Results of Aquatic Toxicity Testing Conducted During 1997-2000 in the Upper Newport Bay Orange County, CA Watershed[1]

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In the late 1980s/early 1990s, it was found that the concentrations of heavy metals in Upper Newport Bay Orange County, CA tributaries (San Diego Creek) and within the Bay occurred in stormwater runoff above US EPA water quality criteria for the protection of aquatic life from toxicity. Bailey, *et al.* (1993) reported at that time that toxicity to *Ceriodaphnia dubia* (a freshwater zooplankton - water flea) was present in stormwater runoff to the Bay. The cause of this toxicity was not identified.

Beginning in July 1996 an Evaluation Monitoring Demonstration Project, was conducted to determine whether San Diego Creek waters entering Upper Newport Bay were toxic to aquatic life. The Evaluation Monitoring Demonstration Project studies (Lee and Taylor, 1997; Silverado, 1997, Jones-Lee and Lee 1998) showed that the stormwater runoff in San Diego Creek as it enters Upper Newport Bay is toxic to *Ceriodaphnia* (freshwater zooplankton) and *Mysidopsis bahia (Americamysis bahia)* a marine zooplankton. San Diego Creek is the primary tributary of Upper Newport Bay. About half of the toxicity was found to be due to the organophosphate pesticides, diazinon and chlorpyrifos, used in urban areas for structural, lawn and garden pest control. The other half of the toxicity is due to unknown causes and appears to originate from residential, agricultural and/or commercial sources such as commercial nurseries in the upper part of the San Diego Creek watershed.

Beginning with the fall of 1997, as part of a US EPA sponsored 205(j) project, a total of seven stormwater runoff events were monitored for *Ceriodaphnia* toxicity in San Diego Creek as it enters Upper Newport Bay as well as at several locations within the Creek's watershed. In addition, three dry weather flow samples were taken of San Diego Creek and its tributaries from the fall of 1997 through August 1998. The monitoring program was expanded to include the Santa Ana Delhi Channel, which is the next largest tributary to Upper Newport Bay. Further, the test organism suite was expanded to include *Mysidopsis*

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1 Reference as, Lee, G. F., and Taylor, S. "Results of Aquatic Toxicity Testing Conducted During 1997-2000 within the Upper Newport Bay Orange County, CA Watershed" Report of G. Fred Lee & Assoicates, El Macero, CA (2001)
http://www.gfredlee.com/Watersheds/295-319-tox-paper.pdf

bahi. A total of 140 toxicity tests were conducted on Upper Newport Bay tributary water through August 1998.

Beginning in September 1999 through May 2000, as part of a US EPA sponsored 319(h) project, two dry weather (September 29, 1999 and May 31, 2000) and three stormwater runoff events (January 25, 2000, February 12, and 21, 2000) were sampled at up to 10 locations in the Orange County, CA, Upper Newport Bay Watershed. A total of about 375 toxicity tests and associated selected chemical measurements were made on these samples. The 10 locations were selected to obtain stormwater runoff from several limited land use activities (residential, agriculture, open space and commercial nurseries) in the watershed upstream of the sampling locations. All stormwater runoff samples were highly toxic to *Ceriodaphnia dubia* and *Mysidopsis bahia*. In general, no toxicity was found to fathead minnow larvae or the alga *Selenastrum.* This report presents a summary of these studies. Further information on these studies is provided in Lee and Tayor (1999) 205(j) and Lee et al. (2001) 319(h) project final reports.

CHARACTERISTICS OF UPPER NEWPORT BAY AND ITS WATERSHED.

Upper Newport Bay is one of the major estuaries/inland bays in southern California. 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. Figure 1 presents the general features of the watershed with respect to San Diego Creek and Upper Newport Bay. The watershed has been greatly altered due to development. 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, commercial, industrial, recreational, and open space land uses. 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. Table 1 summarizes the general land uses within the watershed. The central portion of the Upper Newport Bay 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. Table 2 provides tributary drainage areas and flow rates at locations coincident or near the primary stormwater runoff sampling point (Campus Drive) described in this report.

San Diego Creek at Culver Drive is upstream of the Peters Canyon Channel confluence. Peters Canyon Channel drains an area of about 44.7 square miles; the watershed is comprised of about 50 percent agricultural use and 50 percent urban areas. It is estimated that over half of the remaining agricultural area in the watershed is tributary to Peters Canyon Channel. San Diego Creek at Jamboree Road represents the watershed outlet at Upper Newport Bay. The Creek discharges to Upper Newport Bay about 500 feet west of the Jamboree Road crossing.

