

SUMMARY OF AQUATIC LIFE TOXICITY STUDIES IN UPPER NEWPORT BAY TRIBUTARIES, ORANGE COUNTY, CALIFORNIA DURING 1996/98¹

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During the fall of 1996, the Evaluation Monitoring Demonstration Project (Lee and Taylor, 1997a; Silverado, 1997a) found that stormwater runoff in San Diego Creek at Campus Drive as it enters Upper Newport Bay Orange County, California was toxic to *Ceriodaphnia*. The stormwater runoff contained sufficient concentrations of diazinon and chlorpyrifos (organophosphate pesticides – OP pesticides), as well as some unidentified toxic constituents, to be highly toxic to *Ceriodaphnia* during stormwater runoff events. A dry weather flow sample which was taken of San Diego Creek between the two stormwater runoff events sampled was found to be non-toxic. This report summarizes the results of the aquatic life toxicity studies conducted from October, 1996 through August, 1998 on San Diego Creek and its tributaries. These studies were conducted to confirm aquatic life toxicity in tributaries to Upper Newport Bay and to begin to assess the water quality significance of this toxicity to the beneficial uses of Upper Newport Bay and its tributaries. This report is a condensation of a 210-page comprehensive report (Lee *et al.*, 1999) devoted to these studies. The complete toxicity, chemical analysis, and hydrologic and other background information is presented by Lee *et al.* (1999).

Background

Lee and Taylor (1997b) and Lee *et al.* (1999) have presented a comprehensive review of the information available on Upper Newport Bay water quality. Upper Newport Bay is experiencing a number of significant designated beneficial use impairments. These include excessive fertilization-algal growth, degraded sanitary quality that impairs contact recreation and shellfish harvesting, excessive litter, excessive bioaccumulation of hazardous chemicals, and excessive sediment accumulation. Constituents responsible for the use impairments include: the aquatic plant nutrient nitrogen, sanitary quality indicator organisms-fecal coliforms, sediments (that result in significant sediment accumulation), and hazardous chemicals (such as chlorinated hydrocarbon pesticides and PCBs already present in the Bay and being contributed to the Bay). It also appears that there is sufficient heavy metal input to parts of Lower Newport Bay to cause significantly elevated concentrations of heavy metals in some Bay sediments. Further, the Lower Bay sediments have been found to be toxic to some forms of aquatic life.

¹Reference as Lee, G.F., Jones-Lee, A., Taylor, S., and Neiter, D., "Summary of Aquatic Life Toxicity Studies in Upper Newport Bay Tributaries, Orange County, California During 1996/98," Report of G. Fred Lee & Associates, El Macero, CA, February (1999).

An area of concern for which there is limited information at this time is the input and impacts of potentially toxic chemical constituents such as heavy metals, pesticides, and other organics on the beneficial uses of Upper Newport Bay. Bailey *et al.* (1993) conducted toxicity tests on San Diego Creek and several other tributaries to Upper Newport Bay. They found that San Diego Creek, just above where it enters Upper Newport Bay and upstream of that point, as well as the Santa Ana-Delhi Channel, showed no significant toxicity compared to the controls for fathead minnow larvae. However, the tests conducted with *Ceriodaphnia* (a freshwater zooplankton) for San Diego Creek (Campus Drive and Culver Drive) and the Santa Ana-Delhi Channel waters caused complete mortality of the test organism. The testing with the alga *Selenastrum* showed no inhibition of algal growth. In general, it can be concluded that in late 1992-early 1993, there were toxicants to *Ceriodaphnia* in stormwater runoff in several of the major tributaries of Upper Newport Bay. Bailey *et al.* (1993) did not identify the cause of this toxicity.

Beginning in the fall of 1996, an Evaluation Monitoring Demonstration Project was initiated to specifically assess whether constituents were present in runoff waters which are toxic to aquatic life. The samples taken in the fall of 1996 from San Diego Creek at Campus Drive, just above where the Creek discharges to Upper Newport Bay, were found to be highly toxic (about ten acute toxicity units, TUa) to *Ceriodaphnia* and non-toxic to fathead minnow larvae and the alga *Selenastrum*. These results confirmed the work of Bailey, *et al.* (1993) and identified the cause of about half of the toxicity in the stormwater runoff as it enters Upper Newport Bay as being likely due to the organophosphate pesticides, diazinon and chlorpyrifos. The other half of this toxicity was due to unidentified causes.

Sample Collection and Analysis Procedures

The samples were collected in bottles furnished by the University of California Davis (UCD) Aquatic Toxicology Laboratory (Davis, CA), Pacific Eco-Risk Laboratory (Martinez, CA), and AQUA-Science (Davis, CA) (Neiter and Lee, 1998). At each site, samples for toxicity testing were collected early in the stormwater runoff event. For those situations where multiple samples were taken for chemical analyses for diazinon and chlorpyrifos during the runoff event, the samples were collected in small vials (with a volume of approximately 40 ml). Samples were packed with blue ice in a cooler and shipped overnight for next morning delivery to the toxicity testing laboratories. Upon receipt at UCD the samples were stored in the dark under refrigeration at 4°C. According to L. Deanovic, the UCD Aquatic Toxicology Lab (personal communication, 1997) has found that diazinon and chlorpyrifos samples can be stored for several weeks under these conditions without significant loss of toxicity.

The samples were analyzed by the laboratory using the US EPA standard toxicity testing procedures described in the Quality Assurance Project Plan (QAPP) (Neiter and Lee, 1998). For freshwater samples, the procedures described by Lewis *et al.* (1994) were used in which the fathead minnow larvae *Pimephales promelas*, the zooplankton *Ceriodaphnia dubia* and the alga *Selenastrum capricornutum* were used. For testing the potential toxicity to marine zooplankton, the salinity of the samples was increased to 20 ppt using Forty Fathoms® – bioassay grade and testing was done with *Mysidopsis bahia*. The mysid toxicity testing was done in accord with US EPA (1994) procedures. Mortality rates were examined for all but *Selenastrum capricornutum*, where growth rates were examined. In order to determine whether the toxicity found was likely due to an

organophosphate pesticide, piperonyl butoxide (PBO) was added to some of the duplicate tests. PBO interacts with organophosphate pesticides such as diazinon and chlorpyrifos to eliminate and/or reduce their toxicity (Bailey *et al.*, 1996). Unless otherwise noted, 100 µg/L (ppb) of PBO were added to the test treatment where PBO was added.

The concentrations of diazinon and chlorpyrifos in the samples tested were evaluated using the ELISA (enzyme linked immuno sorbent assay) procedure which has a detection limit for diazinon of about 30 ng/L and for chlorpyrifos of about 50 ng/L. The ELISA procedure is highly specific for the chemicals tested. Its use combined with the use of PBO is part of a toxicity investigation evaluation (TIE) for assessing whether the toxicity in a sample is likely due to an OP pesticide and in particular, diazinon or chlorpyrifos. An estimate of the total toxic units found was made by conducting toxicity tests using dilutions of the test sample using Sierra Spring EPA moderately hard control water (SSEPAMH) (Lewis, *et al.* 1994).

Based on the experience of L. Deanovic (personal communication, 1998) of the University of California, Davis Aquatic Toxicology Lab, 425 ng/L of diazinon and 80 ng/L of chlorpyrifos represent about one acute toxic unit (TUa) each. The toxicities of these two OP pesticides has been found to be additive. Based on the ELISA-measured diazinon and chlorpyrifos concentrations and the dilution series measured toxicity, with and without PBO addition, it is possible to assess the amount of toxicity present in a sample that is not due to OP pesticides and/or diazinon and chlorpyrifos.

Characteristics of The Upper Newport Bay Watershed

The primary tributary of Upper Newport Bay is San Diego Creek. The San Diego Creek watershed is bounded on the north by the Santiago Hills (Loma Ridge) and to the south by the San Joaquin Hills. The major portion of the basin is comprised of the Tustin Plain, a broad alluvial valley occupying the central portion of the watershed. The watershed has been greatly altered due to residential and commercial development. Most of the existing drainage channel features were constructed in the early part of this century to accommodate farming. During the 1960s, easements for many of the principal streams were granted to the Orange County Flood Control District, and interim improvements were made to many of the channels.

The Newport Bay watershed includes an area of about 154 square miles. The San Diego Creek watershed contains about 119 square miles with a mix of residential (15%), commercial (8%), industrial (6%), recreational and open space (23%), agricultural (23%), and transportation/communication/roads (36%). Other major tributaries of Upper Newport Bay include the Santa Ana Delhi Channel with a watershed of about 17 square miles, Big Canyon Wash with a watershed of about 2 square miles, and 16 square miles from other smaller tributaries. The Santa Ana Delhi Channel watershed includes commercial (17%), industrial (8%), recreational (1%), and residential (33%) land uses, with roads (30%) and residential land uses predominant. The Big Canyon Wash watershed is comprised of commercial, recreational, open space, and residential land uses, with residential uses predominant. The remaining area is comprised of commercial and residential uses.

The San Diego Creek portion of the Upper Newport Bay watershed (119 square miles) encompasses elevations that range from a high in the Santiago Hills of 1,775 feet to sea level at Upper Newport Bay. A large portion of the Tustin Plain generally has slopes of less than 1 percent, with steeper slopes occurring near the foothills. Existing land uses in the watershed include agricultural,

open space, residential, commercial, industrial, and recreational. In general, the foothill areas remain as open space, with development generally occurring in the Tustin Plain along the western and eastern watershed boundaries and to the south. The central portion of the watershed retains the most agriculture, although this area is undergoing urbanization at a rapid pace.

Currently, it is estimated that less than 40 percent of the developed Upper Newport Bay watershed is impervious surface. The developed area represents about 50 percent of the total watershed area. Tetterer and Associates (1989) indicated that Orange County has estimated that the ultimate impervious surface in the watershed will be about 60 percent. Urbanization and improvement of the drainage channel system have decreased the watershed runoff lag time, increased the peak discharge as compared to pre-development conditions, and enhanced the ability of the watershed and San Diego Creek to transport chemical constituents and sediment to Upper Newport Bay.

Physical and Hydrologic Characteristics of Newport Bay

Lower Newport Bay extends westward about three miles behind the Balboa Peninsula to Newport Boulevard. The Coast Highway divides the Bay into upper and lower basins. The lower basin is heavily urbanized with numerous islands developed for residential use. The upper basin (about 1,000 acres) remains largely undeveloped within the nominal Bay boundaries with the exception of about the lower one-third, which contains boat docks and other commercial facilities. The remaining area (752 acres) is operated as a State Ecological Reserve by the California Department of Fish and Game.

The Upper Bay is characterized by a semidiurnal tidal pattern of two unequal highs and lows occurring each day. The maximum tidal range is about 9 feet (+7.2 ft MLLW to -1.8 ft MLLW), with little difference in absolute magnitude between the upper and lower Bays. Mudflats comprise the lower portion of the littoral zone below about 3.0 MLLW and are subject to daily inundation. Salt marsh occupies the mid and upper littoral zones up to the extreme high water (EHW) elevation. The salinity in the Upper Bay in 1959 was close to seawater (Gerstenberg, undated). The Bay is becoming progressively more estuarine in character as freshwater inputs to the Bay increase.

Summary of Toxicity Testing Results

The 1996 (Silverado, 1997a and Lee and Taylor, 1997a) monitoring of Upper Newport Bay stormwater runoff from San Diego Creek showed that the Creek waters contain constituents which are highly toxic to some zooplankton, such as *Ceriodaphnia*. During 1996-98, nine stormwater runoff events were monitored. Table 1 presents a summary of the *Ceriodaphnia* toxicity results that have been found in the Upper Newport Bay watershed since the initiation of the Evaluation Monitoring Demonstration Project in the summer of 1996.

