diazinon appears to be responsible for any observed toxicity in Bay Area urban creeks.
- Plan for additional monitoring in subsequent years if the correlations are inconclusive.

For proposed management questions "D", "E" - Is urban runoff the source of any observed toxicity in urban creeks? How does observed pesticide-related toxicity in urban creeks (or pesticide concentrations contributing to such toxicity) vary in time and magnitude across urban creek watersheds?:

• Modify the monitoring plan as needed (to be determined).

In general support of the proposed WQAS management questions, and to address the monitoring requirements of the WQAS as listed above, the following objectives were also included within the CEP's monitoring activities during 2004-05:

- Characterize the urban watersheds and identify representative urban creek locations for long term monitoring.
- Enlist the cooperation of Bay Area stormwater management agencies and others, and coordinate urban creeks monitoring to ensure use of consistent sampling and analytical methods in the selected representative creeks beginning in 2005-06.
- Conduct a preliminary evaluation of the possible use of preventative or preemptive monitoring approaches to complement the planned urban creeks monitoring.
- Develop plans for monitoring program management, including identification of an oversight group and implementation mechanism(s), and establishment of timeline and reporting requirements.
- Modify the monitoring plan for 2005-06 to include the representative monitoring locations and standardized procedures, accounting for the results of the analysis of the 2004-05 monitoring data, and addressing any changes in the management questions or implementation plan of the WQAS.

The CEP Urban Creeks Monitoring Plan is designed to be adaptable and flexible in response to development of new information, including new methods for sampling and analysis of pesticides, as well as to changing environmental conditions, especially those pertaining to patterns of pesticide use.

# Elements of the 2004-05 Monitoring Program

The strategy for adaptive development of the urban creeks monitoring program involved coordinating the monitoring already planned by agencies for 2004-05, supplemented by funding available from the CEP, and using the 2004-05 data as a screening tool to plan for monitoring in subsequent years. A set of representative monitoring locations were selected for long term monitoring of Bay Area urban creeks. The following steps were undertaken to implement the CEP Urban Creeks Monitoring Plan for the 2004-05 monitoring year:

- 1. Identify relevant monitoring of urban creeks planned by local, regional and state agencies and other entities (e.g., the San Francisco Estuary Institute).
- 2. Supplement the monitoring planned by agencies and institutions in the Bay Area as warranted to provide for consistent and coordinated monitoring during wet weather (storm-event-based), including sampling and analysis of creek water for diazinon and toxicity testing.
- 3. Characterize Bay Area urban watersheds and select sites for long term monitoring locations in representative urban creeks.
- 4. Consider the possible use of preventative or preemptive monitoring methods to complement the planned monitoring of urban creeks.
- 5. Compile and analyze the 2004-05 monitoring data.

- 6. Track and assimilate the results of scientific research and studies related to pesticide use in urban watersheds within the Bay Area, chemical concentrations of pesticides in urban creek waters and sediments, and effects of pesticides on water and sediment quality and aquatic life.
- 7. Develop recommendations for monitoring during 2005-06 in the selected, representative urban creeks, including consideration of the proposed monitoring requirements and management questions within the latest version of the WQAS, as well as coordination with regional NPDES stormwater permit monitoring requirements.
- 8. Develop recommendations for program management, including identification of oversight group, implementation mechanism(s), timeline, and reporting.

The results of these activities are reported in this technical memorandum. In follow-up to this memorandum, standardized monitoring protocols will be established for the selected representative urban creek monitoring locations, based on the monitoring results and recommendations derived from the 2004-05 monitoring. The CEP Urban Creeks Monitoring Plan will then be revised for 2005-06 to incorporate the selected representative sites and standardized protocols.

Ongoing scientific research and monitoring studies are expected to provide additional information on the occurrence and effects of pesticides in aquatic environments, as well as improved methodologies for monitoring of replacement pesticides in water and sediment. Tracking and reporting of the results of relevant scientific investigations and water quality monitoring programs is an important function of the UP3 project, which is currently funded by a PRISM grant to the San Francisco Estuary Project. The UP3 project scope provides for funding of these activities through March 2007. The Urban Creeks Monitoring Plan covers interpretation and integration of this information into the updating/revision of the monitoring plan.

# Methods: 2004-05 Urban Creeks Monitoring

Monitoring protocols for CEP-sponsored urban creeks monitoring during 2004-05 are described in the *CEP Urban Creeks Monitoring Plan* (Ruby, 2004). A memorandum summarizing instructions provided to participating agencies, along with a prototype field log sheet, is attached as Appendix A.

#### Site Selection Criteria, 2004-05 Monitoring

The following criteria were developed by the CEP's Diazinon/Toxicity Work Group for selection of creeks to receive supplemental monitoring funding from the CEP during 2004-05:

- Watershed includes at least 50% urban land uses by area
- Watershed includes very limited agricultural land use (avoid those with potted plant nurseries, orchards)
- Creek has been monitored previously
- Storm-based time-proportional composites will be collected

- Trained or trainable monitoring personnel are available
- There is an accessible sampling location above the tidal zone
- Selected creeks are distributed geographically throughout the Bay Area

The work group suggested prioritizing creeks for which previous monitoring was reported in the report, *Diazinon in Surface Waters in the San Francisco Bay Area: Occurrence and Potential Impact* (Katznelson and Mumley, June 1997).

For geographical distribution, the work group suggested exploring the selection of one creek from each of the nine Bay Area counties.

#### Selected Creeks, 2004-05 Monitoring

Based on the work group's site selection criteria, the following creeks were identified for supplemental monitoring funding in 2004-05:

- Marin County: Corte Madera Creek
- Solano County: Blue Rock Springs Creek
- Contra Costa County: Rheem Creek
- Alameda County: Castro Valley Creek
- Santa Clara County: Calabazas Creek
- Santa Clara/San Mateo Counties: San Francisquito Creek
- San Mateo County: Belmont Creek

All of the selected creeks, with the exception of Blue Rock Springs Creek, have historical data and were covered in the 1997 Katznelson/Mumley white paper. Most are also highly urbanized (>50% of the watershed is in urban land uses), with the exception of the San Francisquito Creek watershed, which lies approximately 80% within San Mateo County, and approximately 20% within Santa Clara County. This watershed is considered to be significantly less than 50% urbanized, but has a significant history of monitoring data and a network of permanent, automated monitoring stations.

The list does not include a selected creek for each Bay Area county, as an appropriate creek could not be identified in San Francisco, Sonoma or Napa Counties. There are no qualifying creeks in San Francisco. Napa and Sonoma Counties have relatively lower percentages of urban land uses, and the urban creeks tend to run through substantial agricultural lands and/or open space upstream of the urban areas.

#### Sample Collection Guidance

Monitoring crews were asked to target storms expected to deliver rainfall of at least 0.5 inch within a 12-hour period. Sample collection was to commence when the effects of rainfall runoff were apparent in the creek, generally following a 5-10% increase in depth or flow over base flow conditions.

Time-based composite samples were recommended, with aliquots to be collected by hand or via autosampler at a minimum frequency of one every half-hour.

Sample containers were required to be Teflon or glass, with stainless steel as an alternative aliquot grab container only. Due to concerns regarding potential adsorption problems, plastic tubing or containers could not be used at any point in the sample collection process.

Approximately 20 liters of sample water were requested for toxicity testing and pesticides analyses. Recommended composite containers were 10 liter "pickle" jars or 20 liter glass carboys.

#### Analytical Methods

Funding was provided by the CEP for the following lab analyses for creek water samples:

- Organophosphate pesticides (or diazinon only): via GC/MS or GC (EPA Method 625, 8141 or similar scan), or ELISA
- Pyrethroids: via GC/MS (EPA Method 625 or similar scan)
- Aquatic Toxicity: acute and chronic end points for fathead minnows and *Ceriodaphnia*, chronic end points for *Selenastrum*; tests performed on undiluted (100% concentration) samples only, via standard EPA methods (USEPA, 1990; USEPA, 1991)

Chemical analyses were performed by CRG Marine Laboratories, Torrance, CA. Toxicity testing was performed by Pacific EcoRisk, Martinez, CA.

# **Monitoring Results**

In this section, the results of the CEP-sponsored analyses are presented, followed by summaries of the relevant monitoring results from local agencies and SWAMP.

#### **CEP-Sponsored Monitoring**

CEP-sponsored monitoring was performed during four storm events in the 2004-05 wet season, on the following dates:

- January 25-26: Tuesday-Wednesday
- February 14-15: Monday-Tuesday
- March 18-20: Friday-Sunday
- April 22: Friday

Nine creek samples were collected and analyzed over the course of the four monitoring events. Two of the events occurred on weekdays and two occurred during weekends. All of the targeted creeks were sampled at least once with the exception of Belmont Creek. The results are summarized in Table 1, for detected pesticide concentrations and significant toxic effects only. Lab reports (chemical and toxicity testing) are included in Appendix B; the toxicity lab report appendices are available by contacting the author.

Date	Creek	County	Diazinon (ng/L)	Malathion (ng/L)	Toxicity Test Results (Significant Effects Only)
Jan. 25/26	Blue Rock Springs	Solano	40.9	NA	
	Corte Madera	Marin	ND	NA	
Feb. 14/15	Castro Valley	Alameda	<b>117</b> (a)	ND	Fathead minnow growth Ceriodaphnia reproduction
	San Francisquito	San Mateo	ND	ND	Ceriodaphnia reproduction
Mar. 18/20	Calabazas	Santa Clara	50.3	ND	
	Castro Valley	Alameda	43.8	56.9	
	Rheem	Contra Costa	51.3	<b>219</b> (b)	Ceriodaphnia reproduction
	San Pablo	Contra Costa	ND	61.5	
Apr. 22	Castro Valley	Alameda	ND	<b>435</b> (c)	<i>Ceriodaphnia</i> reproduction <i>Ceriodaphnia</i> survival (50%)

Table 1. Summary of 2004-05 CEP-Sponsored Urban Creeks Monitoring Results\*

\* Detected constituents only. January samples were analyzed for diazinon only; all other samples were analyzed for OP pesticides and pyrethroids. Results for triazine herbicides also were reported for February samples (see text).