Table 1
Land Use—San Diego Creek - (1990 Data)[1]

Land Use	Percent of Watershed	Area (mi^2)
Residential	15.0	17.9
Commercial	8.0	9.5
Industrial	6.3	7.5
Open space/vacant	23.1	27.5
Agriculture/ranching	10.0	11.9
Public	0.3	0.4
Recreation	0.3	0.4
Transportation and communication/utility	1.2	1.4
Roads	35.8	42.6
Sum	100	119.1

[1] Data are based on projections for ultimate buildout.
Source: OCEMA, (1990), and SRWQCB, (2000)

Table 2
Discharges for San Diego Creek

Location	Area (sq. mi.)	Q_{100} (cfs)	Q_2 (cfs)
Near Culver Dr.	42.9	18,050	3,700
At Jamboree Rd.	119.2	34,300	7,000

Source: Simons, Li and Asoociates (1987)

Two discharge frequency values are provided in Table 2, Q_{100} and Q_{2}. The value for Q_{100} represents the discharge at the point indicated for a storm with a hypothetical return period of once every 100 years. A storm of this magnitude has a 1 percent chance of occurring in any given year. A 100-year return frequency represents the design return period used for San Diego Creek flood control improvements.

The Coast Highway divides the Newport Bay into upper and lower basins. Lower Newport Bay extends westward about three miles behind the Balboa Peninsula to Newport Boulevard (see Figure 2). 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 Department of Fish and Game.