Toxicity to *Ceriodaphnia*. Examination of this table shows that, with few exceptions, the undiluted sample of San Diego Creek water during a stormwater runoff event, obtained at Campus Drive just before where the Creek enters Upper Newport Bay killed all *Ceriodaphnia* in the test system within one day. Table 1 also presents a summary of the dilution series tests that were run on some of the samples, as well as an estimate of the total toxicity found in the sample in the "Measured TUa" column. Many of the samples of San Diego Creek taken at Campus Drive have at least three, and often greater than eight, acute toxic units (TUa) to *Ceriodaphnia*. This means that up to a ten-fold

Table 1
Summary of *Ceriodaphnia* Toxicity Test Results for
Upper Newport Bay Watershed Stormwater Runoff and Dry Weather Flow

Date	Location (Treatment)	Duration of Test (days)	% Mortality ^{1,2} (days to 100% kill)	Measured TUa	Ratio TUa(measured):TUa(expected)
10/30/96	San Diego Creek @ Campus	7	100 (1)	> 8	> 3
10/30/96	San Diego Creek @ Campus	1	100		
10/30/96	San Diego Creek @ Campus + PBO	1	100 (1)		
10/30/96	San Diego Creek @ Campus 100%	4	100 (1)		
10/30/96	San Diego Creek @ Campus 50%	4	100 (1)		
10/30/96	San Diego Creek @ Campus 50% + PBO	4	5		
10/30/96	San Diego Creek @ Campus 50% + 200 mg/L PBO	4	5		
10/30/96	San Diego Creek @ Campus 25%	4	100 (2)		
10/30/96	San Diego Creek @ Campus 25% + PBO	4	0		
10/30/96	San Diego Creek @ Campus 25% + 200 mg/L PBO	4	60		
10/30/96	San Diego Creek @ Campus 12.5%	4	5		
11/19/96	San Diego Creek @ Campus Base Flow	7	0	0	0
11/19/96	San Diego Creek @ Campus +PBO Base Flow	7	0		
11/21/96	San Diego Creek @ Campus	1	100 (1)	> 8	> 3
11/21/96	San Diego Creek @ Campus + PBO	1	100 (1)		
11/21/96	San Diego Creek @ Campus 100%	4	100 (1)		
11/21/96	San Diego Creek @ Campus 65%	4	100 (1)		
11/21/96	San Diego Creek @ Campus 65% + PBO	4	100 (1)		
11/21/96	San Diego Creek @ Campus 50%	4	100 (1)		

Table 1
Summary of *Ceriodaphnia* Toxicity Test Results for Upper Newport Bay Watershed
Stormwater Runoff (continued)

Date	Location (Treatment)	Duration of Test (days)	% Mortality ^{1,2} (days to 100%kill)	Measured TUa	Ratio TUa(measured):TUa(expected)
11/21/96	San Diego Creek @ Campus 25%	4	100 (1)		
11/21/96	San Diego Creek @ Campus 25% + PBO	4	100 (3)		
11/21/96	San Diego Creek @ Campus 12.5%	4	100 (2)		
9/25/97	San Diego Creek @ Campus 100%	7	100 (3)	> 2	> 1.3
9/25/97	San Diego Creek @ Campus 100% + PBO	7	0		
9/25/97	San Diego Creek @ Campus 50%	7	100 (7)		
11/13/97	San Diego Creek @ Campus	7	100 (1)	8	3
11/13/97	San Diego Creek @ Campus + PBO	7	100 (2)		
11/13/97	San Diego Creek @ Campus 100%	4	100 (1)		
11/13/97	San Diego Creek @ Campus 50%	4	100 (1)		
11/13/97	San Diego Creek @ Campus 50% + PBO	4	5		
11/13/97	San Diego Creek @ Campus 25%	4	95		
11/13/97	San Diego Creek @ Campus 25% + PBO	4	0		
11/13/97	San Diego Creek @ Campus 12.5%	4	5		
11/13/97	San Diego Creek @ Campus 6.25%	4	0		
11/30/97	San Diego Creek @ Campus	7	100 (1)	4	4
11/30/97	San Diego Creek @ Campus + PBO	7	100 (5)		
11/30/97	San Diego Creek @ Campus 100%	4	100 (2)		
11/30/97	San Diego Creek @ Campus 50%	4	100 (3)		

Table 1
Summary of *Ceriodaphnia* Toxicity Test Results for Upper Newport Bay Watershed
Stormwater Runoff (continued)

Date	Location (Treatment)	Duration of Test (days)	% Mortality ^{1,2} (days to 100%)	Measured TUa	Ratio TUa(measured):TUa(expected)
11/30/97	San Diego Creek @ Campus 50% + PBO	4	5		
11/30/97	San Diego Creek @ Campus 25%	4	5		
11/30/97	San Diego Creek @ Campus 25% + PBO	4	0		
11/30/97	San Diego Creek @ Campus 12.5%	4	0		
11/30/97	San Diego Creek @ Campus 6.25%	4	0		
12/6/97	San Diego Creek @ Campus	7	100 (2)		
12/6/97	San Diego Creek @ Campus + PBO	7	0		
3/24/98 (prestorm)	Santa Ana Delhi Channel Base Flow	7	0		
3/24/98	San Diego Creek @ Campus	7	0		
3/25/98	Peters Canyon Channel @ Barranca	7	100 (1)		
3/25/98	San Diego Creek @ Campus	7	100 (4)		
3/25/98	Santa Ana Delhi Channel	7	100 (4)		
3/25/98	Peters Canyon Channel @ Barranca 100%	4	100 (1)		
3/25/98	Peters Canyon Channel @ Barranca 100% + PBO	4	100 (2)		
3/25/98	Peters Canyon Channel @ Barranca 50%	4	100 (2)		
3/25/98	Peters Canyon Channel @ Barranca 50% + PBO	4	100 (2)		
3/25/98	Peters Canyon Channel @ Barranca 25%	4	100 (2)		
3/25/98	Peters Canyon Channel @ Barranca 25% + PBO	4	20		
3/25/98	Peters Canyon Channel @ Barranca 12.5%	4	90		

Table 1
Summary of *Ceriodaphnia* Toxicity Test Results for Upper Newport Bay Watershed
Stormwater Runoff (continued)

Date	Location (Treatment)	Duration of Test (days)	% Mortality ^{1,2} (days to 100%)	Measured TUa	Ratio TUa(measured):TUa(expected)
3/25/98	Peters Canyon Channel @ Barranca	4	100 (1)		
3/25/98	Peters Canyon Channel @ Barranca + PBO	4	100 (2)		
3/25/98	Peters Canyon Channel @ Barranca 50%	4	100 (2)		
3/25/98	Peters Canyon Channel @ Barranca 50% +50mg/L PBO	4	100 (3)		
3/25/98	Peters Canyon Channel @ Barranca 25%	4	100 (2)		
3/25/98	Peters Canyon Channel @ Barranca 25% +50mg/L PBO	4	5		
3/25/98	Peters Canyon Channel @ Barranca 12.5%	4	100 (3)		
3/25/98	Peters Canyon Channel @ Barranca 12.5% +50mg/L PBO	4	5		
3/25/98	Peters Canyon Channel @ Barranca 6.25%	4	15		
3/25/98	San Gabriel River @ San Gabriel River Pkwy., City of Pico Rivera	7	0		
3/25/98	Malibu Creek @ Piuma Rd., unincorporated area of Malibu	7	0 – impaired reproduction		
3/25/98	Ballona Creek @ Beloit St., Culver City	7	100 (5)		
3/25/98	Project 156 @ Concord St., City of Glendale	7	100 (6)		
3/25/98	LA River Wardlow @ Wardlow Rd., Long Beach	7	0		
3/25/98	Coyote Creek @ Spring St., City of Long Beach	7	100 (2)		

Table 1
Summary of *Ceriodaphnia* Toxicity Test Results for Upper Newport Bay Watershed
Stormwater Runoff (continued)

Date	Location (Treatment)	Duration of Test (days)	% Mortality ^{1,2} (days to 100%)	Measured TUa	Ratio TUa(measured):TUa(expected)
5/5/98	San Diego Creek @ Campus	4	100 (2)		
5/5/98	San Diego Creek @ Campus + PBO	4	0		
5/5/98	Santa Ana Delhi	4	0		
5/5/98	Santa Ana Delhi + PBO	4	0		
5/12/98	San Diego Creek @ Campus	7	100 (1)	7.9	> 8
5/12/98	San Diego Creek @ Campus + PBO	7	100 (1)	7.8	
5/13/98	Santa Ana Delhi Channel	7	0		
5/13/98	Santa Ana Delhi Channel + PBO	7	0		
5/13/98	San Diego Creek @ Campus	4	100 (1)		
5/13/98	San Diego Creek @ Campus + PBO	4	100 (1)		
5/13/98	San Diego Creek (50%) @ Campus	4	100 (1)		
5/13/98	San Diego Creek (25%) @ Campus	4	100 (1)		
5/13/98	San Diego Creek (25%) @ Campus +PBO	4	100 (3)		
5/13/98	San Diego Creek (12.5%) @ Campus	4	100 (2)		
5/13/98	San Diego Creek (6.25%) @ Campus	4	0		
8/13/98	San Diego Creek @Campus (diluted to 2000 mmhos/cm - 66% dilution)	7	0		
8/13/98	San Diego Creek @ Campus (diluted to 2000 mmhos/cm - 66% dilution) + PBO	7	0		
8/13/98	Peters Canyon Channel @ Barranca (diluted to 2000 mmhos/cm - 68% dilution)	7	100 (5)		

Table 1
Summary of *Ceriodaphnia* Toxicity Test Results for Upper Newport Bay Watershed
Stormwater Runoff (continued)

Date	Location (Treatment)	Duration of Test (days)	% Mortality ^{1,2} (days to 100%)	Measured TUa	Ratio TUa(measured):TUa(expected)
8/13/98	Peters Canyon Channel @ Barranca (diluted to 2000 mmhos/cm - 68% dilution) + PBO	7	0		
8/13/98	Hines Channel @ Irvine Creek Dr.	7	100 (1)	32	1.3
8/13/98	Hines Channel @ Irvine Creek Dr. + PBO	7	100 (1)		
8/13/98	Central Irvine Channel	7	100 (1)		
8/13/98	Central Irvine Channel + PBO	7	100 (2)		
8/13/98	Santa Ana Delhi Channel (diluted to 2000mmhos/cm - 74% dilution)	7	10 Impaired Reproduction		
8/13/98	Santa Ana Delhi Channel (diluted to 2000 mmhos/cm - 74% dilution) + PBO	7	0 Impaired Reproduction		
8/13/98	Hines Channel 6.25%	4	100 (1)		
8/13/98	Hines Channel 6.25% + PBO	4	5		
8/13/98	Hines Channel 3.13%	4	100 (4)		
8/13/98	Hines Channel 1.57%	4	0		
8/13/98	Hines Channel 1.57% + PBO	4	5		
8/13/98	Hines Channel 0.78%	4	0		
8/13/98	Hines Channel 0.39%	4	0		
8/13/98	Central Irvine Channel	4	100 (1)		
8/13/98	Central Irvine Channel 50%	4	100 (1)		
8/13/98	Central Irvine Channel 50% + PBO	4	0		
8/13/98	Central Irvine Channel 25%	4	100 (2)		
8/13/98	Central Irvine Channel 12.5%	4	35		
8/13/98	Central Irvine Channel 12.5% + PBO	4	0		

Table 1
Summary of *Ceriodaphnia* Toxicity Test Results for Upper Newport Bay Watershed
Stormwater Runoff (continued)

Date	Location (Treatment)	Duration of Test (days)	% Mortality ^{1,2} (days to 100%)	Measured TUa	Ratio TUa(measured):TUa(expected)
8/13/98	Central Irvine Channel 6.25%	4	20		
8/13/98	Central Irvine Channel 3.13%	4	5		
8/25/98	San Diego Creek @ Campus (diluted to 2000mmhos/cm - 69% dilution)	7	0		
8/25/98	San Diego Creek @ Campus (diluted to 2000mmhos/cm - 69% dilution) + PBO	7	0		
8/25/98	Santa Ana Delhi Channel (diluted to 2000mmhos/cm - 75% dilution)	7	0		
8/25/98	Santa Ana Delhi Channel (diluted to 2000mmhos/cm - 75% dilution) + PBO	7	20		
8/25/98	Hines Channel	7	100 (1)	8	1
8/25/98	Hines Channel + PBO	7	100 (1)		
8/25/98	Hines Channel 25%	4	100 (1)		
8/25/98	Hines Channel 25% + PBO	4	15		
8/25/98	Hines Channel 12.5%	4	50		
8/25/98	Hines Channel 6.25%	4	0		
8/25/98	Hines Channel 6.25% + PBO	4	5		
8/25/98	Hines Channel 3.13%	4	0		
8/25/98	Hines Channel 1.57%	4	0		

¹ 100% sample unless otherwise indicate

² Number in parenthesis indicates number of days to 100% mortality.

* 100µg/L PBO added unless noted otherwise

dilution of San Diego Creek water taken at Campus Drive during a stormwater event could be toxic to *Ceriodaphnia*.

Table 2 presents the results of toxicity testing that was done using *Mysidopsis bahia* as the test organism, where a standard sea salt mixture was added to San Diego Creek water to bring the salinity to 20 ppt. The toxicity results presented in Table 2 are from samples of San Diego Creek water taken at Campus Drive. The undiluted San Diego Creek sample was also toxic to *Mysidopsis*. This indicates that there is a potential for marine zooplankton to be killed by OP pesticides and possibly other pollutants when the San Diego Creek water mixes with the marine waters in Upper Newport Bay during a stormwater runoff event.