NA = not analyzed

ND = not detected

Pesticide concentrations in **bold type** exceeded water quality criteria as follows:

(a) Above TMDL target and USEPA provisional acute/chronic criterion of 100 ng/L

(b) Above USEPA (2002) recommended chronic criterion of 100 ng/L

(c) Above USEPA (2002) recommended chronic criterion of 100 ng/L and DF&G (1998) acute criterion of 430 ng/L

Of the nine creek samples tested, two (the January samples) were analyzed for diazinon only, and the other seven samples were analyzed for OP pesticides (including diazinon) and pyrethroids. Diazinon was detected in five of the nine samples; four of the measured concentrations were in the range of 40-50 ng/L, and one was over 100 ng/L. From the seven OP pesticide scans, there were also four measured values for malathion, ranging from 56 to 435 ng/L. No other OP pesticides were detected, and no pyrethroids were detected in any sample.

Descriptive statistics for the CEP-sponsored monitoring results for diazinon and malathion are shown in Table 2.

Statistic	Diazinon	Malathion
# analyses	9	7
# detected	5	4
Mean *	41.8 ng/L	114 ng/L
Std. Deviation *	39.5 ng/L	177 ng/L
Median	40.9 ng/L	56.9 ng/L
Minimum **	< 10 ng/L	< 10 ng/L
Maximum	117 ng/L	435 ng/L

# Table 2. Descriptive Statistics for Detected OP Pesticides,<br/>CEP Urban Creeks Monitoring, 2004-05

\* Calculated using regression on ordered statistics (ROS) to account for non-detects (see Shumway et al., 2002)

\*\* Analytical reporting limit for both constituents/all samples was 10 ng/L

There were also two measured values for prometon (130 ng/L in the Feb. Castro Valley Creek sample; 206 ng/L in the Feb. San Francisquito Creek sample) and one for simazine (368 ng/L in the Feb. Castro Valley Creek sample); these results were obtained when analytical chemistry results for triazine algaecides/herbicides were inadvertently included in the laboratory report for the February samples.

All nine samples were tested for aquatic toxicity to the EPA standard suite of three freshwater species. Four of the samples were found to have toxic effects on one or more test organisms. There were five statistically-significant chronic toxicity effects: four samples exhibited reductions in *Ceriodaphnia* reproduction, and one exhibited a reduction in fathead minnow growth. There was also one occurrence of statistically-significant acute toxicity, with 50% mortality of *Ceriodaphnia*, in one of the samples that also exhibited reduced *Ceriodaphnia* reproduction.

#### **Comparisons to Water Quality Criteria/TMDL Targets**

Exceedances of relevant water quality criteria are indicated in Table 1 for diazinon and malathion concentrations measured in the CEP-sponsored analyses (see Marshack, 2003 for a compendium of applicable water quality criteria).

For diazinon, the CEP chemistry data were compared to the USEPA draft water quality criterion of 100 ng/L for the protection of aquatic life for both acute and chronic effects (USEPA, 2002). The 100 ng/L criterion also was adopted in the Basin Plan Amendment as the TMDL target for diazinon in urban creeks (as a one-hour average concentration) for both acute and chronic exposure.

The measured concentrations of malathion, another OP pesticide, were compared to the USEPA-recommended chronic criterion (CCC) of 100 ng/l as an instantaneous maximum and the California Department of Fish and Game (DF&G) acute criterion (CMC) of 430 ng/L as a one-hour average, both to protect aquatic life (Siepmann and Slater, 1998).

There are no published water quality criteria for prometon, a triazine herbicide, and the former USEPA criterion for simazine, a triazine algaecide/herbicide, was 10,000 ng/L for acute effects, as an instantaneous maximum, according to Marshack (2003).

Only one measured diazinon concentration exceeded the TMDL target and draft USEPA acute/chronic criterion of 100 ng/L. Two of the measured malathion concentrations exceeded the USEPA recommended chronic criterion of 100 ng/L for malathion, with one sample also exceeding the DF&G acute criterion of 430 ng/L.

For toxicity, the urban creeks TMDL targets are summarized as follows:

Pesticide-related acute and chronic toxicity in urban creek water and sediment, as determined through standard toxicity tests, shall not exceed 1.0 TU<sub>a</sub> or 1.0 TU<sub>c</sub>, where TU<sub>a</sub> = 100/NOAEC and TU<sub>c</sub> = 100/NOEC. "NOAEC" and "NOEC" refer to the "no observable (adverse) effect concentration," which is the highest tested concentration of a sample that causes no observable effect to exposed organisms during an acute or chronic toxicity test, respectively. NOAEC and NOEC are expressed as the percentage of ambient sample tested (e.g., an undiluted sample has a concentration of 100%). In both cases, an observable effect must be statistically significant.

Given that four of the nine 2004-05 CEP samples exhibited chronic and/or acute toxicity to test organisms at statistically-significant levels in tests of undiluted samples (100% concentration), those samples can be presumed to exceed the 1.0 TU TMDL targets.

However, the Basin Plan Amendment also states, "If toxicity exists in urban creeks but pesticides do not cause or contribute to the toxicity, these targets do not apply." Because TIEs were not performed on the toxic samples, it is difficult to determine with certainty whether pesticides caused or contributed to the toxic effects observed; see related discussion below under Chemistry/Toxicity Correspondences.

## Other Bay Area Urban Creeks Monitoring, 2004-05

Additional monitoring of Bay Area creeks was performed during 2004-05 by local agencies and by Water Board personnel under SWAMP. The results of this monitoring are summarized below.

#### Local Agency Results

The following creeks were monitored in the Bay Area by the local agencies indicated:

- Castro Valley Creek Alameda Countywide Clean Water Program (ACCWP): three wet weather samples, during rainfall/runoff events in October, November and December, 2004
- Several creeks in Santa Clara Valley watershed Santa Clara Valley Urban Runoff Pollution Prevention Program (SCVURPPP): 12 dry weather samples, during late September/early October 2004 and January 2005
- San Francisquito Creek City of Palo Alto: five wet weather samples during three storm events in December 2004, and one each in March and April 2005

Results from these monitoring efforts were provided for this analysis by local agency staff or consultants. As the results were generally provided prior to publication of final reports, they are related here in summary fashion only. Readers who wish to review specific data should contact the author of this tech memo or the individual agencies responsible.

A total of 28 creek water samples were collected by local agencies during various wet and dry weather conditions throughout 2004-05 and analyzed for OP pesticides. Of those 28 samples, three (11%) were found to have measurable (i.e., "detected") concentrations of diazinon. The range of measured sample concentrations was 30-51 ng/L (note that where duplicate samples were analyzed, the initial sample result, as opposed to the "duplicate" result, is reported here).

Nine of the samples were also analyzed for pyrethroids; no pyrethroids were detected in any of the samples.

All three of the measured diazinon results occurred during wet weather sampling, in samples from Castro Valley Creek. All five of the San Francisquito Creek wet weather samples and all 20 of the Santa Clara Valley dry weather samples were determined to be non-detect for diazinon. The San Francisquito Creek watershed is less urbanized than those of the other creeks.

Twelve water samples from Santa Clara County creeks were also tested for three species aquatic toxicity by SCVURPPP. All samples were collected in dry weather conditions, with six collected during late September/early October 2004, and six collected during January 2005. Of the 12 samples tested, three (25%) exhibited toxic effects, including two of the fall samples and one of the winter samples. All three toxic samples reduced *Selenastrum* algal growth. One of the three samples also exhibited acute and chronic effects on *Ceriodaphnia*, and one of the three toxic samples was also acutely toxic to fathead minnows.

#### SWAMP Results

The Surface Water Ambient Monitoring Program tested 36 creek water samples for three species aquatic toxicity in 2004-05. Samples were collected in January, April, and June

2005, covering both wet and dry weather conditions. The January samples were collected during rainfall/runoff that occurred on January 10-11, with approximately 0.4" of rain falling each day. The April samples were collected during dry weather conditions on April 11-12, approximately three days after a storm event totaling 0.4-0.6" of rainfall. The June samples were collected during typical early dry season conditions.

Preliminary toxicity testing data were provided by SWAMP staff from the Water Board. Of the 36 samples tested, nine (25%) exhibited statistically-significant toxic effects. The seasonal breakdown of the toxic samples is fairly even: four of the ten January samples, two of the thirteen April samples, and three of the thirteen June samples exhibited toxicity to one or more of the test species. The toxic effects observed in those nine samples were distributed among the three test species as follows:

- Fathead Minnows (*Pimephales*): 1 case of acute toxicity and 5 cases of chronic toxicity
- Water Flea (*Ceriodaphnia*): 3 cases of chronic toxicity
- Algae (Selenastrum): 3 cases of chronic toxicity

The number of toxic effects observed is greater than nine because some samples exhibited toxic effects on more than one test species. There was no apparent pattern in the seasonal distribution of toxic affects for the three species. Chemistry data were not yet available for the SWAMP samples at the time of preparation of this tech memo. TIEs were not performed on the toxic samples.

#### **Results - Summary**

As expected, contemporary concentrations of diazinon are much lower than those observed in monitoring of Bay Area creeks during the 1990s, when levels exceeding 100 ng/L were commonplace. Combining the CEP-sponsored data with other data from local agencies, the majority of creek samples analyzed in 2004-05 did not contain measurable concentrations of diazinon. Only one sample exhibited diazinon at a concentration in excess of 100 ng/L, the TMDL target for diazinon in Bay Area urban creeks.

Malathion was the second-most commonly detected pesticide in the 2004-05 urban creek samples. Two samples exceeded the USEPA-recommended chronic water quality criterion of 100 ng/L, and one exceeded the DF&G acute criterion of 430 ng/L.

The shift to lower diazinon concentrations was accompanied by a corresponding shift in the pattern of toxicity to aquatic organisms. Whereas creek samples tested in the 1990s were commonly found to be acutely toxic to Ceriodaphnia, very little acute toxicity was observed in the samples tested in 2004-05. Only one sample was acutely toxic to *Ceriodaphnia*, while several showed chronic toxic effects (reduced reproduction) in the *Ceriodaphnia* test organisms. There were also toxic effects to fathead minnows and algae in several samples; most of the statistically-significant effects were sub-lethal (chronic) effects. One local agency sample and one SWAMP sample were acutely toxic to fathead minnows. In all, four of nine CEP-sponsored samples, three of 12 local agency samples, and nine of 36 SWAMP samples exhibited some level of toxic effect.