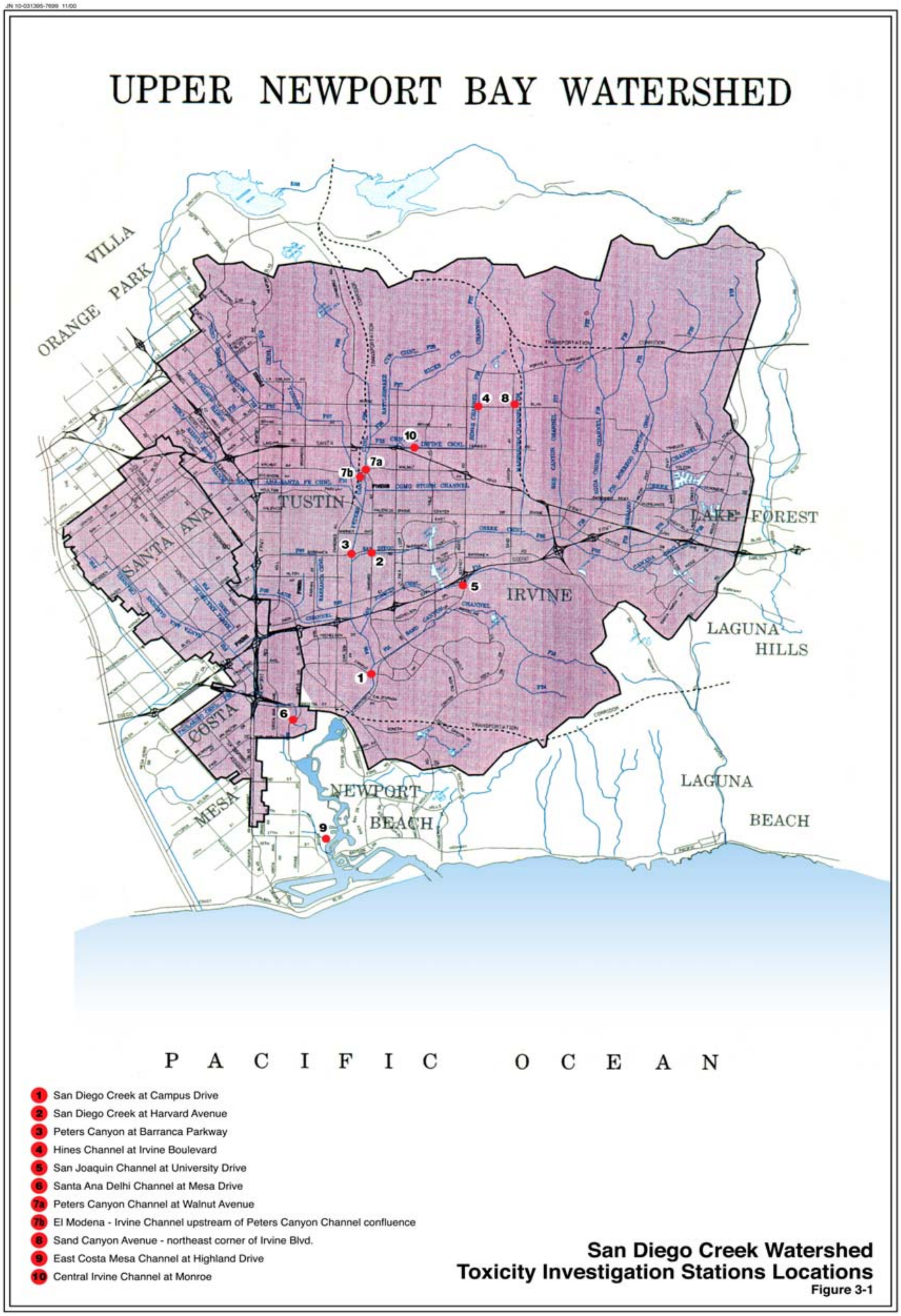


Figure 1 Map of Upper Newport Bay Watershed

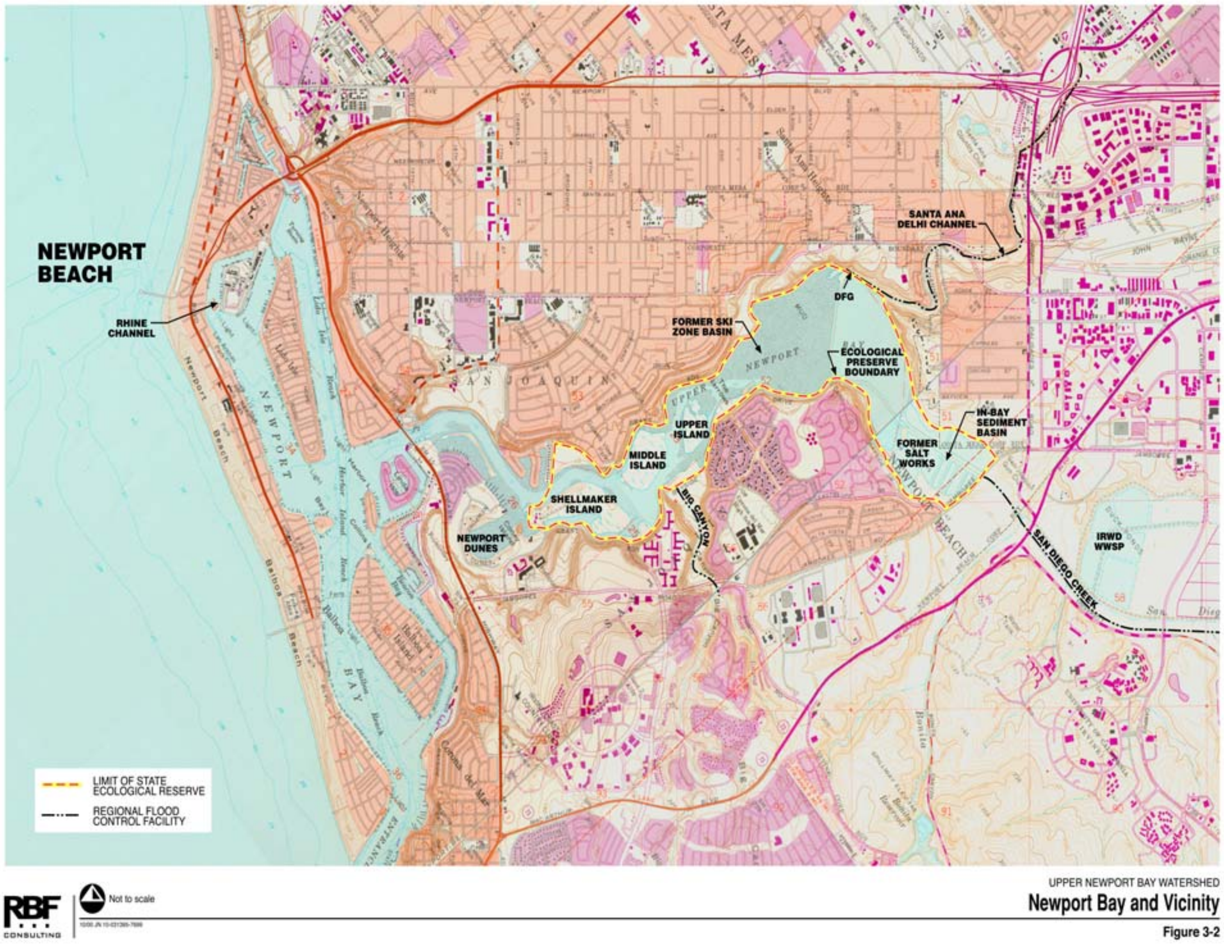


Figure 2 Upper Newport Bay area

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.