Table 2
Summary of *Mysidopsis bahia* Toxicity Results for
San Diego Creek Stormwater Runoff at Campus Drive

Date	Location (Treatment)	% Mortality 7 days	Measured TUa	Calc. TUa Based on Chlorpyrifos Concentrations	Ratio TUa (measured): TUa(expected)
11/30/97	San Diego Creek	88	8	2	4
11/30/97	San Diego Creek 100%	50			
11/30/97	San Diego Creek 50%	10			
11/30/97	San Diego Creek 12.5%	5			
11/30/97	San Diego Creek 6.25%	0			
12/6/97	San Diego Creek	62			
5/12/98	San Diego Creek 100%	100	>8	1.5	>5
5/12/98	San Diego Creek 50%	100			
5/12/98	San Diego Creek 25%	65			
5/12/98	San Diego Creek 12.5%	5			
5/12/98	San Diego Creek 6.25%	5			

The toxicity testing of San Diego Creek water at Campus Drive using *Ceriodaphnia* during dry weather flow conditions was found to be non-toxic, indicating that the toxicity was associated with land runoff from residential, commercial and/or rural areas. In general, with the exception of the samples taken on August 25, 1998, under dry weather flow conditions, no toxicity to fathead minnow larvae or algae has been found in San Diego Creek waters at Campus Drive.

In March 1998 toxicity was found to fathead minnow larvae in Santa Ana Delhi Channel water under low flow conditions, indicating the possibility of illegal or illicit discharges to this Channel. Also, fathead minnow larvae toxicity was found in Hines Channel at the Irvine Boulevard sampling station in the August 1998 samples. This sampling station is just downstream from two large commercial nurseries which may have discharges or fugitive waters containing toxic constituents entering the Channel.

The Table 1 data for *Ceriodaphnia* toxicity indicate that the addition of PBO to the San Diego Creek samples, especially those that have been diluted somewhat, reduced the amount of *Ceriodaphnia* toxicity. This is an indication that the toxicity found is due, at least in part, to OP pesticides.

Estimated Toxicity of Diazinon and Chlorpyrifos. Table 3 presents a summary of information on the respective toxicities (LC₅₀) of diazinon and chlorpyrifos to *Ceriodaphnia* and *Mysidopsis*. These values are used to estimate the toxicity of the samples based on the concentrations of diazinon and chlorpyrifos measured in the samples.

Table 3
Toxicity of Diazinon and Chlorpyrifos to *Ceriodaphnia* and *Mysidopsis*

Constituent	<i>Ceriodaphnia</i> LC ₅₀ (ng/L)	<i>Mysidopsis</i> LC ₅₀ (ng/L)
Diazinon	450	4,500
Chlorpyrifos	80	35

Diazinon and Chlorpyrifos Concentrations. Table 4 presents the results of the ELISA and GC analysis of the Upper Newport Bay watershed samples that have been collected in this study. The data in this table show that frequently the concentrations of diazinon and chlorpyrifos in San Diego Creek waters as they enter Upper Newport Bay that contain stormwater runoff are sufficient, individually and/or when mixed to be toxic to *Ceriodaphnia*.

Table 4 also presents the expected acute toxicity units (TUa) based on the sum of the diazinon and chlorpyrifos concentrations, divided by the LC₅₀ for the respective compounds. Examination of Table 4, calculated expected TUa values, shows that frequently the sum of the diazinon and chlorpyrifos concentrations should result in several acute toxic units for *Ceriodaphnia* in San Diego Creek water as it enters Upper Newport Bay.

Toxicity to *Mysidopsis*. The November 30, 1997 San Diego Creek Campus Drive sample contains sufficient chlorpyrifos to cause about two acute toxic units to *Mysidopsis*. A similar situation exists for the May 12, 1998 San Diego Creek Campus Drive sample, where there is an expected 1.5 TUa to *Mysidopsis* due to chlorpyrifos. The concentrations of diazinon found in this study at the San Diego Creek Campus Drive sampling point are not sufficient to be toxic to *Mysidopsis* (see Table 3). The data presented in Table 2 show that there is appreciable toxicity to *Mysidopsis* in the San Diego Creek water during a stormwater runoff event that cannot be potentially accounted for based on the chlorpyrifos concentrations measured in the sample that was tested for toxicity. The cause of this toxicity to *Mysidopsis* is, at this time, unknown. However, as discussed in subsequent sections, it appears that it may be due to toxic constituents discharged from one or more large commercial nurseries, and possibly agricultural tailwater, present in the headwaters of the San Diego Creek watershed.

First Flush Effects. During several of the stormwater runoff events that have been monitored during 1998, samples were taken at several times during the runoff to evaluate potential changes in diazinon and chlorpyrifos concentrations during the runoff event. The results of these analyses are presented in Table 4. They show that, in general, the grab samples of San Diego Creek water collected at Campus Drive taken during a runoff event are representative of what is found over the runoff event

Table 4
Summary of Diazinon and Chlorpyrifos Concentrations in
Upper Newport Bay Watershed

Date	Location (Time – hrs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)	Expected TUa
10/30/96	San Diego Creek @ Campus	370	157	3
11/19/96	San Diego Creek @ Campus Base Flow	164	ND	0.5
11/21/96	San Diego Creek @ Campus	359	133	2.5
9/25/97	San Diego Creek @ Campus	155	106	1.5
11/13/97	San Diego Creek @ Campus	462	161	3
11/30/97	San Diego Creek @ Campus	226 ¹	63 ¹	1
11/30/97	San Diego Creek @ Campus	278 ²	90 ²	2
12/06/97	Peters Canyon Channel @ Barranca (1040)	277	102	2
12/06/97	Peters Canyon Channel @ Barranca (1350)	426	94	2
12/06/97	Peters Canyon Channel @ Barranca (1715)	202	84	1.5
12/06/97	San Diego Creek @ Campus (1345)	257 ¹	57 ¹	1
12/06/97	San Diego Creek @ Campus (1345)	197 ²	<50 ²	1
12/06/97	San Diego Creek @ Campus (0910)	215	89	1.5
12/06/97	San Diego Creek @ Campus (1640)	195	82	1.5
12/06/97	Rain Water (0910)	13	23	0.3
3/24/98	Santa Ana Delhi Base Flow	140	ND	0.3
3/24/98	San Diego Creek @ Campus Base Flow	148	ND	0.3
3/25/98	San Diego Creek @ Campus (1140)	196	ND	0.4
3/25/98	San Diego Creek @ Campus (1730)	462	50	1.5
3/25/98	San Diego Creek @ Campus (2300)	294	ND	0.5
3/26/98	San Diego Creek @ Campus (0900)	250	ND	0.5
3/25/98	Peters Canyon Channel @ Barranca (1300)	367	ND	0.5
3/25/98	Peters Canyon Channel @ Barranca (1710)	288	ND	0.5
3/25/98	Peters Canyon Channel @ Barranca (2240)	378	ND	0.8
3/26/98	Peters Canyon Channel @ Barranca (0925)	266	ND	0.5
3/25/98	Santa Ana Delhi (1220)	202	ND	0.5
3/25/98	Santa Ana Delhi (1750)	192	ND	0.5

Table 4
Summary of Diazinon and Chlorpyrifos Concentrations in
Upper Newport Bay Watershed (continued)

Date	Location (Time – hrs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)	Expected TUa
3/25/98	Santa Ana Delhi (2215)	155	ND	0.3
3/26/98	Santa Ana Delhi (0830)	64	ND	0.1
3/25/98	Ballona Creek *	298	50	1.5
3/25/98	Project 156 *	375	ND	0.8
3/25/98	Coyote Creek *	586	102	2.5
5/5/98	Santa Ana Delhi	170	ND	0.5
5/5/98	San Diego Creek @ Campus	136	ND	0.3
5/13/98	Santa Ana Delhi (6:45)	96	41	0.7
5/13/98	Santa Ana Delhi (11:45)	203	36	0.9
5/13/98	Santa Ana Delhi (18:00)	104	55	0.9
5/13/98	San Diego Creek @ Campus (19:00)	375	65	1.5
5/13/98	San Diego Creek @ Campus (7:10)	375	57	1.5
5/13/98	San Diego Creek @ Campus (12:05)	371	57	1.5
5/13/98	San Diego Creek @ Campus (17:40)	253	58	1.3
8/13/98	San Diego Creek @ Campus ³ Base Flow	117	67	1.5
8/13/98	Peters Canyon Channel @ Barranca ³ Base Flow	470	57	2
8/13/98	Central Irvine Channel ³	840	281	5.5
8/13/98	Central Irvine Channel ²	620	260	4.5
8/13/98	Hines Channel ³	10,000	47	23
8/13/98	Hines Channel ²	12,000	67	28
8/13/98	Santa Ana Delhi ³	85	5	0.2
8/25/98	San Diego Creek @ Campus ²	492	11	1
8/25/98	Central Irvine Channel ³	620	260	4.5
8/25/98	Hines Channel ²	2,500	97	7
8/25/98	Hines Channel ³	2,500	110	7
8/25/98	Santa Ana Delhi ²	340	18	1

ND = Not Detected. Detection limits for ELISA analyses are 50 ng/L for chlorpyrifos and 30 ng/L for diazinon.

1. UCD
 2. Pacific Eco-Risk
 3. AQUA-Science
- * Los Angeles County, CA

(hydrograph). There was no observed first flush effect for the San Diego Creek samples taken at Campus Drive. This is to be expected based on the nature of the San Diego Creek watershed.

Estimates of Unknown-Caused Toxicity. Table 1 presents the ratio of the measured T_{Ua} based on toxicity testing using dilutions of the San Diego Creek sample to the expected toxicity based on using the LC₅₀ values for diazinon and chlorpyrifos, summed for additive toxicity. Examination of this column in Table 1 shows that in most of the samples where dilutions of the San Diego Creek water taken at the Campus Drive testing was done, that there is appreciable toxicity to *Ceriodaphnia* that cannot be accounted for based on the concentrations of diazinon and chlorpyrifos. These results are somewhat different than what is being found in stormwater runoff in the San Francisco Bay area, and in the Sacramento area, for urban stormwater runoff toxicity to *Ceriodaphnia*. In the San Francisco Bay and Sacramento areas, the diazinon and chlorpyrifos concentrations typically account for the measured *Ceriodaphnia* toxicity found. The principal difference between the Upper Newport Bay/San Diego Creek situation and that of the San Francisco Bay and Sacramento urban creeks, is that the San Diego Creek stormwater not only contains runoff from residential areas, but also contains runoff from agricultural areas, as well as several large commercial nurseries.

TIE Studies On Unknown-Caused Toxicity. In an effort to begin to address the nature and sources of the *Ceriodaphnia* toxicity being found at San Diego Creek Campus Drive sampling location that is due to unidentified causes, selective sampling was initiated in the spring of 1998 within the San Diego Creek watershed to try to identify the source of the known (OP pesticide) and unknown-caused toxicity. It was observed that the samples of stormwater runoff taken where Barranca Parkway crosses Peters Canyon Channel had higher concentrations of unknown-caused toxicity than were found in the San Diego Creek samples taken at Campus Drive. Peters Canyon Channel is one of the primary tributaries of San Diego Creek. This led to conducting additional TIE work on the Peters Canyon Channel Barranca Parkway samples. Dr. Jeff Miller, of AQUA-Science, Davis, CA, was provided samples of Peters Canyon Channel at Barranca Parkway stormwater runoff for the purpose of conducting more extensive TIEs to try to determine the cause of the unknown toxicity. This work has included fractionating the sample using various column chromatography techniques and subjecting the fractions to GC/MS analysis. A summary report of this work is included in Appendix B of Lee *et al.* (1999). Thus far the more comprehensive TIE investigations have not provided definitive results on the cause of the unknown *Ceriodaphnia* toxicity. It appears to be due to a number of chemicals which are not normally present in urban area stormwater runoff.

Pesticides Used in Orange County. In an effort to try to gain some guidance on what could be causing this unknown toxicity, the Orange County Agricultural Commissioner's office was contacted for information on pesticides used in the Peters Canyon Channel watershed. This information is provided in Table 5. A review of Table 5 shows that a wide variety of pesticides are used in the Upper Newport Bay watershed. Many of these contain active agents for which there is no information on their toxicity to *Ceriodaphnia* or *Mysidopsis*. Because of the extensive use of such a variety of pesticides, the information on their use provided by the Orange County Agricultural Commissioner is of limited assistance in helping to identify the potential cause of the unknown-caused toxicity found in Peters Canyon Channel at the Barranca Parkway sampling station.