# **Chemistry/Toxicity Correlations**

The CEP Urban Creeks Monitoring Plan calls for comparisons of chemistry results and toxicity test results in cases where toxic effects are observed, in an effort to evaluate whether pesticides may have caused or contributed to the observed toxicity. This is an important step, as the recently-adopted toxicity targets in the TMDL for diazinon and pesticide-related toxicity in urban creeks do not apply unless a pesticide caused or contributed to the toxicity.

For three of the four CEP-sponsored samples that resulted in statistically-significant toxic effects, diazinon and/or malathion were also present at levels of potential concern. In those three samples, OP pesticides were found at the following levels:

1. *Chemistry*: diazinon (117 ng/L) exceeded the numerical TMDL target (100 ng/L)

Toxic effects: Fathead minnows (chronic); Ceriodaphnia (chronic)

2. *Chemistry*: diazinon (51.3 ng/L) exceeded one-half the numerical TMDL target (100 ng/L), and malathion (219 ng/L) exceeded the USEPA recommended chronic criterion (100 ng/L) and also exceeded one-half the DF&G acute criterion (430 ng/L)

*Toxic effect: Ceriodaphnia* (chronic)

3. *Chemistry*: malathion (435 ng/L) exceeded both the USEPA recommended chronic criterion (100 ng/L) and the DF&G acute criterion (430 ng/L)

Toxic effects: Ceriodaphnia (acute and chronic)

So, in three of the four toxic CEP samples, either diazinon or malathion exceeded an applicable water quality criterion, or both were present at levels of at least one half the applicable criteria. The toxic effects of diazinon have been shown to be cumulative (additive or synergistic) with those of other pesticides (c.f., Bailey et al., 1997; Denton et al., 2003). No OP pesticides were detected in the fourth toxic sample.

However, the measured concentrations of diazinon in these samples were generally well below the concentrations known to produce toxic effects in test species. The reported LC50 values for diazinon in invertebrate toxicity studies range upwards of 200 ng/L (250-590 ng/L for *Ceriodaphnia dubia*) (USEPA, 2002). For malathion, the measured concentrations for all but one of the samples were well below the concentrations known to produce toxic effects. The reported LC50 values for invertebrate species for malathion range upwards of 270 ng/L (1140-3180 ng/L for *Ceriodaphnia dubia*), although one study did report a 24-hour EC50 for malathion of 98 ng/L for *Daphnia magna* (see summary in TDC Environmental, 2003)

Three of the 12 dry weather creek samples tested by SCVURPPP also were toxic; however, there were no detected pesticides in those samples. Nine of 36 samples tested by SWAMP also exhibited toxicity, but corresponding SWAMP water chemistry data were not available for evaluation at the time of preparation of this technical memorandum.

# Are the TMDL Targets Met?

The CEP's Diazinon/Toxicity Work Group debated at length the appropriate methods by which to determine whether the TMDL targets for diazinon and toxicity are met, given the ever-present issues of spatial and temporal variability. The Work Group reached consensus on the following points:

- Monitoring data for all Bay Area urban creeks should be combined, as opposed to a creek-by-creek approach, to maximize the value of limited monitoring data.
- The statistically-based approach included in the statewide Section 303(d) Listing Policy (SWRCB, 2004) can be used to assess whether the TMDL targets are met in Bay Area creeks. The Policy allows for a graduated number of exceedances of a given criterion, based on the total number of data points available over a running three year averaging period (for toxic pollutants).

This technical memorandum summarizes just one year of monitoring data (2004-05). For that one year, combining data from all sources, and using the allowable numbers of exceedances specified in Table 4.1 of the Listing Policy, the following preliminary answers can be drawn for urban creeks in the Bay Area:

#### A. Are the diazinon concentration targets being met?

Yes, based on the 2004-05 data. Only one diazinon test result out of 37 total Bay Area urban creek samples exceeded the 100 ng/L TMDL target (per Table 4.1 of the Listing Policy, three exceedances are allowed with 37 samples). Two additional years of data would be required to make a more definitive determination based on the three year return period inherent in the criterion upon which the target is based.

#### B. Are the toxicity targets being met?

Undetermined, based on the limited 2004-05 data available. Assuming that a statisticallysignificant toxicity test result in any full-strength sample represents a toxicity level greater than 1 T.U., then 16 of 57 urban creek samples tested in 2004-05 exceeded the TMDL toxicity target of 1 T.U.; this is greater than the allowable number of exceedances per Table 4.1 of the Listing Policy (four exceedances are allowed for 57 samples). However, available chemistry data are insufficient to establish pesticides as the cause of the observed toxicity. For three of the toxic samples, corresponding chemical constituent data indicate that organophosphate pesticides may have caused or contributed to the observed toxic effects, as discussed above. For other toxic samples, evidence for causation is unavailable. Once the SWAMP water chemistry become available, it may be possible to draw some inferences regarding causes of toxicity in the nine SWAMP samples that exhibited toxic effects.

It is also not currently possible to definitively answer the question of whether the toxicity targets are being met for urban creek *sediments* in the Bay Area, using the Listing Policy evaluation criteria as presented above. Recent trends in pesticide use and the results of recent scientific research point to the need to assess the quality of sediments in urban creeks, and to determine whether the toxicity targets are being met in sediments. Evidence has been presented to the CEP Diazinon/Toxicity Work Group and to other

audiences (Amweg and Weston, 2005; Amweg and You, 2005), implicating pyrethroid pesticides as the cause of toxicity to invertebrate test organisms in sediment samples from urban creeks in the Bay Area and elsewhere. However, the Bay Area sediment study results are not yet published, and the specific data are not available for evaluation.

# **Other Research - Summary**

To aid in the interpretation of the water quality monitoring results and in development of recommendations for future monitoring of urban creeks, the results of recent scientific research and studies pertinent to pesticides and water quality impacts in the Bay Area are summarized in this section.

The recent UP3 Project report, "Pesticides in Urban Surface Water; Annual Research and Monitoring Update, 2005" (TDC Environmental, 2005a), provides a useful summary of recent research and scientific studies pertinent to pesticide uses and urban surface water quality. Significant conclusions from this report include:

- Common replacements for diazinon and chlorpyrifos, including pyrethroids, carbaryl, and malathion, may cause adverse impacts in urban creeks, with sediment toxicity being of particular concern.
- Pesticides and other pollutants such as copper, which is also an ingredient in certain pesticides may act additively or synergistically to produce toxic effects in aquatic environments affected by urban runoff.
- New urban pesticide products such as fipronil and polyhexamethylene biguanide (PHMB) have the potential to cause or contribute to pesticide-related toxicity in surface waters, urban runoff and wastewater treatment plant effluents.
- Analytical capabilities for measuring environmentally-relevant concentrations of pyrethroids and other pesticides in water and sediment and their effects on aquatic organisms are still lacking; improvements are needed and relevant research is underway in the areas of sample collection, chemical analysis, and toxicity testing (especially relating to TIEs).
- A mechanism is needed to coordinate and disseminate results from the various monitoring efforts that are undertaken in the Bay Area pertinent to pesticide levels and related impacts in local waters.

From these observations, it can be inferred, relative to the urban creeks TMDL/WQAS, that diazinon will continue to decrease as a significant cause of toxicity in urban creeks, while malathion and other pesticides may present an increasing threat to water quality. At the same time, it is becoming essential to assess the quality of sediments in urban creeks, and to determine the extent to which sediment-dwelling organisms are impacted. Significant aspects of the relevant research are summarized below.

#### DPR Sales and Use Data

Pesticide sales data are compiled annually by the California Department of Pesticide Regulation (DPR), based on a state tax paid by manufacturers at the wholesale point of

sale. Certain pesticide uses – principally applications by licensed pest control operators (PCOs) – are also required to be reported to county agricultural commissioners, who in turn report the use data to DPR. Based on the most recently available (2003) DPR sales and use data, as summarized in a recent UP3 Project report, "Pesticides in Urban Surface Water; Urban Pesticides Use Trends Annual Report, 2005" (TDC Environmental, 2005b), and updated by a summertime retail shelf survey (TDC Environmental, 2005c), the following trends are apparent:

- Pyrethroid sales have increased while diazinon and chlorpyrifos sales have decreased during the period 1999-2003.
- Urban uses of the following eight pyrethroids were found to have the potential to release environmentally meaningful quantities of active ingredient into surface water: bifenthrin, cyfluthrin (including beta-cyfluthrin), cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, and tralomethrin.
- Three pyrethroids (bifenthrin, cyfluthrin [including beta-cyfluthrin], and cypermethrin) account for most of the toxic equivalents of pyrethroids applied through urban uses in the San Francisco Bay Area. These three pyrethroids have been found to be the biggest contributors to the total pyrethroid toxic units found in Northern California urban creek sediments (Weston et al., 2005).
- The most common use of pyrethroids in California urban environments involves pest control around buildings by professional pest control operators (PCOs).
- Urban uses of other pesticides of concern relative to water quality, including malathion, fipronil, and PHMB, also have increased during 2001-2003.

The above-referenced report contains a lengthy list of recommendations for a wide range of activities bearing on control of water quality impacts from urban pesticide uses, including monitoring and research. The recommendations most directly relevant to Bay Area urban creeks monitoring are:

- Conduct surveillance monitoring of California urban surface waters (including sediment) for toxicity and for specific pesticides that have the potential to cause adverse effects in aquatic ecosystems (e.g., pyrethroids, carbaryl, malathion, PHMB, and fipronil).
- Report all pesticide-related toxicity incidents and provide all pesticide-related monitoring data to U.S. EPA and DPR.

#### Sediment Testing

The results of chemical and toxicity testing of agricultural and urban sediments in the Central Valley have been recently published by Don Weston and his colleagues at the University of California, Berkeley (Weston et al., 2004; Weston et al., 2005). Additional data relating to findings of pyrethroid-based toxicity in Bay Area urban creek sediments that are not yet in print have been presented to the CEP's Diazinon/Toxicity Work Group and at a recent scientific conference (Amweg and Weston, 2005; Amweg and You, 2005). This research involved sediment toxicity testing using standard test procedures (USEPA, 2000) with *Hyalella azteca* as the test organism, along with low-detection-level

analytical chemistry for pyrethroids, organochlorine pesticides, and chlorpyrifos (an organophosphate pesticide).

In these studies, significant sediment toxicity was found in samples from agricultural creeks in the Central Valley, as well as from urban creeks in Roseville (a suburb of Sacramento), and Contra Costa County and other East Bay locations. Concurrent chemical analysis revealed that pyrethroids were present at levels capable of causing toxic effects in most of the toxic samples. These correlations, together with additional data analysis and toxicity testing conducted by the researchers, strongly suggest that pyrethroids contributed significantly to the observed toxicity.