AQUATIC LIFE TOXICITY IN UPPER NEWPORT BAY TRIBUTARIES 1997 - 1999

A total of nine storm events were sampled during the 1997-99 winter seasons. Runoff from the first three storm events was sampled at San Diego Creek at Campus Drive. The storms occurred on September 25, November 12, and November 30, 1997. Subsequently, sampling locations were expanded to include Peters Canyon Channel at Barranca Parkway for storms occurring on December 6, 1997 and March 25, 1998. Sampling locations were further expanded to the Santa Ana Delhi Channel at Mesa Drive for the May 5 and May 12, 1998 storms. Sampling on November 8, 1999 further included sampling at Hines Channel at Irvine Boulevard and San Diego Creek at Harvard Avenue. Sampling on January 25-29 occurred at San Diego Creek at Campus Drive and at five stations in Upper Newport Bay.

A total of 5 dry weather low flow samples were collected. Dry weather flow sampling occurred on March 24, August 13 and August 25, 1998 at the Santa Ana Delhi Channel at Mesa, Hines Channel at Irvine Boulevard, the Central Irvine Channel just above where it confluences with Peters Canyon Channel at the I-5 crossing, Peters Canyon Channel at Barranca Parkway, and San Diego Creek at Campus Drive. The Peters Canyon at Barranca Parkway sample was taken just upstream of where Peters Canyon Channel confluences with San Diego Creek. "Dry weather" sampling took place on January 21st at San Diego Creek at Campus Drive, the Santa Ana Delhi Channel at Mesa Drive and at Hines Channel at Irvine Boulevard. While this sample was intended to be a dry weather sample, and there was no measured precipitation from rain gages just before or on January 21, 1999, the specific conductivity of San Diego Creek at Campus Drive indicated that it was somewhat less than what it should be for a true dry weather sample. At the time of sampling there was a light mist, which could have resulted in stormwater runoff from paved areas. The fact that this sample was toxic indicates that it may not be indicative of true dry weather conditions in San Diego Creek. "Dry weather" sampling also occurred on January 29th, exclusively at San Diego Creek at Campus Drive. The January 29th "dry weather" – low flow sampling occurred immediately following the January 25-27 storm event and may have been influenced by that event.

SAMPLE COLLECTION AND ANALYSIS PROCEDURES

The samples were collected in prewashed 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 were collected in three 1-gallon amber bottles 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). Field readings for electrical conductivity, pH and temperature were taken using a Hydac 900 portable meter, calibrated per manufacturer's instructions.

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 +/-1°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 impact 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 (1991) 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.

Summary of Results

The 1996 (Silverado, 1997 and Lee and Taylor, 1997) 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, eleven stormwater runoff events were monitored. In general the stormwater runoff samples were none toxic to fathead minor larve and the algal test organism. Table 3 presents a summary of the *Ceriodaphnia* toxicity results that have been found in the Upper Newport Bay watershed 1996-1998. 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 3 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 dilution of San Diego Creek water taken at Campus Drive during a stormwater event could be toxic to *Ceriodaphnia*.

Table 4 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 5 are from samples of San Diego Creek water taken at Campus Drive. The undiluted San Diego Creek sample was also toxic to *Mysidopsis bahia*. 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.

The toxicity testing of San Diego Creek water at Campus Drive using *Ceriodaphnia* during dry weather flow conditions during 1996 and 1997 were 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 toxicity to *Ceriodaphnia* found in the January 21, 1999 low flow sample was likely due to runoff from areas where the toxicants were used, as well as discharges from upstream sources such as the commercial nurseries. While the January 21, 1999 sample was intended to be a dry weather low flow sample, the fact that the specific conductance of the sample was lower than normal low flow conditions indicates that there was some dilution of the San Diego Creek base flow with surface runoff.