Forensic Studies On Unknown-Caused Toxicity Sources. In an effort to define possible sources of the unknown caused toxicity, limited scope forensic studies were done in the Peters Canyon

Table 5
Agricultural Pesticides Used Within the San Diego Creek Watershed

Pesticide Trade Name	Active Chemical Ingredient(s)
Princep Caliber 90	Simazine
Roundup	Glyphosphate
Activator 90	No chemical information
Buffercide	No chemical information
Gramoxone Extra	Paraquat Dichloride
Silwet L-77	No chemical information
LI 700	No chemical information
Pyrellin E.C.	Pyrethrins, rotenone and other related
Neemix 4.5 Botanical Agri	Azadirachtin
Xentari Biological Insecticide	Bacillus thurgiensis (berliner), subst aizawai serotype H-7
Miller NU – Film – P	No chemical information
Tenn – Cop 5E	Copper salts of fatty and rosin acids
Javelin WG Biological Insecticide	Bacillus thuringiensis (berliner), subsp kurstaki, strain SA-11
Micro Flo Captec 4L	Captan, captan and other related
Stik	No chemical information
Drexel Captan 50W	Captan, captan and other related
Du Pont Lannate Insecticide	Methomyl
Unifilm B	No chemical information
Rovral 4 Flowable	Iprodione
Dipel 2X Worm Killer Wettab	Bacillus thuringiensis (berliner) subsp kurstaki, serotype 3A,3B
Goal 2XL Herbicide	Osyfluorfen
Unifilm 707 N.F.	No chemical information
MVP II Bioinsecticide	Encapsulated delta endotoxin of bacillus thuringiensis var. karstaki
Brigade WSB Insecticide/Mit	Bifenthrin
Clean Crop Carbaryl Bait	Carbaryl
Agri-Mek 0.15 EC Miticide/I	Avermectin
Uni-Par	Petroleum oil
Vapam HL Soil Fumagant	Metam-sodium
Leaf Act 80B Buffer Stread	No chemical information
First Choice Thiram 65% Wet	Thiram
Champ Formula 2 Flowable	Copper hydroxide
Ridomil Gold EC	Mefenoxam
Admire 2 Flowable	Imidacloprid

Pesticide Trade Name	Active Chemical Ingredient(s)
Tatto C Suspension Concentrate	Chlorothalonil, propamocarb hydrochloride
Colton Hydrated Lime	Calcium hydroxide
Clean Crop Thiolux Dry Flow	Sulfur
Basicop	Copper sulfate
Bravo 720	Chlorothalonil
Du Pont Manzate 200 DF Fungicide	Mancozeb
Quadris Flowable Fungicide	Azoxystrobin
Kocide 101	Copper hydroxide
Ambush Insecticide	Permethrin
Provado 1.6 Flowable	Imidacloprid
Lasso Herbicide	Alachlor
Du Pont Benlate SP Fungicide	Benomyl
Clean Crop Malathion 8 Aqua	Malathion
Ornalin FL Liquid Flowable	Vinclozolin

Source: Orange County Agricultural Commissioner (1998)

Channel watershed in which dry weather flow samples were taken during August 1998 to specifically target potential discharges of pesticides from several large commercial nurseries located in this watershed. Nurseries are known to use large amounts of a variety of conventional and exotic (less commonly used) pesticides. One of the sampling stations selected for dry weather sampling on August 13, 1998 was the Hines Channel at the Irvine Boulevard crossing. This sampling station is just waters into a channel which apparently, based on the information currently available, contributes flow to the Hines Channel. At this time, the flow patterns have not been fully defined, since they occur, in part, in below-ground pipes.

As shown in Table 4, the August 13, 1998 sample of Hines Channel analyzed by two different analytical procedures and labs had from 10,000 to 12,000 ng/L of diazinon, representing a potential *Ceriodaphnia* toxicity of 23 to 28 TUa. Because of this very high concentration of diazinon, the Hines Channel at Irvine Boulevard was sampled again on August 25, 1998. This time the diazinon was present at 2,500 ng/L. The same analytical result was obtained by both labs using two different procedures. It was also found that there was enough chlorpyrifos in these samples to be highly toxic to *Ceriodaphnia*. The total predicted diazinon plus chlorpyrifos toxicity for the August 25th sample was 7 TUa.

The August 13, 1998 sample of the Hines Channel, as well as the August 25, 1998 sample of Hines Channel water, as expected, killed all *Ceriodaphnia* in one day. Both the August 13 and August 25 samples were taken under dry weather flow conditions which apparently represented flow derived from primarily the El Modena Nursery and/or possibly groundwater flow into the channel. Further work on the hydrology of this system upstream of the Hines Channel sampling point at Irvine Boulevard is needed.

A dilution series of the August 13, 1998 sample of Hines Channel water showed that the 3.13% dilution of this sample killed all *Ceriodaphnia* in four days. The 1.57% sample of Hines Channel water

did not kill *Ceriodaphnia*. This indicates that the measured *Ceriodaphnia* TUa was about 32. Since the predicted August 13, 1998 Hines Channel water had an expected 25 *Ceriodaphnia* TUa, based on diazinon and chlorpyrifos concentrations, apparently there was appreciable toxicity in this sample due to unknown causes.

It is of interest to find that the addition of PBO to the 1.57% Hines Channel sample collected on August 13, 1998 caused a low level of toxicity to *Ceriodaphnia* that was not found in the same dilution of this sample without PBO. A similar result was found for the Santa Ana Delhi Channel sample collected on August 25, 1998. This is a possible indication of a PBO-activated toxicity such as that associated with pyrethrins. It would not be surprising to find nurseries and/or agriculture using pyrethrin-based pesticides to control certain types of pests in their nursery stock or crops.

The August 13, 1998 Hines Channel sample was nontoxic to fathead minnow larvae. It did, however, show toxicity to the alga *Selenastrum*. It appears that the nurseries and/or other dischargers to the Hines Channel may be using a herbicide(s) that is toxic to *Selenastrum*. The August 25, 1998 sample of Hines Channel water, however, as well as the San Diego Creek at Campus Drive sample, were both toxic to fathead minnow larvae. This is the only time that toxicity to fish larvae was found during this study in the San Diego Creek watershed. The March 1998 Santa Ana Delhi dry weather flow sample was toxic to fathead minnow larvae; however the August 25, 1998 sample, which was also a dry weather flow sample, was nontoxic to fathead minnow larvae.

A review of the August 13, 1998 and August 25, 1998 dry weather flow conditions samples taken at the Hines Channel, Central Irvine Channel, and San Diego Creek at Campus Drive locations data presented in Table 4, shows that the toxicity decreased from the Hines Channel downstream to the San Diego Creek sampling location. This reflects a situation where the primary source of toxicity is upstream of the Hines Channel at Irvine Boulevard.

Summary of Toxicity Testing Results. Overall, the August 1998 dry weather flow sampling of the San Diego Creek watershed, focusing on the Peters Canyon Channel, the Central Irvine Channel, and the Hines Channel established that high levels of *Ceriodaphnia* toxicity are present immediately downstream of two large commercial nurseries. The sampling at other times during the past year indicated that this situation is likely occurring year-round, and that the Hines Channel is likely one of the sources, if not the primary source of unknown-caused toxicity that is found during stormwater runoff events at the San Diego Creek at Campus Drive sampling point, as well as at the Peters Canyon Channel sampling point at Barranca Parkway.

The two nurseries (Hines Nursery and El Modena Nursery) are near the headwaters of the Hines Channel. Based on field reconnaissance and the results of the toxicity testing and chemical analysis, the El Modena Nursery and possibly the Hines Nursery appear to be contributing substantial toxic constituents that are being carried with some dilution into Upper Newport Bay. It is also possible, however, that orchards in the headwaters area of Hines Channel may also be contributing toxic constituents to the Channel. In addition, agricultural drains and possibly groundwater discharge to the Channel are likely sources of constituents that cause *Ceriodaphnia* toxicity. This situation needs further investigation.

The stormwater runoff sampling that has been conducted since the fall of 1996 at various locations in the San Diego Creek watershed has demonstrated that with each stormwater runoff event, there is appreciable *Ceriodaphnia* and *Mysidopsis* toxicity contributed from the San Diego Creek watershed to Upper Newport Bay. Substantial parts of this toxicity (on the order of 50%) are likely

due to diazinon and chlorpyrifos. The remainder of the toxicity is due to causes unknown at this time, which apparently are related to commercial nursery use of chemicals for pest control or other purposes, as well as agricultural use of pesticides. The Hines Channel discharges which are believed to be due to nursery sources contain high concentrations of diazinon, and contain chlorpyrifos at toxic levels.

The studies conducted during the fall of 1996, 1997, and 1998 show high levels of aquatic life toxicity in San Diego Creek and in various tributaries to the Creek. Very high levels of toxicity were found in the Hines Channel area, which is a tributary of Central Irvine Channel, which in turn is a tributary of Peters Canyon Channel. Peters Canyon Channel is a tributary of San Diego Creek. The past studies have not attempted to determine the toxicity of the upper branches of San Diego Creek above where it confluences with Peters Canyon Channel. From the data collected during August, 1998 under low flow conditions, it appears that San Diego Creek above Peters Canyon Channel confluence is of lower toxicity since it diluted the toxicity found in Peters Canyon Channel at the Barranca Parkway, which is just above where this Channel confluences with San Diego Creek.

The current studies focused on the Peters Canyon Channel and its tributaries, since high levels of unknown-caused toxicity were found at Barranca in previous studies. There is need in future studies to separately sample the San Diego Creek watershed that does not include Peters Canyon Channel flow under stormwater runoff conditions. It is likely, based on the past data that, under stormwater runoff conditions, there would be appreciable *Ceriodaphnia* toxicity present in San Diego Creek before it confluences with Peters Canyon Channel. This assessment is based on the fact that Silverado (1997a) and Lee and Taylor (1997a) have reported that the primary uses of diazinon and chlorpyrifos in the Upper Newport Bay watershed are associated with structural and lawn and garden use in residential areas. There is appreciable residential area in the San Diego Creek watershed that is likely contributing diazinon and chlorpyrifos during stormwater runoff events. Also, there are several commercial nurseries and appreciable agricultural drainage in the headwaters of San Diego Creek that do not discharge to Peters Canyon Channel or its tributaries.

The November 1998 stormwater runoff sample of San Diego Creek at Harvard Avenue showed appreciable *Ceriodaphnia* toxicity which contained substantial constituents that contribute toxicity that are not accounted for by the concentrations of diazinon and chlorpyrifos (unknown caused toxicity). The more intensive sampling of the various components of the San Diego Creek watershed should be done as part of the US EPA 319(h) project that has been recently activated. That project provides funds to do further work on determining the specific sources of toxic components within the Upper Newport Bay watershed.

Fall 1998 Preliminary Results. It has been found that the first stormwater runoff event of the fall 1998/99 season, which occurred on November 8, 1998, showed similar results in terms of toxicity levels to *Ceriodaphnia* and *Mysidopsis* and lack of toxicity to fathead minnow larvae and *Selenastrum* (algae), as was found in the first fall and subsequent stormwater runoff event sampled in 1996 and 1997. The November 8, 1998 sample of San Diego Creek water just above where it enters Upper Newport Bay was found to contain in excess of 16 TUa for *Mysidopsis*. The November 8, 1998 samples of San Diego Creek water taken at various locations was found to contain from 16 to 32 *Ceriodaphnia* TUa. In addition to having 670 ng/L diazinon and 430 ng/L of chlorpyrifos this sample contained a variety of other OP pesticides and carbamate pesticides. Table 6 presents a listing of the OP and carbamate pesticides that have been found in 1997 and 1998 in San Diego Creek stormwater

runoff using dual column GC with the US EPA 8141 Special Low-Level List of OP pesticides and US EPA Method 632 for carbamate pesticides.

At this time there is no information available on the toxicity of many of the pesticides listed in Table 6 to *Ceriodaphnia* and/or *Mysidopsis*. It is possible that part of the unknown-caused toxicity that has been repeatedly found in these studies is due to one or more of these pesticides.

A dry weather sample taken of San Diego Creek at Campus Drive in January 1999, after several months of no appreciable runoff, was found to be highly toxic to *Ceriodaphnia*. This sample contained a variety of OP pesticides and carbamate pesticides that had not been found at this location in the previous studies. The data from the November 1998 and January 1999 samples will be reported in the final report for the 205(j) project, which will be available in the summer of 1999.

Table 6
OP and Carbamate Pesticides Found in November 8, 1998 San Diego Creek
Sample Taken at Campus Drive

dimethoate	290 ng/L
fensulfothion	320 ng/L
prowl	180 ng/L
benomyl	500 ng/L
carbaryl	3,100 ng/L
methomyl	6,200 ng/L
diuron	2,200 ng/L
oryzalin (surfalan)	20 to 30 µg/L
metalaxyl (ridomil)	5 to 10 µg/L
simazine	3,200 ng/L

Also, at other times the following pesticides have been found in San Diego Creek/Upper Newport Bay tributaries:

dimethoate	7,100 ng/L
malathion	200 ng/L
merphos	140 ng/L
prowl	1,200 ng/L
stirophos	140 ng/L
benomyl (carbendazim)	500 ng/L

While of limited scope, the studies of Bailey *et al.* (1993), which showed *Ceriodaphnia* toxicity in stormwater runoff to Upper Newport Bay, indicates that the OP pesticide-caused aquatic life toxicity problem that now exists in the Upper Newport Bay watershed is a longstanding problem that has been occurring for many years without being detected by other stormwater runoff monitoring programs. The water quality significance of the toxicity, from one or more nurseries and/or agricultural use located in the headwaters of the Hines Channel, is an issue that needs to be addressed. There is need to do more detailed sampling on other channels in the San Diego Creek watershed during various runoff conditions to determine if this type of problem is occurring elsewhere in the San Diego Creek watershed.