Importantly, related research has found that pyrethroid toxicity tends to be mitigated by higher levels of organic carbon (Amweg et al., 2005; Gan et al., 2005). For that reason, in the above-cited studies the relative toxicity of individual pyrethroids is determined on a TOC-normalized basis.

# Conclusions

The preceding analysis of 2004-05 Bay Area urban creeks monitoring data and related research and scientific information leads to the following conclusions:

- 1) Diazinon levels have decreased. As only one measured diazinon concentration out of 37 urban creek samples exceeded the 100 ng/L TMDL target, the 2004-05 monitoring data provide support for the delisting of Bay Area urban creeks for diazinon. However, two additional years of data are required to make a more definitive determination, based on the three year return period inherent in the water quality criteria upon which the target is based.
- 2) Some aquatic toxicity persists. Bay Area urban creeks continue to exhibit toxicity to aquatic test organisms. Over 25% of 2004-05 Bay Area creek samples (16 of 57) were toxic to one or more test species. Most of the toxic effects were of a chronic rather than acute nature, but effects were observed on all three test species. In some of the toxic CEP-sponsored samples, chemical analyses suggested that the OP pesticides diazinon and malathion may have contributed to the observed toxicity.
- **3)** Other pesticides may cause water quality impacts. Based on pesticide use data and related information, diazinon is expected to continue to decline as a significant cause of aquatic toxicity in urban creeks, while other pesticides, including malathion, carbaryl, fipronil, and PHMB, may become more problematic.
- 4) Sediment testing is essential. Due to the well-documented rise in urban uses of pyrethroid pesticides, and recent discoveries of pyrethroid-caused toxicity in urban creek sediments, pesticide-related impacts on sediment quality may be significant, and warrant further investigation.

#### Next Steps

Given that aquatic (water column) toxicity continues to be observed in Bay Area urban creeks, and given the association of some of the toxicity observations with elevated concentrations of pesticides, per the Urban Creeks Monitoring Plan, the next steps are to address the subsequent WQAS monitoring questions:

#### C. Is toxicity observed in urban creeks caused by a pesticide?

Per the discussion presented above, the 2004-05 CEP-sponsored monitoring data are inconclusive as to whether a pesticide or combination of pesticides caused or contributed to the observed toxicity. The Urban Creeks Monitoring Plan calls for a combination of additional monitoring and TIEs, where technically feasible, to identify the cause(s) of the observed toxicity.

#### D. Is urban runoff the source of any observed toxicity in urban creeks?

Given that urban runoff is a major contributor to flows in most Bay Area urban creeks, it is expected that in some measure urban runoff will be found to be a source of the observed toxicity, and possibly the principal source. Some monitoring to characterize urban runoff contributions to in-stream pesticide levels may be necessary. Alternatively, estimates of the relative contributions of urban runoff to in-stream water column pesticide concentrations may be calculated based on existing water quality and hydrology information.

# E. How does observed pesticide-related toxicity in urban creeks (or pesticide concentrations contributing to such toxicity) vary in time and magnitude across urban creek watersheds?

The 2004-05 monitoring data provide some information pertinent to this question; however, additional, follow-up monitoring should be planned to further address this question once it is determined more definitively to what extent the observed toxicity is due to pesticides. To achieve better geographical distribution of data throughout the Bay Area, it is important to include monitoring of an urbanized watershed in San Mateo County, as specified in the recommended list of sites for long term monitoring (Laurel Creek in San Mateo is the creek selected for this purpose; see Recommendations for 2005-06 Urban Creeks Monitoring, below).

#### Sediment Assessment

Because of the rise in urban uses of pyrethroid pesticides, as well as recent evidence of toxicity in urban creek sediments in the Bay Area and elsewhere in northern California, it is considered important to begin assessment of sediment quality in Bay Area urban creeks. The research performed by Weston and associates on sediment toxicity in Bay Area urban creeks, once published, will provide a significant starting point for this assessment. The Recommendations for 2005-06 Urban Creeks Monitoring (see below) include annual monitoring of Bay Area creek sediments, involving sediment chemistry and toxicity testing. The same set of questions applied above to urban creek waters will then need to be addressed for sediments, if it is found that the TMDL toxicity targets are not met for urban creek sediments.

### **Recommendations for 2005-06 Urban Creeks Monitoring**

Based on the analysis presented in this technical memorandum, the following recommendations are made for monitoring of Bay Area urban creeks in 2005-06.

1) Continue to monitor urban creek waters at selected sites throughout the Bay Area (see recommended list of locations below). Collect samples during rainfall/runoff from two wet season events (one early season and one mid-to-late season) and one dry season event per year. Perform chemical analyses for OP pesticides and pyrethroids, plus carbaryl, fipronil, and PHMB. Conduct three-species aquatic toxicity testing for acute and chronic end points as applicable. Perform TIEs where technically feasible to identify causative agents in toxic samples.

Collect samples from representative long term monitoring locations as identified by the CEP's Diazinon/Toxicity Work Group (organized by county, clockwise around the Bay Area beginning with Marin County):

- Marin County: Corte Madera Creek at Sir Francis Drake Blvd./Lagunitas Rd., behind the City of Ross Fire Dept.
- Solano County: Blue Rock Springs Creek at Admiral Callaghan La., at Avery Greene culvert in Vallejo
- Contra Costa County: Rheem Creek at Giant Rd., City of Richmond
- Alameda County: Castro Valley Creek at ACCWP Site "S3", by footbridge off N. 3<sup>rd</sup> St. behind Hayward senior center, at the USGS gauging station
- Santa Clara County: Calabazas Creek at Lakeside Dr. in Sunnyvale (on border with Santa Clara)
- Santa Clara/San Mateo Counties: San Francisquito Creek at Newell Rd. in Palo Alto
- San Mateo County: Laurel Creek at Laurie Meadows Park, off Casanova Dr. in the City of San Mateo

For a detailed description of the selection criteria and process used in selecting the creeks listed above, see the relevant Memorandum to the Diazinon/Toxicity Work Group, included herein as Appendix C. This list does not include a selected creek for each Bay Area county, as an appropriate creek could not be identified in San Francisco, Sonoma or Napa Counties.

**2)** Add sampling and analysis of sediments for pyrethroids and fipronil, plus toxicity testing (with *Hyalella azteca* as the test organism), from each site, once during each dry season. Include analysis for sediment TOC to facilitate data interpretation.

**3)** Coordinate the monitoring to the extent feasible to ensure consistency in methods and comparability of results.

**4) Prepare an analysis of the monitoring data** from all agencies/sites, incorporating relevant results from other programs such as SWAMP, as available, at the conclusion of

the monitoring year. Compare the results to TMDL targets and address the WQAS monitoring questions as feasible.

**5) Incorporate preventative/pre-emptive monitoring techniques** to identify and address potential threats to water quality before impacts occur, to the extent feasible. The measures recommended by the CEP's Diazinon/Toxicity Work Group include the following:

- Continue to review the scientific literature, government reports, and monitoring data to identify which pesticides pose the greatest threats to urban surface water quality. Continue to track and analyze DPR pesticide use and sales data for pesticides of concern relevant to water quality. Conduct retail store shelf surveys and assess other relevant information sources to supplement the DPR data. Analyze potential water quality impacts based on evaluations of the available use data and scientific information. (Note that through early 2007 these functions are effectively covered through the UP3 Project. Development of a means for continuing this work following expiration of the UP3 Project grant is essential.)
- Evaluate the potential effects on water quality of significant proposed regulatory measures affecting pesticide uses, in light of the available scientific information.
- When timely information is needed regarding professional pesticide applications on the local or regional level, agency staff may request the latest available pesticide use reports from PCOs through the offices of county agricultural commissioners. Potential impacts to local and/or regional water quality may be assessed through evaluation of the current pesticide use information, in light of the available scientific information.
- Plan to conduct some reconnaissance-level monitoring at selected upstream locations in urban watersheds for pesticides identified as threats to surface water quality.
- Use ELISA techniques for monitoring of targeted pesticides when available. Contact ELISA test manufacturers to encourage development of needed tests – for water and sediment samples as appropriate – based on information on potential threats to water quality provided by analysis of pesticide use data and regulatory imperatives (per first and second items above).
- Apply pressure on USEPA to perform adequate water quality impacts assessments as part of the routine pesticide registration process. Encourage USEPA to require pesticide manufacturers to conduct runoff quality studies to evaluate the potential effects of their products on surface water quality.
- Enhance cooperation and coordination between the Water Board and DPR regarding monitoring and assessment of the effects of pesticide applications, and appropriate uses of available evidence of water quality impacts.

A detailed discussion of the issues related to these recommended preventative/preemptive monitoring measures is contained in a Memorandum to the Diazinon/Toxicity Work Group, included herein as Appendix D.

### **Recommendations for Monitoring Program Management**

The local municipal stormwater agencies are currently engaged in negotiations with the Water Board for a new, region-wide NPDES stormwater permit. This permit will include monitoring requirements, which will presumably also be regionally-based. The development of the regional permit and regional monitoring requirements are compatible with the recommended elements of the urban creeks monitoring program for 2005-06, including the recommended monitoring sites, as detailed above.

BASMAA has a standing Monitoring Committee; it would seem appropriate to assign responsibility for regional monitoring oversight to this committee. To ensure effective coordination of the monitoring efforts and incorporation of all the recommended elements of the monitoring program, and to facilitate joint compilation and analysis of the monitoring results from each local agency, it would seem necessary for the committee to assign the responsibility for implementing these activities to an individual with relevant knowledge and expertise.

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APPENDIX A

MEMORANDUM RE: 2004-05 URBAN CREEKS MONITORING

Memo to:	Monitoring Personnel – CEP-Funded Urban Creeks Analysis
From:	Armand Ruby, CEP Diazinon/Toxicity Work Group Coordinator
Date:	January, 2005
Subject:	Urban Creeks Monitoring Guidance

## Overview

The Clean Estuary Partnership (CEP) is providing funding for supplemental monitoring of urban creeks to support the implementation of the *Diazinon and Pesticide-Related Toxicity in Urban Creeks Water Quality Attainment Strategy and Total Maximum Daily Load.* The CEP will cover the costs of analysis for specific pesticides and toxicity testing for creek samples from selected urban creeks (see list below) during winter/spring of the 2004-05 wet season. Funding is available to cover analytical costs for approximately three monitoring events per selected site. The following specifications describe how samples should be collected and logistical details for sample analysis.