Table 3
Summary of *Ceriodaphnia* Toxicity Test Results for Upper Newport Bay Watershed

Date	Location (Treatment)	Duration of Test (days)	% Mortality[1,2] (days to 100% kill)	Measured TUa	Ratio TUa(meas): 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 µg/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 µg/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)		
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)		

Table 3
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(meas): TUa(expected)
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)		
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)		

Table 3
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(meas): TUa(expected)
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		
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% +50µg/L PBO	4	100 (3)		
3/25/98	Peters Canyon Channel @ Barranca 25%	4	100 (2)		
3/25/98	Peters Canyon Channel @ Barranca 25% +50µg/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% +50µg/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 3
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 µmhos/cm - 66% dilution)	7	0		
8/13/98	San Diego Creek @ Campus (diluted to 2000 µmhos/cm - 66% dilution) + PBO	7	0		
8/13/98	Peters Canyon Channel @ Barranca (diluted to 2000 µmhos/cm - 68% dilution)	7	100 (5)		

Table 3
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(meas): TUa(expected)
8/13/98	Peters Canyon Channel @ Barranca (diluted to 2000 µmhos/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 2000µmhos/cm - 74% dilution)	7	10 Impaired Reproduction		
8/13/98	Santa Ana Delhi Channel (diluted to 2000 µmhos/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 3
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 2000µmhos/cm - 69% dilution)	7	0		
8/25/98	San Diego Creek @ Campus (diluted to 2000µmhos/cm - 69% dilution) + PBO	7	0		
8/25/98	Santa Ana Delhi Channel (diluted to 2000µmhos/cm - 75% dilution)	7	0		
8/25/98	Santa Ana Delhi Channel (diluted to 2000µmhos/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		
11/8/98	San Diego Creek at Campus	7	100 (1)	>16	>3
11/8/98	Peters Canyon Channel at Barranca	7	100 (1)	>16	>3
11/8/98	Peters Canyon Channel at Barranca + PBO	7	100 (1)		
11/8/98	Harvard Ave	7	100 (1)		
11/8/98	Harvard Ave + PBO	7	100 (1)		
11/8/98	Hines Channel	7	100 (1)	>16	>1.5
11/8/98	Hines Channel + PBO	7	100 (1)		
11/8/98	Santa Ana Delhi Channel	7	100 (4)		

Table 3
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)
11/8/98	Santa Ana Delhi Channel + PBO	7	20		
11/8/98	25% San Diego Creek at Campus	4	100 (1)		
11/8/98	25% San Diego Creek at Campus + PBO	4	100 (1)		
11/8/98	12.5% San Diego Creek at Campus	4	100 (1)		
11/8/98	6.25% San Diego Creek at Campus	4	100 (2)		
11/8/98	3.13% San Diego Creek at Campus	4	0		
11/8/98	1.57% San Diego Creek at Campus	4	0		
11/8/98	25% Peters Canyon Channel at Barranca	4	100 (1)		
11/8/98	25% Peters Canyon Channel at Barranca + PBO	4	100 (1)		
11/8/98	12.5% Peters Canyon Channel at Barranca	4	100 (2)		
11/8/98	6.25% Peters Canyon Channel at Barranca	4	100 (4)		
11/8/98	3.13% Peters Canyon Channel at Barranca	4	5		
11/8/98	25% Harvard Ave	4	100 (1)		
11/8/98	25% Harvard Ave + PBO	4	100 (1)		
11/8/98	12.5% Harvard Ave	4	100 (1)		
11/8/98	6.25% Harvard Ave	4	100 (2)		
11/8/98	3.13% Harvard Ave	4	0		
11/8/98	25% Hines Channel	4	100 (1)		
11/8/98	25% Hines Channel + PBO	4	100 (2)		
11/8/98	12.5% Hines Channel	4	100 (1)		
11/8/98	6.25% Hines Channel	4	100 (2)		
11/8/98	3.13% Hines Channel	4	5		

Table 3
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):TU a(expected)
11/8/98	12.5% San Diego Creek at Campus	4	100 (1)		
11/8/98	12.5% San Diego Creek at Campus + PBO	4	20		
11/8/98	12.5% Peters Canyon Channel at Barranca	4	100 (1)		
11/8/98	12.5% Peters Canyon Channel at Barranca + PBO	4	5		
11/8/98	12.5% Harvard Ave	4	100 (2)		
11/8/98	12.5% Harvard Ave + PBO	4	0		
11/8/98	12.5% Hines Channel	4	100 (1)		
11/8/98	12.5% Hines Channel + PBO	4	10		
11/8/98	Hines Channel C8 Solid Phase Extracted Water	4	100 (1)		
11/8/98	San Diego Creek at Campus C8 Solid Phase Extracted Water	4	60		
1/21/99	San Diego Creek at Campus	7	100 (1)	>2	>1
1/21/99	Hines Channel	7	100 (1)	12.5	>1
1/21/99	Santa Ana Delhi Channel	7	90		
1/21/99	100% San Diego Creek at Campus	4	100 (1)		
1/21/99	50% San Diego Creek at Campus	4	100 (2)		
1/21/99	25% San Diego Creek at Campus	4	10		
1/21/99	12.5% San Diego Creek at Campus	4	5		
1/21/99	6.25% Hines Channel	4	100 (1)		
1/21/99	3.13% Hines Channel	4	63		
1/21/99	1.56% Hines Channel	4	0		
1/21/99	0.78% Hines Channel	4	5		
1/21/99	100% San Diego Creek at Campus	4	100 (1)		