Regulating Aquatic Life Pesticide Toxicity

One of the issues that will likely influence the control of the aquatic life toxicity in Upper Newport Bay and its tributaries is that the Santa Ana Regional Water Quality Control Board has listed San Diego Creek Reach 1 (lower reach) on the 1998 303(d) list of impaired waterbodies due to the presence of “pesticides” in the Creek waters. This Board has listed San Diego Creek Reach 2 (upper reach) on the 303(d) list because of “unknown toxicity.” Both of these listings are given a high priority for Total Maximum Daily Load (TMDL) development. According to the TMDL process, the Reach 1 TMDL for the control of pesticides is to be started on January 1, 1999 and completed by January 1, 2002. The unknown toxicity TMDL for Reach 2 has the same start and completion dates.

Regulatory Requirements. The US EPA Region IX, as part of settling a lawsuit filed by an environmental group concerned about protecting the beneficial uses of Upper Newport Bay, entered into a consent decree which requires that TMDLs be developed for all Santa Ana Regional Board-listed Upper Newport Bay use impairments within a limited specified time period. If the Santa Ana Regional Water Quality Control Board does not meet this extremely short timetable for developing a TMDL for such complex issues as control of toxics, the US EPA Region IX will develop the TMDL and impose the requirements on the Santa Ana Regional Board for enforcement.

The 1998 303(d) list developed for the Upper Newport Bay Ecological Reserve, which is the upper part of the Upper Bay, includes the development of TMDLs for “pesticides” as a high-priority item that is to begin on January 1, 1999 and be completed by January 1, 2002. Toxicity is not listed as a use impairment of the Upper Newport Bay. However, in discussing this matter with H. Smythe of the Santa Ana Regional Water Quality Control Board, the listing of Upper Newport Bay as being impaired by pesticides is based on the work of Bailey *et al.* (1993) in which they found *Ceriodaphnia* toxicity to be due to unknown causes. It is now clear from the studies conducted in this project that diazinon and chlorpyrifos are the cause of at least a substantial part of this toxicity. However, a significant part of the toxicity at times is due to unknown causes, which may not be due to pesticides.

The development of a TMDL for pesticides and pesticide-caused toxicity will be difficult and is controversial. The controversy stems from the fact that pesticides are regulated differently than other toxicants. While various Regional Water Quality Control Board Basin Plans all have a toxicity control requirement of “no toxics in toxic amounts,” the application of this Basin Plan requirement to pesticides is controlled by a Management Agency Agreement (MAA) between the Cal EPA Department of Pesticide Regulation and the State Water Resources Control Board. The initial phase of the MAA (DPR, 1997) focuses on achieving voluntary control of the use of pesticides associated with agricultural use to control the runoff and aerial drift of pesticides from agricultural applications, which results in pesticides entering the state’s waters in sufficient concentrations to be toxic to aquatic life. Ciba *et al.* (undated) have discussed what they term best management practices for protecting water quality in California from pesticides used as a dormant spray in orchards. It is unlikely that the application of these BMPs on a voluntary basis will be effective in controlling the discharge of pesticides to sufficiently low concentrations so that the discharge/runoff waters are non-toxic to aquatic life.

The US EPA Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) pesticide use regulations governing restricting the use of pesticides can allow aquatic life toxicity to non-target organisms provided that this does not cause significant adverse impacts on the beneficial uses of a waterbody. In addition, the State Water Resources Control Board’s (WRCB, 1997) draft approach

for implementation of the California Toxics Rule (CTR) proposes to allow aquatic life toxicity in the state's waters provided it is not significantly adverse to the beneficial uses of the waterbody.

There is a fundamental conflict between Clean Water Act requirements of no toxics in toxic amounts, as currently required in some regional board basin plans, and the pesticide use regulations governing aquatic life toxicity control due to pesticides, as well as the SWRCB's proposed toxicity control under the CTR. The latter two focus on controlling aquatic life toxicity that is significantly adverse to the beneficial uses of a waterbody. The Santa Ana Regional Water Quality Control Board's toxicity control requirements will allow laboratory based toxicity to occur provided it is not significantly adverse to the beneficial uses of the waterbody. At this time it is not clear that the SWRCB's (WRCB, 1997) proposed approach will be adopted in the final regulations governing the implementation of the CTR. Further, in several years, based on the MAA, if toxicity is still present in the state's waters due to pesticide applications in agricultural use, the regional water quality control boards will become responsible for controlling the pesticide-caused aquatic life toxicity through appropriate regulatory means. Such control could include curtailment of use for certain purposes.

An emerging area that could significantly influence the use of OP pesticides is the Food Quality and Protection Act (FQPA) that was adopted by the U.S. Congress in August, 1996. The FQPA replaced the Delaney clause governing the evaluation of the public health hazards associated with pesticide use. According to the FQPA, by August, 1999 the US EPA is to develop a revised approach for determining the health hazards associated with pesticide use considering the potential for cumulative impacts. While the OP pesticides diazinon and chlorpyrifos are not particularly toxic to people, because of their widespread use, the cumulative exposure to people may be judged to be excessive, and thereby represent a health threat. If this occurs, then through the FQPA there could be a significant curtailment in OP pesticide use.

Pesticide Use Patterns. Significant problems are likely to develop in curtailing the use of OP pesticides because of their widespread use in both agricultural and especially urban areas. Silverado (1997a) and Lee and Taylor (1997a) reported, based on Department of Pesticide Regulation data, that on the order of 60,000 pounds per year of diazinon and chlorpyrifos were applied in the Upper Newport Bay watershed during 1995. The 1995 data are the latest data available from the Department of Pesticide Regulation at this time. While there have been some changes in pesticide use patterns over the past three years, these changes would not be expected to have significantly changed the overall magnitude of use and the purpose of use of diazinon and chlorpyrifos in the Upper Newport Bay watershed. From the information available, based on diazinon and chlorpyrifos use within the San Diego Creek watershed, it appears that the primary use of these pesticides is residential, industrial, and commercial use for structural, lawn, and garden pest control. There is also input of these pesticides in stormwater runoff from agricultural use within the San Diego Creek watershed.

Based on 1995 pesticide use data obtained from the Cal EPA Department of Pesticide Regulation, as reported by Lee and Taylor (1997a) and Silverado (1997a), about 2,000 pounds of diazinon and 1,400 pounds of chlorpyrifos were used for agricultural purposes in Orange County during that year. The remainder of the use was for landscape, commercial, and structural pest control. These types of uses represented about 91% of the 21,500 pounds of diazinon used in Orange County during 1995. The 1995 agricultural use of chlorpyrifos represented about 3% of the 41,800 pounds used in Orange County in 1995. It is estimated, based on land use, that about half of the Orange County reported use of diazinon and chlorpyrifos occurs in the San Diego Creek watershed.

Further, it is estimated that the public, through purchases at hardware and garden stores, uses at least an equal amount of diazinon and chlorpyrifos on their residential properties as is applied by commercial applicators (Hill, 1997). It can be concluded that the primary source of diazinon and chlorpyrifos in the San Diego Creek stormwater runoff is derived from landscape and structural applications where, in 1995, 81% of the commercial applicator diazinon use was for structural purposes. Correspondingly, 91% of the commercial applicator use of chlorpyrifos was for structural purposes. It is likely, however, that the public's purchase and use of these chemicals is directed more toward landscape purposes. It is expected that residentially utilized chlorpyrifos is more susceptible to stormwater wash-off than structurally utilized chlorpyrifos.

In summary, approximately 90% of the diazinon and chlorpyrifos use in the Upper Newport Bay watershed is for structural, landscape and commercial use purposes. Agricultural use represents a small part of the total usage. It is estimated that approximately half of the use of diazinon and chlorpyrifos is made for residential purposes, where the pesticide is purchased in hardware or garden stores. Based on the concentrations of diazinon and chlorpyrifos found in these studies in stormwater runoff in San Diego Creek waters at Campus Drive, only a few pounds of the over 60,000 pounds of diazinon and chlorpyrifos used in the Upper Newport Bay watershed each year can cause the levels of aquatic life toxicity and diazinon and chlorpyrifos concentrations found in stormwater runoff to Upper Newport Bay.

Further, as reported by Silverado (1997a) and Lee and Taylor (1997a), based on the work of Scanlin (1997) in Alameda County, California, and Lee (1998) in El Macero, California, normal registered use of these pesticides on residential properties can be a significant source of pesticide runoff from these properties. Therefore, the control of urban stormwater runoff-caused *Ceriodaphnia* toxicity is going to be extremely difficult to achieve without significantly curtailing the use of these pesticides for residential, commercial and agricultural purposes. While it would be possible to curtail the use of these pesticides, there is no assurance that the substitute pesticides would necessarily be any more compatible with the environment than diazinon and chlorpyrifos.

Water Quality Criteria/Standards for Diazinon and Chlorpyrifos. One of the fundamental aspects of developing a TMDL for diazinon and/or chlorpyrifos is the selection of a target value which is to serve as the goal of the TMDL. Typically the TMDL goal is the elimination of the 303(d) impaired listing of a waterbody due to a particular chemical. The 303(d) listings arise out of the exceedance of numeric or narrative water quality standards (objectives). While, in the early 1980s, the US EPA (1986) developed a water quality criterion for chlorpyrifos, since chlorpyrifos is not listed as a toxic pollutant in the National Toxics Rule, the states are not required to adopt this criterion as a state standard. While the State of California Water Resources Control Board could have adopted this criterion as a state standard years ago, thus far it has chosen not to do so.

The US EPA freshwater acute water quality criterion for chlorpyrifos is 70 ng/L, which is to be implemented on a one-hour average. The US EPA freshwater chronic criterion is 41 ng/L, which is to be implemented on a four-day average. The corresponding US EPA criteria for salt water are acute 56 ng/L and chronic 30 ng/L. A review of the data presented in Table 4 shows that diazinon is frequently present in San Diego Creek or its tributaries at concentrations above the US EPA chronic and acute water quality criterion. Since there is a US EPA criterion value established for chlorpyrifos it is highly likely that this value will become the target value for the TMDL.

With respect to stormwater runoff conditions, it is unlikely that the chronic criterion (based on a four-day average) would be exceeded for urban area stormwater runoff. However, the acute criterion value for both fresh and marine waters based on a one-hour average will frequently be exceeded in San Diego Creek at various parts of the watershed and as it enters Upper Newport Bay.

While the US EPA has been developing a water quality criterion for diazinon since the late 1980s, while periodically announcing that this criterion would be promulgated, thus far the agency has failed to do so, with the result that at this time there is no US EPA criterion for diazinon.

The California Department of Fish and Game (DFG), using US EPA water quality criteria development approaches (US EPA, 1985, 1987a), has developed suggested water quality criteria for diazinon and chlorpyrifos (Menconi and Cox, 1994; Menconi and Paul, 1994). For chlorpyrifos the DFG freshwater chronic suggested criterion is 20 ng/L, and salt water chronic suggested criterion is 10 ng/L. These values are similar to the US EPA water quality criteria for chlorpyrifos.

For diazinon the DFG freshwater acute suggested criterion is 80 ng/L, and the chronic suggested criterion is 40 ng/L. DFG did not develop a salt water criterion for diazinon, evidently, since thus far no marine organism has been found to be highly sensitive to this pesticide. The concentration of diazinon found in this study in the San Diego Creek and its tributaries are typically above the DFG suggested acute water quality criterion. This situation would result in an automatic 303(d) listing of San Diego Creek and many of its tributaries as 303(d) listed impaired waterbodies which would mandate that a TMDL be developed if the DFG suggested water quality criterion is adopted as a state water quality standard/objective.

As typically implemented, in accord with current US EPA guidance, the exceedance of these suggested criterion values in San Diego Creek waters throughout most of the watershed and as they enter Upper Newport Bay by more than any amount once every three years represents a violation of a water quality standard that could result in the waterbody being listed as a 303(d) listed "impaired" waterbody. This listing sets in motion the TMDL process to ultimately achieve the water quality standard (criterion) in the waterbody. Therefore, from the US EPA chlorpyrifos criterion value, the DFG diazinon suggested criterion value, if adopted as a state water quality standard, as well as the narrative no-toxic-in-toxic-amounts water quality objective, it is necessary under the current regulatory requirements to develop a TMDL for control of diazinon and chlorpyrifos as well as aquatic life toxicity from known and unknown causes in the San Diego Creek watershed for Upper Newport Bay.

TMDL Process. As discussed herein, the Santa Ana Regional Water Quality Control Board is obligated under a court consent decree to develop TMDLs for diazinon and chlorpyrifos and unknown-caused toxicity by the year 2002. Normally credible TMDLs should be based on having an understanding of the relationship between the concentration/loads of a regulated constituent or characteristic and a water quality standard. Developing this information requires considerable understanding of the use of a chemical as it influences the concentrations and/or their impacts in a waterbody of concern.

Lee and Jones-Lee (1997) have discussed the approach that should be followed in developing TMDLs that will protect designated beneficial uses of waterbodies without significant unnecessary expenditures for constituent control. Their suggested approach is based on having a good understanding between the use and the aquatic chemistry of the constituents of concern and the impacts of these constituents on the beneficial uses of a waterbody. The US EPA and the states have largely neglected developing this kind of information for any chemical or constituent with the result that crash

programs are now being implemented for TMDL development arising out of litigation settlements, where there is an inadequate database of information upon which to formulate technically valid, cost effective TMDLs.