# **Storm Selection**

**Target: 0.5" within 12 hours or less.** Monitoring crews should target storms that are expected to deliver rainfall of at least 0.5 inch in a 12 hour period. *However, if the sampled storm delivers less than the desired minimum rainfall amount, the sample should still be submitted to the lab provided runoff from the storm was well-characterized by the composite sample, i.e., the composite sample essentially covers the full hydrograph.* 

# Sample Collection

**Sample Type/Timing:** <u>Time-based composite samples</u> are preferred. Creek sampling should commence when the effects of rainfall runoff are apparent in the creek, generally following a 5-10% increase in depth or flow over baseflow conditions. Sampling should be terminated when creek flows return to near-baseflow (pre-storm) conditions.

**Composite Period:** should be <u>at least 4 hours duration</u>; 8 hours minimum is preferred. NOTE: Coverage of full storm hydrograph is ideal, <u>up to a 24 hour maximum</u>; however, the 4 hour minimum duration is acceptable for this program if necessary due to institutional or weather-related limitations.

**Sample Volumes:** Approximately <u>20 liters</u> should be collected for samples that will be tested for toxicity and analyzed for pesticides. This is facilitated by the use of 10 liter glass "pickle" jars or 20 liter glass carboys as composite containers. For the specified toxicity tests, 16 L are needed, and 2 or 4 L are needed for the pesticides, depending on the level of QA/QC to be performed (will be determined by the lab). If you have more than 20L, great - EXTRA SAMPLE VOLUME IS A GOOD THING! *If the composite sample ends up short, bring the composite sample into the lab anyway, and the lab will perform whatever tests/analyses are possible with the volume provided.* 

Aliquot Frequency/Volume: composite sample aliquots should be collected at a minimum frequency of <u>one every half-hour</u>. Aliquots may be collected more frequently (e.g., at 15 or 20-minute intervals). Aliquots may be collected by hand or via autosampler. Aliquot volume should be based on the expected storm duration or the planned composite period, such that the minimum required composite volume (20 L) is collected, at the selected aliquot frequency.

**Sample Containers:** must be <u>Teflon or glass</u>. Stainless steel may be used as an intermediate sampling device (sample aliquot container), if no metals analyses are planned (note that the CEP is covering pesticides and toxicity analysis only). Plastic containers or equipment (other than Teflon) may not be used at any point in the sample collection process. Borosilicate glass pickle jars or carboys (10 or 20L) are ideal for composite sample collection; simply pour each aliquot into the composite container as they are collected.

**Sample Preservation:** <u>Samples must be kept cool (4°C)</u> during and after sample collection. Composite sample bottles may be kept in a refrigerated sampler, or on ice. A simple solution is to purchase a new plastic garbage can of sufficient size to hold the composite carboy, and surround the carboy with ice prior to sample collection. If composite samples are not delivered directly to the lab (i.e., if they are held overnight) they must be refrigerated or iced while awaiting transport to the lab.

**Field Measurements/Field Log:** *If possible,* the field crews are requested to provide flow and rainfall amounts for each sampled storm event, as well as field-measured conductivity and any other available field parameters. A field log form is provided for that purpose. Please send copies of all completed field logs to Armand Ruby (contact info is on the bottom of the form) for CEP data analysis and interpretation.

**Laboratory Notification:** Pacific EcoRisk should be notified (see below) as early as possible prior to each sampling event so that the lab can ensure that adequate stocks of test organisms are available. Contact Armand Ruby for that purpose (a summary of the expected numbers of samples will then be provided to PER. Advance notification is not required for CRG.

#### Selected Creeks:

Marin: Corte Madera Creek Solano: Blue Rock Springs Creek Contra Costa: Rheem Creek Alameda: Castro Valley Creek) Santa Clara: Calabazas Creek Santa Clara/San Mateo: San Francisquito Creek San Mateo: Belmont Creek

Additional Information: Additional information regarding monitoring protocols, including sample handling and field observations, is included in the *CEP Urban Creeks Monitoring Plan*, or contact Armand Ruby.

## Sample Delivery

All samples must be delivered to Pacific EcoRisk ("PER") laboratories in Martinez. <u>Because of the short (36 hour) holding time for toxicity testing, samples must be</u> <u>delivered to Pacific EcoRisk ASAP after sample collection is complete.</u>

#### **PER Contact Information:**

Scott Ogle or Ed Salinas Pacific EcoRisk 835 Arnold Drive, Suite 104 Martinez, CA, 94553-6838 Tel: 925-313-8080 Fax: 925-313-8089

Samples will be split and/or composited at PER as necessary. PER will arrange delivery of samples to CRG Labs for pesticides analysis.

Analytical/Toxicity Testing: The following toxicity tests will be performed:

- Selenastrum chronic toxicity
- Ceriodaphnia acute toxicity
- Ceriodaphnia chronic toxicity
- Fathead minnow larvae chronic toxicity, with measurement of acute toxicity endpoints

Samples will be analyzed for OP pesticides and, if selected, pyrethroids (as the most common substitutes for diazinon and chlorpyrifos).

**Chain of Custody:** Separate COC forms are provided for Pacific EcoRisk (toxicity testing) and CRG Labs (pesticides analysis). *Please fill in sampler name, agency, and telephone #, as well as sample ID information.* The COCs are pre-filled-out with the relevant information on billing and analysis.

**For toxicity testing:** simply check the elongated box in the "ANALYSES REQUESTED" column for each sample; all the listed toxicity tests will then be performed for each of the submitted samples.

**For pesticides analysis:** select one of the options for "REQUESTED ANALYSIS". Select "Pyrethroids + OP Pesticides by GCMS" unless there are institutional reasons why your agency does not want all of the available analyses to be performed.

**Results:** The lab results will be reported to Armand Ruby, who will then compile and report the results to all participants.

**Lab Billing:** The labs will charge the toxicity testing and analytical costs to purchase orders issued by Applied Marine Sciences under contract to the CEP.

# **CEP Urban Creeks Monitoring - Field Log**

Date/Time:	_ Field Crew:					
Monitoring Site:	Site ID:					
Weather Conditions:						
Observations (creek flow, color, odor, floatable materials, etc.):						
SAMPLE COLLECTION						
Sample Type (Composite/Grab):	Collection Method:					
Sample Start Time:	Sample End Time:					
Field Blank Collected? (Y/N):	Time of Blank Collection:					
Observations/Occurrences:						
RAINFALL/FLOW DATA						
Total Event Rainfall:	Rainfall Duration:					
Creek Stage Level Before Sampling:	Creek Stage Level After Sampling:					
Total Event Creek Flow:	Max. Creek Stage Level:					
Observations/Occurrences:						
FIELD MEASUREMENTS						
Time of Measurements:	Conductivity:					
	pH:					
Temperature:						

Please mail, fax or e-mail form to: Armand Ruby, 1032 Morris Cir., Woodland, CA, 95776 Fax: 530-668-5612 (phone must be answered in person); e-mail: armand@armandruby.com

#### APPENDIX B

# ANALYTICAL CHEMISTRY AND TOXICITY TESTING RESULTS: 2004-05 URBAN CREEKS MONITORING

#### NOTE: LABORATORY REPORTS ARE NOT INCLUDED IN THIS PDF.

#### FOR APPENDIX B LAB REPORTS CONTACT THE REPORT AUTHOR, OR VIEW THE FULL REPORT ON THE UPC WEB SITE:

http://www.up3project.org/documents/CEP\_2004-05\_Urban\_Creeks\_Monitoring\_Tech\_Memo.pdf

#### **APPENDIX** C

#### MEMORANDUM RE: SELECTION OF LONG TERM URBAN CREEK MONITORING SITES

Memo to: CEP Diazinon/Toxicity Work Group
From: Armand Ruby, Diazinon/Toxicity Work Group Coordinator
Date: Revised July 29, 2005
Subject: Selection of Urban Creeks for Long Term Monitoring

#### Introduction

This memorandum describes the proposed selection of long term urban creek monitoring sites to support adaptive implementation of the *Diazinon and Pesticide-Related Toxicity in Urban Creeks Water Quality Attainment Strategy and Total Maximum Daily Load* ("the WQAS"; see the Staff Report, SFBRWQCB, 2005). This work is performed in consultation with and under the direction of the Diazinon/Toxicity Work Group ("Work Group") of the Clean Estuary Partnership (CEP).

The CEP provided funding during 2004-05 for monitoring of urban creeks, to supplement that already planned by local agencies. Funding was provided for chemical analysis of creek water samples for OP pesticides and pyrethroids, and testing for three species aquatic toxicity. The monitoring was performed in accordance with the CEP Urban Creeks Monitoring Plan (Ruby, 2004a). The 2004-05 monitoring year is a transitional period prior to formal implementation of the WQAS. Selection of long term monitoring sites is considered necessary to support effective implementation of the WQAS in an adaptive management mode, with monitoring adapted to reflect current conditions.

# **Guiding Principles**

**Pesticides of Concern.** Pesticide use patterns change over time as regulatory actions limit uses of certain chemicals, and others are brought into the marketplace. The means, timing, and placement of pesticide applications in the urban environment differs for different pesticides, leading to varying pathways for potential effects on water quality. For information on specific pesticides consult the UP3 project web site (c.f. TDC Environmental 2003, 2005a, 2005b): <u>http://www.up3project.org/up3\_index.shtml</u>.

**Conceptual Model.** The selection of urban creek monitoring sites is based on the conceptual model of pesticide application, transport, fate and effects as described in the WQAS staff report. In this model, pesticides are applied in urban areas, are subject to physical, chemical, and biological degradation, and in some measure are then available for transport to urban creeks during rainfall/runoff events or in irrigation runoff. In this concept the urban creeks can be seen as collectors of the residual pesticide that is available for transport after application in urban areas. Many pathways are available for pesticides to potentially impact water quality, depending on the nature and timing of pesticides like diazinon and other organophosphates, which tend to attach less to particles and are found more readily in the water column, and those, like pyrethroids, that have greater affinity for particles and tend to be more prevalent in sediments.