Table 3
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)
1/21/99	100% San Diego Creek at Campus + PBO	4	100 (3)		
1/21/99	12.5% Hines Channel	4	100 (1)		
1/21/99	12.5% Hines Channel + PBO	4	100 (2)		
1/25/99	San Diego Creek at Campus (1000hrs)	7	100 (1)		
1/25/99	San Diego Creek at Campus (1530hrs)	7	100 (1)		
1/26/99	San Diego Creek at Campus	7	100 (1)	>4	>1
1/25/99	25% San Diego Creek at Campus (1000hrs)	4	100 (1)		
1/25/99	12.5% San Diego Creek at Campus (1000hrs)	4	20		
1/25/99	6.25% San Diego Creek at Campus (1000hrs)	4	10		
1/25/99	3.13% San Diego Creek at Campus (1000hrs)	4	0		
1/25/99	25% San Diego Creek at Campus (1530hrs)	4	100 (2)		
1/25/99	12.5% San Diego Creek at Campus (1530hrs)	4	0		
1/25/99	6.25% San Diego Creek at Campus (1530hrs)	4	0		
1/25/99	3.13% San Diego Creek at Campus (1530hrs)	4	0		
1/26/99	25% San Diego Creek at Campus	4	100 (2)		
1/26/99	12.5% San Diego Creek at Campus	4	0		
1/26/99	6.25% San Diego Creek at Campus	4	5		
1/26/99	3.13% San Diego Creek at Campus	4	0		
1/25/99	50% San Diego Creek at Campus (1000hrs)	4	100 (1)		

Table 3
Summary of *Ceriodaphnia* Toxicity Test Results for Upper Newport Bay Watershed Stormwater Runoff (continued)

Date	Location (Treatment)	Duration of	% Mortality[1,2]	Measured	Ratio
1/25/99	50% San Diego Creek at Campus (1000hrs) + PBO	4	100 (2)		
1/25/99	50% San Diego Creek at Campus (1530hrs)	4	100 (1)		
1/25/99	50% San Diego Creek at Campus (1530hrs) + PBO	4	100 (2)		
1/26/99	50% San Diego Creek at Campus	4	100 (1)		
1/26/99	50% San Diego Creek at Campus + PBO	4	100 (2)		
1/27/99	San Diego Creek at Campus	7	100 (1)	>4	>2.5
1/27/99	100% San Diego Creek at Campus	4	100 (1)		
1/27/99	50% San Diego Creek at Campus	4	100 (1)		
1/27/99	25% San Diego Creek at Campus	4	100 (3)		
1/27/99	12.5% San Diego Creek at Campus	4	0		
1/27/99	6.25% San Diego Creek at Campus	4	15		
1/27/99	50% San Diego Creek at Campus	4	100 (1)		
1/27/99	50% San Diego Creek at Campus + PBO	4	60		

[1] 100% sample unless otherwise indicate
[2] Number in parenthesis indicates number of days to 100% mortality.
* 100µg/L PBO added unless noted otherwise

Table 4
Summary of *Mysidopsis bahia* Toxicity Results for San Diego Creek Stormwater Runoff at Campus Drive