At this time there is insufficient understanding of how pesticides applied for various uses become part of urban and rural area stormwater runoff to be able to formulate technically valid, cost effective TMDLs. The net result is that somewhat arbitrary approaches will have to be developed for establishing chlorpyrifos and diazinon, as well as toxicity control programs, in implementing the first phase of a TMDL. This phase will likely have to be implemented over at least a five-year period. As discussed by Lee and Jones-Lee (1997), through appropriate monitoring conducted during TMDL Phase I it should be possible to begin to develop an understanding of how pesticides used on residential properties, as well as for agriculture at commercial nurseries, etc., become incorporated into stormwater runoff to a sufficient extent to lead to aquatic life toxicity in the runoff waters.

Water Quality/Ecological Significance of Aquatic Life Toxicity in San Diego Creek and its Tributaries

One of the issues that should be addressed is the water quality/ecological significance of *Ceriodaphnia* and other aquatic organism toxicity, including fathead minnows and possibly *Selenastrum* in the Hines Channel, Central Irvine Channel, Peters Canyon Channel, San Diego Creek above Harvard Avenue, as well as other tributaries of San Diego Creek, under low flow, as well as stormwater flow conditions. While the beneficial uses of these waters are listed as aquatic life-related habitat by the Santa Ana Regional Water Quality Control Board in this Board's Basin Plan, the aquatic life-related resources of the waters in these channels are severely impacted by habitat characteristics. There is need to assess the potential improvement in the beneficial uses of these waters if the high levels of aquatic life toxicity that have been found under both low flow and high flow conditions were eliminated.

It is likely that the high levels of toxicity found on two different sampling days in August 1998 are detrimental to the aquatic life resources of these channels and therefore the apparent discharge of toxic constituents from one or both of the nurseries in their wastewater and fugitive water discharges/releases, as well as stormwater runoff from the nurseries will have to be controlled through limitations on the use of diazinon and chlorpyrifos and other pesticides.

Associated with each stormwater runoff event to Upper Newport Bay is a pulse of toxic water that has a potential to kill certain zooplankton with a sensitivity to OP pesticides similar to *Ceriodaphnia* and mysids. Novartis (1997) has compiled information on the diazinon-caused LC₅₀s for various freshwater and marine organisms. Based on the information available at this time, *Ceriodaphnia* is one of the most sensitive organisms to diazinon toxicity. Based on the review of Menconi and Paul (1994), there is no evidence from the literature that the organophosphate pesticides at the concentrations being found in this study in San Diego Creek waters as they enter Upper Newport Bay are toxic to adult or larval fish. There is, however, some limited un-corroborated work that chlorpyrifos is toxic to the Korean prawn, *Palaemon macrodactylus*, at 10 ng/L (Earnest, 1970). The Korean prawn is not a native species in the US, but has been introduced to the San Francisco Bay, Sacramento/San Joaquin River Delta. According to S. Dawson (personal communication, 1998) of the Santa Ana Regional Water Quality Control Board, the Korean prawn has not been found in Upper Newport Bay. Further work needs to be done to determine if the limited scope study, which indicates a potential for OP pesticide toxicity to certain types of shrimp, is reliable. Also, work needs to be done

to determine if Upper Newport Bay has organisms that are key parts of the food web for the overall ecosystem that could be impacted by OP pesticide toxicity and/or the toxicity due to the unknown-caused toxicity found in this study.

Since the zooplankton present in San Diego Creek water will be killed in Upper Newport Bay as the Creek water mixes with the 30 ppt marine waters due to salinity, the water quality significance of the toxic pulses becomes one of assessing whether there are marine organisms present in the Bay waters that will be mixed into, or migrate into, the San Diego Creek waters that are present as a fresh water lens on top of the Bay marine waters during and following a stormwater runoff event. This relationship is shown in Figure 1. If it is assumed that the worst-case condition for toxicity to marine zooplankton would be that 10 TUa units of acute toxicity could be present in San Diego Creek water as it enters Upper Newport Bay, then under these conditions the toxic waters that could affect marine zooplankton are those with a salinity less than 3 ppt. Any salinity greater than this amount would dilute the 10 TUa San Diego Creek water to non-toxic levels.

A fundamental issue that needs to be assessed is whether there is a significant amount of water present in Upper Newport Bay associated with stormwater runoff events with salinities less than 3 ppt that would persist for at least one to two days. Another issue is whether marine zooplankton could be mixed into, or migrate into the freshwater marine water lens with salinities less than 3 ppt and stay in this lens. This assumes that the zooplankton persisted for a sufficient period of time to receive a toxic exposure to the toxic constituents in the San Diego Creek water that has been diluted by the Bay's marine waters. In order to review this situation an analysis of the currently available information on the mixing of San Diego Creek waters with Upper Newport Bay waters has been undertaken.

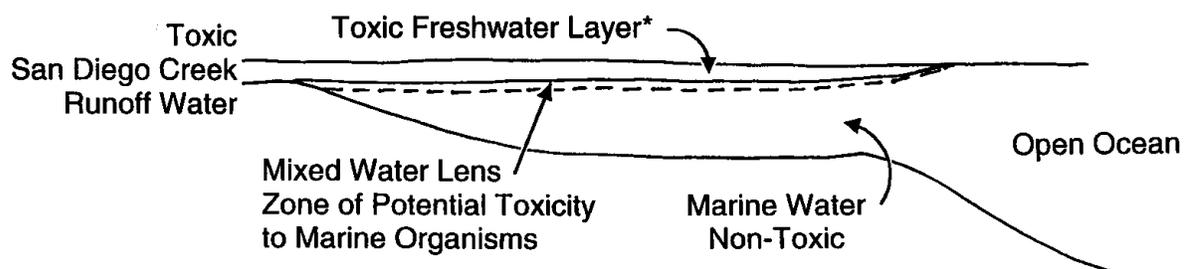
Mixing of San Diego Creek and Upper Newport Bay

The water quality and ecological significance of the toxicity identified in San Diego Creek and the Santa Ana Delhi Channel stormwater runoff in Upper Newport Bay is a function of the level of mixing that occurs between the runoff waters and the Bay water. Conductivity data from the County of Orange municipal stormwater monitoring effort in the Bay would tend to suggest that stratification occurs during significant runoff events, wherein freshwater remains as a 'lens' on the surface of the Bay marine waters. The stratification of Upper Newport Bay during stormwater runoff events was investigated by Limno-Tech (1998) as part of a study devoted to defining the fate and persistence of nutrients associated with low flows and stormwater runoff input to Upper Newport Bay.

Limno-Tech conducted an investigation of the quantity of water necessary to cause significant salinity stratification in Newport Bay (creation of a freshwater 'lens'). Their analysis incorporated an estuarine stratification classification system using salinity stratification and water circulation patterns. This classification system was developed by Hansen and Rattray (1996). The system involves the calculation of two parameters at two points along a main estuary channel. The two locations chosen were an upper station near San Diego Creek (UNSBC) and a lower bay station near Harbor Island (HIR). Lee *et al.* (1999) have provided a discussion of the application of the Limno-Tech mixing model for the Upper Newport Bay. Based on this review Upper Bay area appears to be well mixed

Figure 1

Upper Newport Bay OP Pesticide Aquatic Life Toxicity Situation



Toxic Freshwater Mixes with Non-Toxic Marine Water

* Under "Steady State" Conditions with Minimum Flow of 1500 cfs. At Lower Flow Rates, Bay May Be Only Partially Stratified, or, in Upper Bay, Fully Mixed, with Unknown Toxicity.

depending on tide conditions. In reviewing County of Orange conductivity data, it also appears reasonable to assume that the lower Bay is largely unaffected by flows of less than about 50 cfs (urban runoff) from San Diego Creek and the Santa Ana Delhi Channel and is fully mixed. These conclusions are valid regardless of tidal stage. Between Creek discharges of 50 cfs and about 1,500 cfs, the influence of tide would appear to be important, and partial stratification (mixed condition) occurs in the Lower and Upper Bay, depending on tide conditions. Above about 1,500 cfs, the Bay would appear to be fully stratified at all locations and for all tide conditions. The LTI report upon which these conclusions are based is provided in Lee *et al.* (1999) Appendix E.

Preliminary conclusions on the extent of stratification may be drawn relative to this project's 1997-98 sampled storm events using the stratification analysis of the Bay. Table 7 provides a description of the estimated time that the Bay would be stratified vs. the time it would be mixed for selected storm events during the 1997-98 season.

The stormwater runoff is assumed to remain in a relatively confined prism as it moves through the Bay. The data and analysis compiled to date have not explicitly examined the question of the potential for lateral mixing of the stratified freshwater plume. This assumption will need to be verified through actual in-Bay testing.

Table 7
Estimated Time of Stratification during Sampled Storm Events

Storm Date	Location	Period Flow Is Stratified (hrs)	Period Flow Is Mixed (hrs)	Total Storm Time of Runoff (hrs)
9/25/97	Campus	17	9	26
11/13/97	Campus	24	9	33
11/30/97	Campus	19	10	29
12/6/97	Campus	45	4	49
3/25/98	Campus	36	6	42
5/5/98	Campus	28	13	41
5/12/98	Campus	60	3	63
3/25/98	Santa Ana Delhi Channel	13	9	22
5/5/98	Santa Ana Delhi Channel	6	18	24
5/12/98	Santa Ana Delhi Channel	18	24	42

If the flow is stratified or partially so above 50 cfs, then the time when it is more fully mixed with the Bay waters and the dilution during this time may become critical from the perspective of potential harm to organisms in the water from the measured toxicity. An estimate of the relative volumes of stormwater runoff vs. Bay water for these low flow conditions may be made by assuming a control volume in the Bay and computing the total stormwater runoff volume during the period when the flow is likely to be mixed.

The LTI report provided estimates of a flow ratio parameter as part of their analysis. The value is a ratio of tidally induced flow to river flow. Such a flow ratio provides a good estimate with respect to estimating the dilution (and assessing the associated toxicity) of the stormwater runoff and Bay water. The tidal prism represents the mass of water that moves in and out of the estuary with the tide.

The tidal prism is a reasonable control volume to use as a basis to assess dilution of the stormwater runoff within the estuary/Bay.

Upper Newport Bay marine waters typically exhibit a salinity of about 30 ppt. During a portion of a storm event there will be a zone in the Bay waters where the salinity drops significantly, the time this zone will exist depends on several variables. A salinity of about 3 ppt or less is considered critical with respect to mysid mortality based on the salinity threshold and an assumed toxicity of 10 toxic units associated with the incoming stormwater discharge.

The extent and time of mixed versus stratified flow in the Bay is highly variable, depending on the volume of stormwater entering the Bay versus the tide stage, the time of direct runoff of the stormwater hydrograph, and the peak discharge of the stormwater hydrograph, and to a lesser extent the temperature differential of the Bay and stormwater, the amount of sediment in the stormwater, and the shape of the hydrograph. In addition, lateral mixing of storm flow and Bay waters is also impacted by wind direction and magnitude. The information provided in Table 7 can be used as an indicator to determine if a potential problem exists for exposure of marine organisms to stormwater runoff that has been determined to be toxic.

It is reasonable to assume that the time where a substantial zone of water in the range of 3 ppt of salinity or less, would be during full or partial mixing of storm flow with Bay water. Conditions with full stratification may be less problematic for marine organisms, since they are not originally present in the stormwater runoff and may not tend to migrate into the freshwater lens. Therefore, if the critical time is assumed to be during the hours when the flow is estimated to be fully mixed, it can be seen from the data in Table 7 that this occurs on average about 10.5 hours per storm event (using 1997-98 storm season data). The average time of direct storm runoff into the Bay (again using 1997-98 data) is about 37 hours per storm. This average contact time (10.5 hrs) is potentially significant relative to toxicity to marine organisms in the Bay. Based on this analysis, it is clear that the toxicity from San Diego Creek and the Santa Ana Delhi Channel could impact some forms of aquatic life in Newport Bay.

Further study is needed to confirm the preliminary conclusion of the significance of the toxicity associated with the stormwater runoff. It is expected that under low flow conditions this interface will be hard or impossible to locate and a fully mixed condition will occur. Samples will be taken under this condition to investigate the magnitude of the toxicity as well as the extent. Samples will also be taken at other points in the runoff hydrograph in an attempt to validate the method used to develop the data in Table 7, as well as to define the lateral extent of the freshwater lens as it moves through the Bay. This study will be undertaken by sampling at defined cross sections within the Bay, and at defined depths for each sampling point on the cross section. Sampling at the cross sections will be completed for several points throughout the storm hydrograph.