**"Worst Case" Approximation.** The Work Group's intention in developing site selection criteria for long-term monitoring was to select creeks that are highly urbanized and can therefore provide evidence of pesticide-related water quality impacts in the creeks most likely to be affected by urban pesticide applications. At their downstream reaches those urban creeks presumably represent the greatest accumulation of pesticide loads prior to discharge to the Bay. Based on the results of monitoring at such worst case locations, adaptive management actions can then be taken as necessary to prevent significant impacts in less urbanized – and presumably less impacted – creeks.

**Current Conditions.** Based on data from the CEP-sponsored monitoring of urban creeks in 2004-05, OP pesticides continue to be sporadically present at measurable levels in urban creeks, including diazinon at low to moderate levels, and malathion at moderate to fairly high levels. There have been several instances of mild, chronic toxicity effects (reduced reproduction in *Ceriodaphnia*; reduced growth in fathead minnows) and one instance of acute toxicity (*Ceriodaphnia* mortality).

No pyrethroids were detected in the creek water samples. However, recent work by researchers from UC Berkeley has indicated that sediments from urban creeks in the East Bay exhibit elevated concentrations of pyrethroids and acute toxic effects on test organisms in a majority of cases (Weston and Amweg, 2005).

Information on urban pesticide use in the Bay Area indicates that pyrethroid use is on the rise and that pyrethroids have effectively replaced diazinon in structural pest control and on store shelves (TDC Environmental, 2005a).

# Site Selection Criteria

Following the guiding principles, the Work Group developed criteria for selection of creeks for long term monitoring in support of the WQAS. These criteria are revised somewhat from those developed by the Work Group for selection of creeks to receive supplemental monitoring funding from the CEP during 2004-05 (Ruby, 2004b). The long-term site selection criteria are as follows:

1) Land Use Characteristics. Selected watersheds should:

- include at least 50% urban land uses by area
- include very limited agricultural land use (avoiding those with potted plant nurseries, orchards)
- represent a "reasonable range" of urban land uses (commercial, industrial, and residential high and low density)

**2)** Geographical Distribution. Selected creeks should be distributed geographically throughout the Bay Area. The Work Group has, both for regulatory purposes and to provide for an equitable distribution of effort and responsibility, proposed the selection of one creek from each of the nine Bay Area counties, where feasible.

3) Site Accessibility/Safety. Selected sites must have sampling locations that are:

- Safely accessible to sampling personnel
- Have safe parking for field vehicle available nearby
- Amenable to collection of storm-based composite samples; i.e., either automated equipment is or can be in place, or the site should be accessible to sampling personnel throughout the course of typical (non-flooding) rainfall/runoff events

**4)Hydrological Characteristics.** Selected creeks should be undisturbed by flow modifications at the point of sample collection:

- The sample collection site should be above the tidal zone
- There should be no dam or other significant flow-regulating structure upstream that could affect creek water quantity/quality
- The watershed must be of sufficient size to generate flow during smaller rainfall events and provide a reasonable window for sampling; 500 acres was used as a rule of thumb

**5)** Sediment Sampling Capability. Because of the increased use of pyrethroids and the documented presence of pyrethroid contamination in sediments, with associated toxic effects, it is important for the urban creek sites to provide the opportunity for collection of sediment samples, to the extent feasible.

### 6) Other Considerations:

**Previous Monitoring History.** The work group had previously prioritized creeks for which monitoring by public agencies had occurred previously, but due to the changing nature of pesticide use and urban runoff characteristics, and the general difficulty in identifying long term trends for any specific creek, this criterion was reduced as a priority. The availability of previous monitoring data is considered to be an advantage.

**Presence of Automated Monitoring Stations.** Where automated equipment is installed, sample collection is facilitated in a wider range of conditions and circumstances, as sample collection can proceed unattended by field personnel.

# Land Use Information

The Work Group's highest priority – to identify creeks with highly urbanized watersheds – has been difficult to implement due to a lack of consistent land use information for Bay Area watersheds. Several resources were consulted in an attempt to address this criterion. Those resources included:

- San Francisco Bay Area Stormwater Runoff Monitoring Data Analysis, 1988-1995 (Woodward-Clyde Consultants, 1996)
- Contra Costa Creeks Inventory and Watershed Characterization Report (Dovzak and Sommers, 2004)

- The Contra Costa Watershed Forum's Watershed Atlas (see: <u>http://www.cocowaterweb.org/</u>)
- Watershed Characteristics Report, Watershed Management Plan, Volume One, Unabridged 2003 Revision (Santa Clara Basin Watershed Management Initiative, 2003 (see: <u>http://www.valleywater.org/\_WMI/Related\_report/Wcr2003r.cfm</u>)
- Characterization of Imperviousness and Creek Channel Modifications for Seventeen Watersheds in San Mateo County (EOA, 2002)
- Oakland Museum of California Guide to San Francisco Bay Area Creeks, Creek and Watershed Maps (see: <u>http://www.museumca.org/creeks/index.html</u>)
- Marin County Department of Public Works (Liz Lewis, personal communication)
- Vallejo Sanitation and Flood Control District (Jack Betourne, personal communication)

The results of the search for land use data to characterize the candidate watersheds is summarized in Table 1 for the proposed long term creek monitoring watersheds.

# **Creek Selection**

Based on the work group's site selection criteria, the following creeks are proposed for long term monitoring, ordered by county (clockwise from Marin County).

**Marin: Corte Madera Creek** at Sir Francis Drake Blvd./Lagunitas Rd., behind City of Ross Fire Dept. – this creek is highly urbanized in its lower watershed but has an area of open space in the upper reaches. Overall, urban uses comprise nearly 50% of the total watershed area. Sediment is readily available and there is safe access to the sampling site at USGS gauging station. Monitoring was performed in 2004-05 and prior.

**Solano: Blue Rock Springs Creek** at Admiral Callaghan La., Avery Greene culvert in City of Vallejo – urban creek with a readily accessible and safe monitoring location in a highly urbanized, mixed use watershed. Sediment is readily available and there is safe access to the sampling site. Monitoring was conducted during 2004-05.

**Contra Costa: Rheem Creek** at Giant Rd., City of Richmond – urban creek with a readily accessible and safe downstream monitoring location in a highly urbanized, mixed use watershed. Sediment is readily available and there is safe access to the sampling site through locked gate. Monitoring was conducted during 2004-05 and prior.

**Alameda: Castro Valley Creek** at ACCWP Site "S3", by footbridge off N. 3<sup>rd</sup> St. behind Hayward senior center, at USGS gauging station – urban creek with automated monitoring equipment in a highly urbanized, mixed use watershed. Monitoring was conducted during 2004-05 and prior. Rocky substrate with limited sediment.

**Santa Clara: Calabazas Creek** at Lakeside Dr. in Sunnyvale (on border with Santa Clara) – urban creek in a highly urbanized, mixed use watershed. Monitoring was

conducted during 2004-05 and prior. Concrete channel with limited sediment. Locked gate with ramp into channel.

**Santa Clara/San Mateo: San Francisquito Creek** at Newell Rd. in Palo Alto – urban land uses in lower watershed, large areas of open in upper watershed. Overall, 36% of the watershed is in urban land uses. Watershed has a multi-station, automated monitoring network in place, historical data, and ongoing local funding and staffing for monitoring. The network includes sites above and below the principal urban area (City of Palo Alto), which allow for upstream/downstream comparisons. This creek is included in the long term network to provide for comparisons with the more highly urbanized sites, given its other advantages.

**San Mateo: Laurel Creek** at Laurie Meadows Park, off Casanova Dr. – urban creek in a highly urbanized, mixed use watershed. Easy access to channel with plenty of sediment.

**San Francisco/Napa/Sonoma Counties:** This list does not include a selected creek for each Bay Area county. An appropriate creek could not be identified in San Francisco, Sonoma or Napa Counties.

For the North Bay counties of Napa and Sonoma, Napa and Sonoma Creeks appear to be the best candidates in terms of urban exposure, but neither meets the 50% urban land use criterion. Napa and Sonoma Creeks run through the cities of Napa and Sonoma, respectively, but their watersheds also include significant areas of open space and agricultural land use. These counties have relatively lower percentages of urban land uses, and neither Napa nor Sonoma were Phase 1 stormwater communities.

These creeks could be included to provide information on inputs to the Bay from mixed agricultural and urban land uses, and provide information on the extent to which agricultural uses contribute to pesticide and/or toxicity levels in urban creeks. Data from such sites also may be useful in development and implementation of the upcoming WQAS for diazinon and pesticide-related toxicity in the Bay.

**Summary of Selected Creeks:** The results of the assessment of candidate creeks are summarized in Table 2. Photos of the selected sites are shown in Attachment A. Notes regarding Table 2:

- Summary includes only recommended creeks and alternates; creeks not meeting the criteria are not included
- The table does not represent an exhaustive list of potentially-acceptable creeks; alternates are only listed for counties where some question exists with respect to the recommended creek due to little or no prior sampling experience

None of the selected creeks have upstream dams or other flood control structures except San Francisquito Creek, which has Searsville Dam and other flood control structures upstream of the larger urban areas. All sampling sites are above the tidal zone. All selected creeks except Laurel Creek have some prior data.

#### Page 6

#### Table 1. Land Use Information for Recommended Creeks and Alternates

			Land Uses As Percentage of Watershed Area							
Creek	County	Area (acres)	Comm'l.	Indust.	Resid.	As Percen	Public, Parks, Schools, Golf Courses	Transp.	a Sum: Urban Land Uses	Agric.
Corte Madera	Marin	16117	2.8%	0.1%	35.8%		8.2%		46.9%	
Blue Rock Springs	Solano		1.4%		47.3%		26.3%		75.0%	0%
Rheem	Contra Costa	1790		7.0%	42.0%	30.0%			79.0%	0%
Castro Valley	Alameda	3489	6.4%		74.3%			2.0%	82.7%	0%
Calabazas	Santa Clara	13400	8.8%	14.1%	54.5%		6.1%	1.7%	85.2%	0.3%
San Francisquito Laurel *	San Mateo/ Santa Clara San Mateo	27400 2950	1.8% 6.2%	0.1%	29.6% 41.9%		4.1% 3.1%	0.8%	36.4% 52.5%	1.8% 0%
Alternates:										
Adobe Mills *	Santa Clara San Mateo	7260 784	5.7% 1.4%	2.0% 2.8%	46.5% 46.8%		4.0% 4.5%	0.9% 2.2%	59.1% 57.7%	0.3% 0%

\* Land Use percentages shown are impervious acreages as percent of watershed area; actual land use area percentages are higher.