Date	Location (Treatment)	% Mortality (days)	Measured TUa	Calc. TUa Based on Chlorpyrifos Concentrations	Ratio TUa (measured): TUa(expected)
11/30/97	San Diego Creek	88 (7)	8	2	4
11/30/97	San Diego Creek 100%	50 (7)		2.5	
11/30/97	San Diego Creek 50%	10 (7)			
11/30/98	San Diego Creek 25%	10 (7)			
11/30/97	San Diego Creek 12.5%	5 (7)			
11/30/97	San Diego Creek 6.25%	0 (7)			
12/6/97	San Diego Creek	62 (7)		2.5	
3/25/98	San Diego Creek (C) 100%	12 (7)		0	
3/25/98	San Diego Creek (D) 100%	10 (7)		0	
5/12/98	San Diego Creek 100%	100 (1)	>8	2	>5
5/12/98	San Diego Creek 50%	100 (2)			
5/12/98	San Diego Creek 25%	65 (3)			
5/12/98	San Diego Creek 12.5%	5 (7)			
5/12/98	San Diego Creek 6.25%	5 (7)			
11/8/98	San Diego Creek	100 (1)	>16	14	>1
11/8/98	San Diego Creek 100%	100 (1)			
11/8/98	San Diego Creek 50%	100 (1)			
11/8/98	San Diego Creek 25%	100 (1)			
11/8/98	San Diego Creek 12.5%	100 (2)			
11/8/98	San Diego Creek 6.25%	100 (4)			
1/25/99	San Diego Creek C2 100%	100 (2)	3	1.5	2
1/25/99	San Diego Creek C2 50%	100 (3)			
1/25/99	San Diego Creek C2 25%	10 (7)			
1/25/99	San Diego Creek C2 12.5%	5 (7)			
1/25/99	San Diego Creek C2 6.25%	20 (7)			

Table 5 presents a summary of information on the respective toxicities (LC_{50}) of diazinon, chlorpyrifos, methomyl, carbaryl, and malathion to *Ceriodaphnia* and *Mysidopsis bahia*. These values are used to estimate the toxicity of the samples based on the concentrations of diazinon and chlorpyrifos and the other pesticides for which there is LC_{50} data measured in the samples. The Table 3 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.

Table 5
Toxicity of Diazinon and Chlorpyrifos to *Ceriodaphnia* and *Mysidopsis bahia*

Constituent	*Ceriodaphnia* LC_{50} (ng/L)	*Mysidopsis bahia* LC_{50} (ng/L)
Diazinon	450	4,500
Chlorpyrifos	80	35
Methomyl	5,560	-
Carbaryl	3,500 – 5,200	-
Malathion	1,400	-

- No information available.

Table 6 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 shows that frequently the concentrations of diazinon and chlorpyrifos in the 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 6 also presents the expected acute *Ceriodaphnia* toxic units (TUa) based on the sum of the diazinon and chlorpyrifos concentrations, plus other pesticides for which LC_{50} data was available, divided by the LC_{50} for the respective compounds. Examination of Table 6, 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.

The November 30, 1997 San Diego Creek Campus Drive sample contains sufficient chlorpyrifos to cause about two acute toxic units to *Mysidopsis bahia*. 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 bahia* 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 bahia* (see Table 5). The data presented in Table 4 shows that there is appreciable toxicity to *Mysidopsis bahia* in the San Diego Creek water during a stormwater runoff event that cannot be accounted for based on the chlorpyrifos concentrations measured in the sample that was tested for toxicity. The cause of this toxicity to *Mysidopsis bahia* 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 present in the headwaters of the San Diego Creek watershed.

During several of the stormwater runoff events that have been monitored during 1998-99, 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 3. They show that, in general, the grab samples of San Diego

Table 6
Summary of Diazinon and Chlorpyrifos Concentrations in Upper Newport Bay Watershed Tributaries

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 6
Summary of Diazinon and Chlorpyrifos Concentrations in Upper Newport Bay Watershed Tributariescontinued)

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
5/25/98	Hines Channel	2,500	110	6.5
8/13/98	San Diego Creek @ Campus[3] Base Flow	117	67	1.5
8/13/09	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
11/8/98	San Diego Creek at Campus	<50	500	5.5
11/8/98	Peters Canyon Channel at Barranca	670	430	6
11/8/98	Hines Channel	4,100	140	10.5

Table 6
Summary of Diazinon and Chlorpyrifos Concentrations in
Upper Newport Bay Watershed Tributariescontinued)

Date	Location (Time – hrs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)	Expected TUa
11/8/98	Santa Ana Delhi Channel	<50	<50	<1
11/8/98	Harvard Ave	<50	400	4.5
1/21/99	Hines Channel	1,400	670	10.5
1/21/99	San Diego Creek at Campus	570	70	2
1/25/99	San Diego Creek at Campus (1000hrs)	960	<50	2
1/25/99	San Diego Creek at Campus (1530hrs)	910	<50	2
1/26/99	San Diego Creek at Campus	880	<50	2

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

Creek water collected at Campus Drive taken during a runoff event are representative of what is found over the runoff event (hydrograph).

Table 3 presents the ratio of the measured TUa based on toxicity testing using dilutions of the San Diego Creek sample to the expected toxicity based on using the LC_{50} values for diazinon and chlorpyrifos, summed for additive toxicity. Examination of this column in Table 3 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/Stockton 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/Stockton 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.