Using salinity gradients as a measure of mixing San Diego Creek water with Upper Newport Bay water in order to estimate the persistence of the toxic constituents and toxicity in the Bay following a runoff event assumes that the toxic constituents measured in the laboratory test of toxicity will be conservative, i.e., remain unaltered, in Upper Newport Bay. Since chlorpyrifos is likely the constituent of greatest concern, and since it tends to sorb on other particulates, it is possible that part of chlorpyrifos entering the Bay will be in non-toxic forms. This is based on the fact that the WRCB BPTCP/EMAP studies of Upper Newport Bay conducted in 1994 (Anderson *et al.*, 1997) found chlorpyrifos in the Bay sediments near where San Diego Creek enters Upper Newport Bay. There is no information at this time, however, that the mysid toxicity that has been found in San Diego Creek

waters as it enters Upper Newport Bay is affected by sorption or other reactions which would affect its fate, persistence and toxicity. There is need to conduct field studies during and following stormwater runoff events to determine the actual persistence of chlorpyrifos and toxicity in the Bay. These results should be compared to those predicted based on salinity profiles, assuming that the chlorpyrifos and other toxic constituents are conservative – non-reactive.

Samples were taken in mid-January 1999 during a storm event to define the freshwater lens for a given set of conditions, and measure the toxicity associated with the freshwater inflow. Particular attention was given to examining the freshwater/salt water interface at various flow and tide conditions. The results of this study are not yet available. They will be reported in the final report for the 205(j).

Recommendations For Future Studies

The results from the Evaluation Monitoring Demonstration Project and the first year of this 205(j) project have developed sufficient results to define several areas that need additional studies to further define the magnitude of the aquatic life toxicity problem that exists in the Upper Newport Bay watershed and the Bay. Of particular importance is the need to conduct specific investigation of the fate/persistence of toxicity of the OP pesticides, diazinon and chlorpyrifos. Also of concern is the persistence of the unknown toxicity in the Bay. Information on the persistence of the aquatic life toxicity in the Bay is the key to evaluating the potential water quality/ecological significance of the toxicity discharged to the Bay with each stormwater runoff event.

The other major area of needed future studies is the definition of the sources of the known (OP pesticide) and unknown caused toxicity. Of particular importance is an assessment of the relative magnitude of the contributions of toxicity from residential, agricultural and commercial nurseries that persist in the tributary waters to the Bay and within the Bay. Also there is need to define the specific uses and formulations of pesticides and other chemicals in each of these known principal sources that leads to the greatest loss of toxic components to stormwater runoff that persists in the Bay.

This project considers aquatic life toxicity as an entity that may need to be controlled irrespective of whether the cause of the toxicity is identified. As discussed in Lee et al. (1999) Section 4 and Appendix B, after considerable TIE efforts, there is substantial toxicity caused by unidentified constituents. It may not be possible with the funds available to identify the specific constituents responsible for all of the unknown caused toxicity. However, as demonstrated thus far in this project through toxicity, diazinon and chlorpyrifos forensic based studies of samples taken in various parts of the watershed during dry weather flow and during runoff events, it is possible to determine the source of the unknown caused toxicity without specifically identifying the chemicals responsible. The commercial nurseries that discharge/release water to the Hines Channel have been tentatively identified as potentially significant sources of the unknown caused toxicity.

Through the use of US EPA toxicity reduction evaluations (TREs) approaches, the nurseries and for that matter other identified sources of unknown toxicity can be required to control this toxicity through the elimination of certain chemical applications and/or modification of water management practices. Therefore, in accord with the TMDL toxicity control requirements, the development of toxicity control approaches for the unknown caused toxicity will be a key component of the future efforts in this project.

The development of the needed information through the recommended follow-up studies will provide the technical base of information that the Santa Ana Regional Water Quality Control Board

can use to formulate the Phase 1 total maximum daily loads (TMDLs) for toxicity, diazinon and chlorpyrifos.

Evaluation of The Water Quality/ecological Significance of The Stormwater Runoff Toxicity.

The water quality/ecological significance of the stormwater runoff associated *Ceriodaphnia*/mysid toxicity is a key factor that could be highly influential in determining the degree of control of OP pesticides and other toxic constituents that are now causing San Diego Creek and its tributaries to be toxic to *Ceriodaphnia* and certain other forms of aquatic life during stormwater runoff events. A key issue that must be resolved is whether the regulation of this toxicity will be based on its likely causing a significant adverse impact to the beneficial uses of the tributary waters as well as in the Bay. If the toxicity is judged to be of water quality significance to the aquatic life related beneficial uses of the Bay and/or its tributaries, then the degree of toxic constituent control needed to protect the designated beneficial uses without unnecessary restriction on use of the pesticides or other chemicals responsible for the toxicity will need to be assessed.

The information presented on the current degree of mixing of San Diego Creek water with Upper Newport Bay water during and following a stormwater runoff event shows that there are conditions where marine zooplankton could receive an acute toxic exposure provided that there are marine organisms that will migrate into the low (less than 3 ppt) salinity and stay in this water for a day or more. Bay studies will be conducted to verify persistence of the San Diego Creek water in the Bay following a stormwater runoff event. While one in Bay study has been conducted there is need to conduct addition studies in which salinity profiles will be taken at various locations in the Bay during stormwater runoff events of various magnitudes will be conducted. Also, selected sampling should be conducted for the presence of diazinon, chlorpyrifos and aquatic life toxicity at various locations within the Bay

Based on the information available which is derived from work conducted by Limno-Tech (LTI) (Limno-Tech, 1998) relative to investigation of the conditions under which Newport Bay becomes stratified (freshwater in a defined lens on top of marine water). Stratification occurs when the large tributaries to the Bay (San Diego Creek, and to a lesser extent the Santa Ana Delhi Channel) discharge stormwater to the Bay.

It will be important to monitor stormwater runoff events that result in runoff from San Diego Creek of at least 1500 cfs to allow validation of the LTI estimates. The sampling plan will generally be based on the following criteria:

- Samples will be taken in the Upper Bay at selected stations. Each station is defined as a cross section, taken normal to the stormwater flow.
- Three stations have been identified in the Upper Bay. One near the entrance of San Diego Creek to the Bay (Jamboree Road, OCPFRD Station “UNBJAM”), one about mid-way between Jamboree Road and the Pacific Coast Highway bridge (OCPFRD Station “UNBBCW”), and the third near the Pacific Coast Highway bridge (OCPFRD Station “UNBCHB”).
- Three locations will be selected at each station. Two locations will be near each shore, the third location will be in the middle of the Bay. Nearshore locations will be in active flow areas, as opposed to ineffective flow areas (i.e., in small channels on the leeward side of islands). Four samples will be taken at each location. The samples will be taken at various depths and be spaced between the surface and the sediments of the Bay, dependent on the salinity profiles. Tide and wind

will be noted for each of the samples, and the influence of these variables will be included in the data analysis.

- Salinity will be measured at each sampling location. Samples for toxicity testing, when taken, will be collected at the center Bay locations.
- Sampling will be carried out at several times over the runoff hydrograph. One sampling time will be completed when the inflow from San Diego Creek is estimated to be below 1500 cfs. The other sampling sets will be taken at other times during the runoff hydrograph.
- It is anticipated that for some storms, a total of 108 salinity measurements could be made. The number of samples to be taken for toxicity and diazinon and chlorpyrifos measurements will be determined based on the data obtained.

The stations will be identified at existing OCPF RD in-Bay locations, and the cross sections will be identified using landmarks at each station location so that subsequent samples may be taken at approximately the same location each time. Sampling will be limited to daylight hours. These data will be used to refine the existing information on the rate of mixing San Diego Creek water with the Bay water during stormwater runoff events.

During several of the salinity profiled monitored stormwater runoff events, samples of the Bay waters will be taken at several locations in the Bay to determine the relationship between the predicted mysid toxicity, diazinon and chlorpyrifos concentrations based on salinity – San Diego Creek toxicity and the in-Bay measured values. Attempts will be made to make these measurements in the upper part of Upper Newport Bay, mid Upper Newport Bay and lower Upper Newport Bay near the Pacific Coast Highway associated with one or more major stormwater runoff events that occur in 1999. Samples will be taken of the low salinity surface waters, the fresh water/marine water lens with a salinity between 1 and 3 ppt and in the near bottom marine waters. This information will be used to evaluate the conservative characteristics of the known caused and unknown caused toxicity as well as the OP pesticides, diazinon and chlorpyrifos.

One of the issues that may need to be investigated if it appears that there is a significant potential for marine zooplankton to receive a toxic exposure and if the decision to regulate the toxicity is based on there being significant adverse impacts to the aquatic life beneficial uses of the Bay, is whether there are marine zooplankton that migrate into the low salinity toxic San Diego Creek/ Bay marine waters and stay in these waters for one or more days. As discussed, the current regulatory requirements are unclear as to whether OP pesticide caused toxicity will be regulated based on significant adverse impacts or simply based on the presence of toxicity. If toxicity that causes significant adverse impacts to the beneficial uses of the Bay is the regulatory approach adopted, then studies will need to be conducted during subsequent years as part of renewal of this project that involve trawling for zooplankton in the potentially toxic fresh water/ marine water lens. The purpose of these studies is to determine the types of organisms present in the areas where the toxicity is present for sufficient duration to be potentially adverse to aquatic life.

If potentially significant marine zooplankton are present in the Bay toxic waters, then caged organism and/or laboratory studies may need to be conducted to determine if they are sensitive to the conditions that are toxic to the standard test organism used in these studies, mysids. The caged organism studies where exposure occurs during a runoff event would provide information on whether the marine zooplankton that migrate into the potentially toxic fresh water/marine water lens are killed during the period of time that this lens exists. These studies would need to be done in follow-on studies

to this 205(j) project as part of a renewal of the project beyond the current two-year grant period which ends in the summer of 1999. Consideration will be given to whether there are fresh water zooplankton that enter Upper Newport Bay in a stormwater runoff event that could survive in Upper Newport Bay when the stormwater runoff is mixed with the Bay waters. It is expected that most of the San Diego Creek zooplankton will be killed by the salinity of the Bay when the Creek and Bay waters mix.

If it is established that there are marine zooplankton that are likely killed by the toxic conditions that occur in stormwater runoff events, then an assessment will need to be made on whether the potentially impacted zooplankton are important components of the Upper Newport Bay ecosystem. If they are important, then a reduction in toxicity would lead to significantly improved aquatic life-related beneficial uses of the Bay, where key organisms in the Bay Waters depend on Upper Newport Bay as important nursery grounds for larval forms of the organisms.

Because of the complexity of the regulatory process that depends on demonstrating that the Upper Newport Bay ecosystem is currently being significantly impaired by the OP pesticide and the currently unknown caused toxicity, it is likely that the TMDL for control of toxicity, and diazinon and chlorpyrifos will be based on a Phase 1 assumed percent reduction of the total toxic loads and the OP pesticide loads to Upper Newport Bay by each of the major sources, urban residential, agricultural and commercial nurseries as well as any others that are identified through further studies.

During the remainder of this project the focus of the evaluation of the water quality significance of the aquatic life toxicity will be on Upper Newport Bay and its aquatic life resources. It is being assumed that if the toxicity that is found throughout the Upper Newport Bay watershed is controlled so that it is either not present in San Diego Creek as it enters Upper Newport Bay or is judged to be insignificant to the beneficial uses of Upper Newport Bay, that the potential adverse impacts of this toxicity on the beneficial uses of San Diego Creek and its tributaries will be at least initially adequately addressed. It is possible that as part of the Phase 2 or subsequent phases of the TMDL for toxics and for OP pesticide toxicity control that the toxicity that enters the tributaries of Upper Newport Bay does not persist into the Bay. This is an issue that may need to be addressed in follow-on studies to this project.

An area of particular concern is the very high levels of *Ceriodaphnia* toxicity that were found in August 1998 dry weather flow in the Hines Channel just downstream from the two commercial nurseries. From the limited information that is available it appears that groundwater input to the Hines Channel and downstream channels diluted the high levels of toxicity found in Hines Channel just downstream of the two commercial nurseries. It should be noted however, that at this time no sampling of agricultural irrigation return water (tail water) for aquatic life toxicity has been conducted. It is possible that at some time during the year, but not necessarily at all times, agricultural tail water in the Upper Newport Bay watershed could also be highly toxic to *Ceriodaphnia* and other forms of aquatic life. This is an area that needs to be investigated in subsequent studies.

Sources of Toxicity And OP Pesticides, Diazinon And Chlorpyrifos. Independent of the regulatory approach adopted in the TMDLs that will be implemented by 2002, there is need for information on the sources of known and unknown caused toxicity, diazinon and chlorpyrifos that leads to aquatic life toxicity in Upper Newport Bay tributaries as well as the Bay. Thus far the Evaluation Monitoring Demonstration Project and this 205(j) project have focused the sampling and toxicity assessment on San Diego Creek at Campus Drive as it enters Upper Newport Bay. Selected sampling of other Bay tributaries such as the Santa Ana Delhi Channel as well as within the San Diego Creek watershed has

been conducted. In the future, associated with the Santa Ana Regional Water Quality Control Board's need for information on the sources of aquatic life toxicity and diazinon and chlorpyrifos, a more detailed systematic sampling of the stormwater runoff events should be conducted. This sampling program should be designed to define the major sources of toxicity and diazinon and chlorpyrifos for San Diego Creek and its tributaries. The implementation of the needed watershed monitoring program is beyond the scope and funding of this 205(j) project. A discussion of the components of this program is presented below.