Sources of Land Use Information:

Corte Madera	Lewis, 2005
Blue Rock Springs	Betourne, 2005
Rheem	Dovzak & Sommers, 2004
Castro Valley	WCC, 1996
Calabazas	WMI, 2003
San Francisquito	WMI, 2003
Laurel *	EOA, 2002
Adobe	WMI, 2003
Mills *	EOA, 2002

#### % Urban Land % Agri. Land Use Dam/ Safe Auto. County Acres Uses Use Types \*\* Other? Access? Parking? Equip.? Sediment Creek Corte Madera Marin 16117 47% C, I, R Υ Υ Plenty Unk. Ν Ν Υ **Blue Rock Springs** Solano Ν Υ Plenty Unk. 75% 0% C, R Ν I, R Rheem Contra Costa 1790 79% 0% Ν Υ Υ Ν Plenty Castro Valley Alameda 3489 83% 0% C, R Ν Υ Υ Υ Some C, I, R Ν Calabazas Santa Clara 13400 85% 0.3% Υ Υ Little Ν San Mateo/ Santa Clara 27400 C, I, R San Francisquito 36% 1.8% Υ Υ Υ Υ Plenty San Mateo 2950 53% 0% C, R Ν Υ Υ Ν Plenty Laurel \* Alternates: Santa Clara Adobe 7260 C, I, R Ν Υ Little 59% 0.3% Υ Ν Mills \* San Mateo 784 C, I, R Ν Υ Υ Ν Plenty 58% 0%

#### Table 2. Summary of Site Characteristics for Recommended Creeks and Alternates

\* Land Use percentages shown are impervious acreages as percent of watershed area; actual land use area percentages are higher.

\*\* C = Commercial

I = Industrial

R = Residential

# **References Cited**

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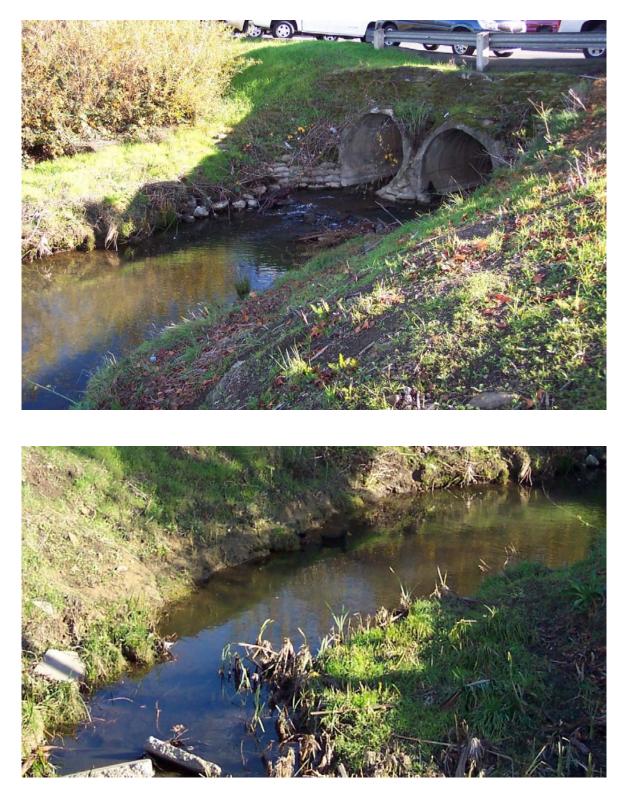
\* Available at: <u>http://www.up3project.org/norcal\_ipm\_documents.shtml</u>

ATTACHMENT A

Photos of Selected Long Term Urban Creek Monitoring Sites



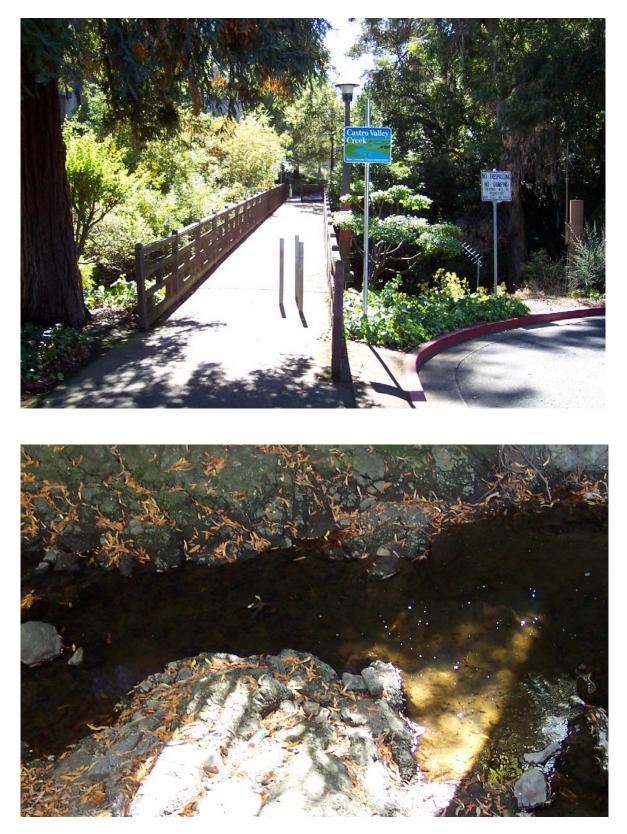
Corte Madera Creek, Ross (Marin County)



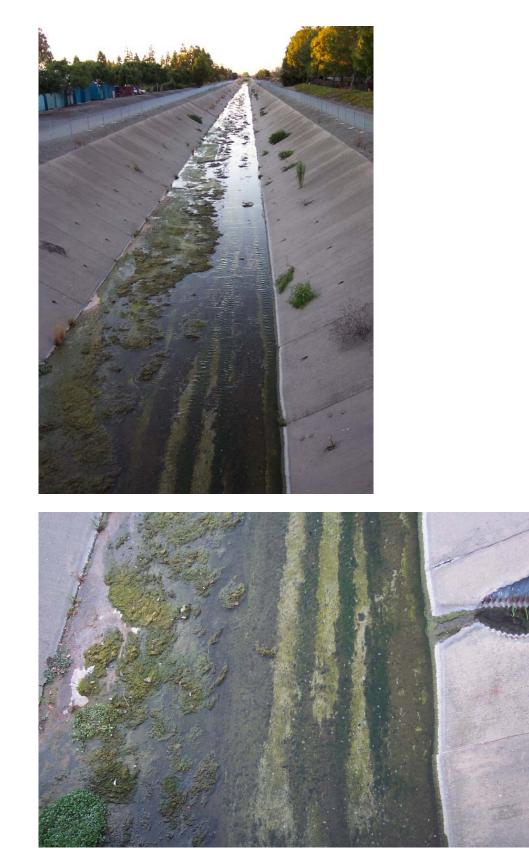
Blue Rock Springs Creek, Vallejo (Solano County)



Rheem Creek, Richmond (Contra Costa County)



Castro Valley Creek, Hayward (Alameda County)



Calabazas Creek, Sunnyvale/Santa Clara (Santa Clara County)





San Francisquito Creek, Palo Alto (Santa Clara/San Mateo Counties)



Laurel Creek, San Mateo (San Mateo County)

## APPENDIX D

MEMORANDUM RE: INCORPORATION OF PREVENTATIVE/PRE-EMPTIVE MONITORING MEASURES

Memo to:	CEP Diazinon/Toxicity Work Group;		
	CEP Technical Committee		
From:	Armand Ruby, Diazinon/Toxicity Work Group Coordinator		
Date:	Aug. 31, 2005; Revised Sept. 8, 2005, Sept. 29, 2005		
Subject:	Inclusion of Preventative/Pre-emptive Monitoring Measures		
	in 2005-06 Urban Creeks Monitoring Plan		

#### Introduction

The Diazinon/Toxicity Work Group of the Clean Estuary Partnership's Technical Committee has been working to support development and implementation of the *Diazinon and Pesticide-Related Toxicity in Urban Creeks Water Quality Attainment Strategy and Total Maximum Daily Load* (the WQAS). The Work Group produced a *CEP Urban Creeks Monitoring Plan* for 2004-05 to guide related monitoring by local agencies, with funding from the CEP for chemical analysis and toxicity testing. The Work Group is in the process of revising and updating that monitoring plan for 2005-06. This memo reflects the Work Group's deliberations as to whether alternative monitoring measures could provide "early-warning" indications of potential violations of the proposed TMDL targets and monitoring benchmarks in urban creeks, whether such monitoring would be cost-effective and logistically advantageous, and how such monitoring would be useful in addressing the proposed WQAS management questions and the proposed WQAS monitoring requirements. The memo describes activities that will be included in the revised *CEP Urban Creeks Monitoring Plan* to address the need for preventative/pre-emptive monitoring.

#### The Issue

There is a need to identify and address emerging threats to water quality in urbanized areas before impacts occur in local receiving waters, including urban creeks, rivers, and embayments. Most monitoring of such waters is of the integrated watershed type, reflecting conditions in the water body at a downstream location – and as such is geared towards identifying impacts that already exist. Such monitoring provides valuable information to regulators and stormwater program managers regarding receiving water health and the existence of water quality impairments, but it also places those managers and regulators in a reactive mode, responding to impacts that are already in progress. Alternative monitoring methods are needed to provide information that will allow managers to adaptively address pollutant sources before they impact beneficial uses. Inclusion of preventative/pre-emptive measures in the planned monitoring of urban creeks can assist in the conversion of urban creeks management from reactive mode to adaptive management mode.

Such measures as interpretation of DPR pesticide sales data, market surveys, and upstream monitoring in urban creek systems may be used to identify potential impacts to creek water quality from pesticides before impacts are apparent via traditional, downstream, water quality monitoring. The real difficulty lies in developing "leading" indicators that are truly useful in identifying water quality impacts *before they occur* (as opposed to identifying impacts before they are readily apparent). In-stream water quality monitoring inherently produces "lagging" indicators, demonstrating impacts that are already in progress. This memo discusses proactive management actions that can be taken to help prevent water quality impacts, as well as actions that can be taken to reduce the severity of in-stream impacts from identified pollutant sources.