Measurements should be made of *Ceriodaphnia* toxicity with and without PBO in a dilution series to assess the total magnitude of the toxicity and the part of the toxicity that can be attributed to diazinon and chlorpyrifos. The diazinon and chlorpyrifos concentrations should be measured using ELISA procedures. This study program should, as in the past, define the magnitude of unknown caused toxicity in the samples.

As in the past, some of the samples should be subject to dual column GC analysis for a more complete scan of OP and carbamate pesticides. In addition to toxicity and chemical measurements, stream flow measurements/estimates should be made. The flow measurements made at the time of sample collection should enable an estimate to be made of the total mass of toxicity and diazinon and chlorpyrifos that passes a sampling location during a runoff event. This approach should be used to attempt to develop a mass balance of the estimated toxicity and OP pesticide loads from various parts of the San Diego Creek watershed compared to the total loads measured at Campus Drive.

Further, some additional ELISA testing of the stormwater runoff samples taken at various times during the hydrograph should be conducted to confirm what has been found in this past year's study, that the diazinon and chlorpyrifos concentrations present in the stormwater runoff do not change significantly during a runoff event. This situation may change as sampling is done closer to the ultimate source of the OP pesticides due to first flush effects.

Grab sampling should be used for all tributary sampling during these studies. It is possible that at an appropriate secured sampling station such as Campus Drive, composite samples should be taken to compare the results of the grab sampling to a composite sample of a runoff event.

It is suggested that samples be collected from several major stormwater runoff events at the following locations:

- San Diego Creek at Campus Drive
- San Diego Creek at Culver Drive,
- Peters Canyon Channel at Barranca Parkway
- Santa Ana – Santa Fe Channel at Peters Canyon Channel Confluence
- Central Irvine Channel at Peters Canyon Channel Confluence
- Rattlesnake Canyon Channel at Peters Canyon Channel Confluence
- Marshburn Channel at San Diego Creek
- Bee Canyon Channel at San Diego Creek
- Borrego Canyon Channel at San Diego Creek
- Serrano Channel at Canada Channel

The sampling program should be an "active" rather than "passive" sampling and data review program (see Lee and Jones 1983) where appropriate modifications of the sampling program should be made as needed based on the results obtained in the previous monitoring. For example, if a particular sampling station shows high toxicity compared to that expected, then additional sampling within that

subwatershed should be undertaken. The sampling sites indicated above will allow an assessment of the relative magnitudes of toxicity from the major portions of the watershed, with the goal of providing information to develop a TMDL for toxics.

Since residential use of the OP pesticides, diazinon and chlorpyrifos, are the primary uses in the Upper Newport Bay watershed, a special purpose study program should be conducted to determine the potential significance of various residential uses, structural for termite and ant control versus lawn and garden pest control, as a source of stormwater runoff associated toxicity. As delineated in DPR (1995) pesticide use data for Orange County, by far the greatest use of the OP pesticides diazinon and chlorpyrifos applied by commercial applicators is for structural purposes. At this time, however, it is unclear whether such uses represent significant sources of OP pesticides that lead to stormwater runoff toxicity. It is possible that if properly applied by a commercial applicator, the OP pesticides used for termite and ant control do not represent a significant source of stormwater runoff associated toxicity. However, it is likely that any use of the OP pesticides for lawn and garden pest control by commercial applicators and/or the public can lead to stormwater runoff associated toxicity. Therefore, it will be important to determine at several locations within the Upper Newport Bay watershed the significance of various residential uses of the OP pesticides as a cause of aquatic life toxicity in stormwater runoff. The details of these studies remain to be developed. They should involve measurement of stormwater runoff associated pesticides and toxicity on residential properties where a controlled application of the pesticides has taken place.

Thus far this project has focused on the OP pesticides diazinon and chlorpyrifos as a potential cause of the *Ceriodaphnia* toxicity found in the stormwater runoff that is measured at San Diego Creek as it enters Upper Newport Bay. Since there has been readily measurable amounts of unknown causes of toxicity in stormwater runoff in the Upper Newport Bay watershed, some samples of the San Diego Creek stormwater runoff have been submitted for dual column GC analysis in order to determine whether there are other OP pesticides or carbamate pesticides that are causing *Ceriodaphnia* toxicity. It was through this approach that methomyl, a carbamate pesticide was discovered at sufficient concentrations in San Diego Creek as it enters Upper Newport Bay during a fall 1996 stormwater runoff event, to be acutely toxic to *Ceriodaphnia*. The use of methomyl in the Upper Newport Bay watershed in 1995 was exclusively for agricultural purposes on cabbage, corn, strawberries, lettuce, beans and tomatoes.

There could be a variety of other OP as well as other types of pesticides used in the Upper Newport Bay watershed by residential, agricultural and commercial institutions including nurseries which are responsible for the *Ceriodaphnia* and mysid toxicity that is found in San Diego Creek as it enters Upper Newport Bay. It has been found that only a small amount of pesticide loss (about a pound or so over the year) from the point of application compared to the total pesticide applied can account for the *Ceriodaphnia*/mysid toxicity found in this study in San Diego Creek stormwater runoff. While typically pesticide investigation programs focus on large uses of pesticides, some of the smaller uses could be important sources causing *Ceriodaphnia*/mysid toxicity.

As an example, about 4,000 pounds of methomyl were applied to agricultural crops in Orange County in 1995, yet it was detected as a potential toxicant above the LC₅₀ for *Ceriodaphnia* in San Diego Creek water as it enters Upper Newport Bay. Propetamphos is an example of an OP pesticide that is being used in the Upper Newport Bay watershed for residential pest control purposes that could be responsible for part of the unknown caused toxicity in San Diego Creek as it enters Upper Newport

Bay. This pesticide can only be used by commercial applicators. In 1990, which is the most recent information available from DPR, over 7,800 pounds were applied for structural pest control in Orange County. Another 23 pounds were applied that year for regulatory pest control. No information is available on the toxicity of this pesticide to *Ceriodaphnia*. Further, it has been found that the conventional GC scan for OP pesticides is not typically set up to detect this chemical. Therefore this is one of possibly many OP pesticides that could be present in residential stormwater runoff that could be contributing to the unknown caused *Ceriodaphnia* toxicity in Orange County.

It will be important in any Upper Newport Bay pesticide source studies to examine each of the sources of *Ceriodaphnia* and mysid toxicity to determine whether there is unknown caused toxicity that cannot be accounted for by diazinon and chlorpyrifos. This type of study could reveal that there are a variety of other OP as well as other pesticides used in residential, agricultural and commercial nurseries that are contributing to the *Ceriodaphnia*/mysid toxicity problem that is occurring in San Diego Creek water as it enters Upper Newport Bay.

A new area of potential concern with respect to pesticide impacts on San Diego Creek and Upper Newport Bay is the recent finding that fire ants have become established in Orange County. This could lead to the use of one or more pesticides as part of an effort to try to eradicate fire ants before they spread further through the County. It will be important to keep track of what pesticides are used and where and when this use takes place in any fire ant control program. Also it may be desirable to do some stormwater runoff monitoring from areas that are treated for fire ant control.

Future TIE Studies. Toxicity investigation evaluations (TIEs) have been used throughout the Evaluation Monitoring Demonstration Project and this 205(j) project to gain insight into the cause of the *Ceriodaphnia* and mysid toxicity that is found in San Diego Creek watershed stormwater runoff as it enters Upper Newport Bay. The use of PBO with the ELISA testing is a highly directed, fairly specific TIE for OP pesticides and in particular, diazinon and chlorpyrifos. Further the recently completed expanded conventional TIE that was conducted on the San Diego Creek stormwater runoff collected at Campus Drive for the November 8, 1998 storm, demonstrated that heavy metals are not likely a significant cause of the toxicity that was found in this sample. There is, however, a substantial amount of the *Ceriodaphnia* and mysid toxicity that at this time is due to unknown causes. As reported by Dr. J. Miller Lee et al.(1999) Appendix B, efforts to identify the cause of this toxicity have thus far proven to be unsuccessful. Therefore, one of the issues that needs to be addressed is what further work should be done to identify the cause of the unknown caused toxicity.

A substantial part of the unknown-caused toxicity appears to be derived from the use of pesticides and other chemicals by one or both commercial nurseries that are located just upstream of the Hines Channel sampling point. It appears from the data available that a part of an unknown caused toxicity that has been measured at the San Diego Creek Campus Drive station and the Peters Canyon Channel Barranca Parkway station is derived from the Hines Channel and likely the commercial nurseries and/or upstream agricultural areas. A set of samples was obtained in the San Diego Creek watershed on November 8, 1998 that provides information on other sources of unknown caused toxicity.

The testing of the November 8, 1998 runoff waters for toxicity to *Ceriodaphnia* showed that San Diego Creek at Campus Drive and Harvard Avenue, Peters Canyon Channel at Barranca Parkway and Hines Channel were highly toxic where 12.5% dilution killed all *Ceriodaphnia* in 24 hours. PBO only partially neutralized this toxicity on the highly diluted samples. The total *Ceriodaphnia* toxicity

in these samples was on the order of 16 toxic units. This is the first time that San Diego Creek above where it confluences with Peters Canyon Channel has been tested in this study. It is of interest to find that there were high levels of *Ceriodaphnia* toxicity in the main stem of San Diego Creek above where it confluences with Peters Canyon Channel and, most importantly, that there were high levels of *Ceriodaphnia* toxicity that could not be neutralized by PBO, indicating that there is a source(s) of unknown-caused toxicity in the San Diego Creek watershed that is not associated with the Hines Channel. The complete results from the November 8, 1998 stormwater runoff testing will be presented in the final 205(j) report which should be available this summer.

The watershed studies that should be conducted in a separate project should attempt to identify other sources of unknown caused toxicity, as well as to quantify how much of the unknown caused toxicity that is present in the Peters Canyon Channel and its tributaries branch of the San Diego Creek watershed is derived from the Hines Channel. Also, studies need to be conducted on the sources of the unknown caused toxicity in San Diego Creek above where it confluences with the Peters Canyon Channel.

There is need to determine if any further efforts should be made to identify, through more comprehensive TIEs, the specific chemicals responsible for the unknown caused toxicity that is present in the Hines Channel just downstream from the commercial nurseries and agricultural areas. There is concern about devoting the limited funds available to this area, since large amounts of funds (\$10,000 per full TIE) could be spent for this purpose, in conducting full TIEs which may not identify all or even a substantial part of the cause of the unknown caused toxicity found in the samples in the Hines Channel sampling location. Further it is likely that the pesticide or other chemical mix that is responsible for the unknown caused toxicity, changes from season-to-season and could change from year-to-year as pesticide use is modified.

Further TIE work should be devoted to examining the cause(s) of the unknown caused toxicity if any is found in the stormwater runoff from the residential areas as well as from agricultural areas. For those situations where substantial amounts of unknown caused toxicity are found in stormwater runoff for more restricted types of land use, more comprehensive TIEs should be used to try to identify the cause(s) of this toxicity. The planning and implementation of this effort should be closely coordinated with the Santa Ana Regional Water Quality Control Board to best use the limited funds available.

An important aspect of further TIE work is an understanding of the uncertainty that exists in assessing the magnitude of the unknown caused toxicity present in a sample. The approach that has been used to estimate the toxicity due to the organophosphate pesticides involved dividing the ELISA measured concentrations by the LC_{50} and adding the two quotients to assess the known toxicity is subject to considerable variability. The LC_{50} s for *Ceriodaphnia* or mysids are not fixed, precise values but are subject to a number of factors that can influence their magnitude. These include the inherent variability in the toxicity tests used, as well as an ambient water effect on toxicity associated with how toxicity by a chemical such as diazinon is manifested to a test organism such as *Ceriodaphnia* in various types of ambient waters. The ambient water effects can be both positive or negative depending on the constituents in the water. Dr. Miller of AQUA-Science (personal communication, 1998) has indicated that he is finding enhanced toxicity of diazinon to *Ceriodaphnia* in certain ambient waters, compared to the toxicity found in standard laboratory waters. Such findings would reduce the magnitude of the unknown toxicity in a sample, proportionate to the enhanced toxicity associated with the ambient water

effects on toxicity. The net result is that the so-called known toxicity that is obtained by the procedures used in this investigation can easily vary \pm one or more toxic units.

There is also considerable uncertainty about the magnitude of the total toxicity present in the sample, based on the dilution series toxicity testing that is done. Another factor is that many of the analytical procedures used to identify unknown toxic components in a sample yield variable results, especially at low concentrations of constituents.

These factors result in a situation where any efforts to try to identify unknown caused toxicity through a TIE procedure should only be directed toward samples that repeatedly show at least a three toxic unit difference between the total toxicity measured in a sample through a dilution series and the estimated toxicity based on dividing the measured concentrations of diazinon and chlorpyrifos by the LC_{50} values.

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