## WQAS Monitoring/Management Questions

The proposed WQAS contains the following monitoring/management questions:

- Is the diazinon concentration TMDL target being met?
- Are the toxicity monitoring benchmarks being met?
- Is any toxicity observed in urban creeks caused by a pesticide (or something else)?
- Is urban runoff the source of any observed toxicity in urban creeks?
- How does any observed pesticide-related toxicity in urban creeks (or pesticide concentrations contributing to such toxicity) vary in time and magnitude across urban creek watersheds, and what types of pest control practices contribute to such toxicity?
- Are actions already being taken to reduce pesticide discharges sufficient to meet the targets/benchmarks, and if not, what should be done differently?

The CEP 2004-05 Urban Creeks Monitoring Plan lays out a stepwise process for addressing these questions; this process has continued during 2005 as a topic of the Diazinon/Toxicity Work Group. The principal purpose for inclusion of preventative/preemptive monitoring measures would be to provide early warning of potential water quality impacts to urban creeks, so that appropriate management actions could be taken before new impacts occur.

## Work Group Deliberations Re: Preventative/Pre-emptive Monitoring

The Work Group concurred that pesticide use data can be useful in gauging potential water quality impacts. The primary source of such information is the pesticide sales and use data available from the California Department of Pesticide Regulation. Other relevant information sources include local pesticide retail shelf surveys, manufacturers' product line information, pesticide use surveys conducted by universities and government agencies, and information available from professional staff at regulatory agencies and in academia. The major limitations to the use of such information in a preventative or preemptive way are the timing and resolution of the data. That is, there is a substantial time lag between pesticide application and the official availability of pesticide use data (greater than one year, typically), and the finest spatial resolution for DPR use data is the county level, limiting its predictive usefulness on a local watershed scale. Nonetheless, pesticide use information, in conjunction with an analysis of the characteristics of specific chemicals and their environmental effects, has proven to be a valuable complement to water quality monitoring in identifying threats to water quality.

In the near term, much of the relevant pesticide use information and associated analysis is supplied by the Urban Pesticide Pollution Prevention (UP3) Project, in particular through the *Annual Research and Monitoring Update* and the *Urban Pesticides Use Trends Annual Report*. The former report provides a synthesis of the available scientific findings

on pesticides and water quality effects relevant to urban surface waters. The latter report includes information on pesticide application techniques and use patterns. These reports will be available annually through the UP3 project for two more years (through 2007). This set of steps is considered to be cost-effective, logistically-advantageous, and useful in addressing the proposed WQAS monitoring/management questions. The analysis is also a highly valuable complement to ongoing creek water/sediment quality monitoring. However, given that the pesticide use information is generally assessed after the pesticides are already in use, impacts may be occurring before the analysis of potential impacts is available.

Advance warning of potential pesticide impacts could potentially be gained from information regarding what pesticides the professional pest control operators are *planning to use*, and what products retail stores are *planning to stock*. This information, together with information on chemical characteristics and likely application patterns, would provide material that could be used to derive a true leading indicator of potential water quality impacts. Pesticide manufacturers, distributors, sales people, and pest control advisors would be potential sources of such information. Of course this is likely to be difficult to achieve, as the information may be difficult to obtain, and would require a significant degree of informed analysis to predict water quality impacts.

Another potential leading indicator could be derived from evaluations of the potential effects of significant regulatory actions. The obvious contemporary example of this is the EPA phase-out of allowable uses of diazinon and chlorpyrifos, analysis of which lead to the predicted impacts of pyrethroid pesticides – impacts that are now being observed in urban and agricultural streams. As all significant federal and state regulatory actions are subject to public review in advance of implementation, this affords an opportunity for predictive analysis. Again, the analysis would need to incorporate relevant information on chemical characteristics and expected uses.

PCOs are required to notify county agricultural commissioners of pesticide use monthly. This information is in turn reported to DPR, and then made available to the public. Because there is a delay of up to two years in public availability of this information, the Work Group explored ways by which local or regional authorities could acquire the information in a more timely manner. Setting up a means of direct reporting of pesticide uses to local stormwater agencies was deemed to be duplicative, and would represent an unwelcome additional administrative burden to PCOs and local agencies. However, local and regional agencies can request access to the information directly through the offices of the county ag commissioners, on an as-needed basis. Interpretation of the pesticide use information vis-à-vis potential water quality impacts would require access to knowledge regarding pesticide characteristics and environmental effects commensurate with that provided through the UP3 project reports, however.

The Work Group also discussed the possibility of sampling urban runoff at upstream locations in urban watersheds, such as street gutters or at pipe discharges to creeks. This may be considered also as a potential leading indicator of water quality impacts. However, in typical urban drainages, once pesticides are in the gutter, they are generally

bound to end up in the creek in short order. Such monitoring is most useful as a means of identifying or tracking sources. Higher pesticide concentrations may in some cases occur at such upstream locations, perhaps permitting detection of pesticides that are not at detectable levels downstream. ACCWP did such sampling in the 1990s and successfully tracked diazinon upstream. However, the target pesticide (diazinon) was known, and the ACCWP analysis was performed using the ELISA test, which permits cost-effective, chemical-specific analysis at very low detection limits. ELISA tests are not available for all pollutants of concern, such as pyrethroids, but such methods are under development for some pesticides. Local and regional agency personnel can contact manufacturers and encourage them to develop tests for pesticides considered to be at high risk for water quality impacts (this information can be derived from the UP3 reports). For pyrethroids, development of commercially-available, low-level methods is also necessary for testing of sediments.

The Work Group considers sediment testing to be an important tool in the assessment of emerging threats to water quality from pesticides. The importance of sediment testing is demonstrated in the recent discovery by UC Berkeley researchers of toxicity in Bay Area urban creek sediments, attributable largely to pyrethroid pesticides.

Preferably, runoff testing and analysis would be performed by manufacturers before any pesticide is registered for use, and the USEPA would base the analysis of impacts on such studies. Ideally, through a thorough consideration of potential water quality impacts during the pesticide registration process, many potential water quality impacts would be identified and prevented. As it is, the urban environment acts as a real-world laboratory for assessment of the water quality impacts of pesticides that have been approved and registered for legal uses.

Improved coordination by the Water Board with DPR regarding observations of water quality impacts, and follow-up action by DPR through the pesticide reevaluation/review process is also essential. However, DPR is likely to take action to modify allowable pesticide uses only when clear evidence of water quality impacts has been provided. Again, this type of action serves to reduce impacts once they are already known and documented.

#### Recommended Preventative/Pre-emptive Elements of the 2005-06 Urban Creeks Monitoring Plan

The following elements are proposed for inclusion in the 2005-06 CEP Urban Creeks Monitoring Plan:

 Continue to track and analyze DPR pesticide use and sales data, and analyze potential water quality impacts based on evaluations of the available scientific information. Conduct retail store shelf surveys and assess other relevant information sources to supplement the DPR data. See Attachment A for details. (For the next two years these functions are effectively covered through the UP3 Project. Development of a means for continuing this work following expiration of the UP3 Project grant is essential.)

- 2. Evaluate the potential effects on water quality of significant proposed regulatory measures affecting pesticide uses, in light of the available scientific information, using a process similar to that outlined in Attachment A.
- 3. When timely information is needed regarding professional pesticide applications on the local or regional level, agency staff may request the latest available pesticide use reports from PCOs through the offices of county agricultural commissioners. Potential impacts to local and/or regional water quality may be assessed through evaluation of the current pesticide use information, in light of the available scientific information, using a process similar to that outlined in Attachment A.
- 4. Identify high-priority pesticides through the assessments recommended above, and plan to conduct some reconnaissance-level monitoring at selected upstream locations in urban watersheds for those pesticides.
- 5. Use ELISA techniques for monitoring of targeted pesticides when available. Contact ELISA test manufacturers to encourage development of needed tests – for water and sediment samples as appropriate – based on information on potential threats to water quality provided by analysis of pesticide use data and regulatory imperatives (per items #1 and #2 above).
- 6. Apply pressure on USEPA to perform adequate water quality impacts assessments as part of the routine pesticide registration process. Encourage USEPA to require pesticide manufacturers to conduct runoff quality studies to evaluate the potential effects.
- 7. Enhance cooperation and coordination between the Water Board and DPR to reevaluate allowable pesticide uses and take appropriate action to restrict uses based on available evidence of water quality impacts.

## ATTACHMENT A

The following describes a process of identifying pesticides that may impact creek water quality through an evaluation of the available scientific information, coupled with an analysis of the available information on pesticide uses.<sup>1</sup> The process is illustrated in a schematic that follows the text (courtesy of Kelly Moran, TDC Environmental).

#### **Evaluate Scientific Information**

Prepare an annual update of scientific information on pesticides and urban surface water quality. Relevant tasks include:

- Track government (especially DPR, U.S. EPA, and USGS), university, and private scientific investigations and water quality monitoring programs, including interagency science programs like the San Francisco Bay Area Clean Estuary Partnership and CalFed and PRISM and other grant-funded projects. Monitor U.S. EPA risk assessments for urban pesticides.
- Identify California 303(d) listings, incidents of pesticide-related POTW discharge toxicity attributable to pesticides, and other relevant water quality agency decisions about adverse effects of pesticides in surface waters.
- Conduct an annual pesticide/water quality literature review.
- Summarize major findings and interpret information such that it is immediately usable for adaptive management of urban pesticide-related water quality problems.

### Assess Pesticide Use Information

Prepare an annual urban pesticide market report. The report should have two sections: (1) pesticide use estimates and (2) an assessment of leading indicators for current and future pesticide use. The following tasks should be included:

- Using DPR pesticide use reporting and sales data, estimate Bay Area pesticide use for pesticides that may impact water quality.
- Assess urban pesticide sales and use trends; evaluate water quality implications.
- Complete an annual shelf survey of major pesticide retailers.
- Consult with county agriculture commissioners regarding current trends in reported pesticide use.
- Identify active ingredients in retail and professional products in the marketplace (use Internet site and other sources).
- Track pesticide regulatory developments; assess potential impacts of significant regulatory actions on urban pesticide uses.
- Consider other types of surveys and leading indicators to identify trends in pesticide use by professional applicators.

### Develop "Watch" List

Prepare an annotated list of pesticides of concern pertinent to water quality. Evaluate data from the scientific and pesticide use reports, using a weight-of-evidence approach to identify those pesticides of greatest concern for urban surface water quality.

<sup>&</sup>lt;sup>1</sup> Modified from the UP3 Project scope of work.