In an effort to begin to address the nature and source 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. 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 and Taylor (1999) Thus far the more comprehensive TIE investigations have not provided definitive results on the cause of the unknown *Ceriodaphnia* toxicity.

In an effort to define possible sources of the unknown caused toxicity, limited scope forensic studies were done in the Peters Canyon 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 downstream of two large commercial nurseries, one of which (Hines Nursery) exists on each side of the Channel just upstream of the sampling location. The other (El Modena Nursery) discharges runoff 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 6, 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 25 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.

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.

The November 8, 1998 study of the Upper Newport Bay watershed of the first major stormwater runoff event for the fall of 1998 showed somewhat similar results to the August 1998 studies, where high concentrations of OP pesticides and aquatic life toxicity were found in Hines Channel just downstream from the nurseries. In excess of 16 TUa of *Ceriodaphnia* toxicity was found in the November 8, 1998 Hines Channel runoff waters. About 20 TUa could be accounted for based on diazinon, chlorpyrifos and methomyl.

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 pyrethroid based psesticides.

The August 13, 1998 Hines Channel sample was nontoxic to fathead minnow larvae. It did, however, show toxicity to the algae, *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 presented in Table 3, 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.

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.

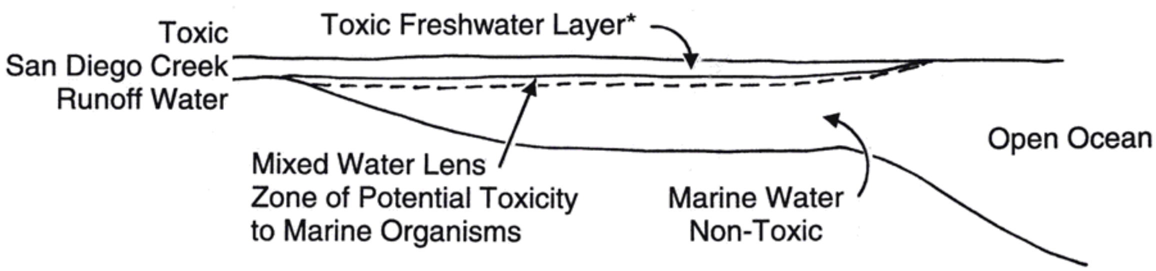
The stormwater runoff sampling that has been conducted since the fall of 1996 at various locations in the San Diego Creek watershed has demonstrated that with each stormwater runoff event, there is appreciable *Ceriodaphnia* and *Mysidopsis* toxicity contributed from the

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. Further, the Hines Channel water in August 1998 and January 21, 1999 was found to contain substances that were toxic to *Selenastrum*.

EVALUATION OF THE WATER QUALITY SIGNIFICANCE OF STORMWATER RUNOFF *CERIODAPHNIA*/MYSID TOXICITY TO UPPER NEWPORT BAY

Since the zooplankton present in San Diego Creek water will be killed due to salinity in Upper Newport Bay as the Creek water mixes with the 30 ppt marine waters, 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 fresher water lens on top of the Bay marine waters during and following a stormwater runoff event. This relationship is shown in Figure 3. If it is

Figure 3



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.

assumed that 10 TUa of acute toxicity is 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.

During the fall 1998/January 1999 studies an excess of 16 TUa for *Ceriodaphnia* and mysids was found in stormwater runoff to Upper Newport Bay. This means that the expected lower-most salinity, which should be toxic to organisms with mysid sensitivity, would be about 6 to 10 ppt. Salinities greater than this amount would not be expected to be toxic to mysids.

Lee et al (2000) discussed that is need 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 to 10 ppt that would persist for at least two to three 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. These results were presented by Lee and Taylor (1999). They show that under certain stormwater runoff conditions there could be substantial water in Upper Newport Bay that would be present as a "fresh water" lense where the Bay waters could be toxic to some marine zooplankton.

319(H) PROJECT RESULTS

As part of developing the Clean Water Act 303(d) list of impaired waterbodies in the Upper Newport Bay Watershed, the Santa Ana Regional Water Quality Control Board (SARWQCB) listed Upper Newport Bay and its tributaries as Clean Water Act 393(d) impaired, based on excessive concentrations of heavy metals, excessive bioaccumutlation of organochlorine legacy pesticides such as DDT, PCBs (OCls) and aquatic life toxicity. This listing led to establishing total maximum daily loads (TMDLs) to control the aquatic life toxicity, excessive OCl bioaccumulation and excessive heavy metals.

A US EPA 319(h) grant was obtained to determine the occurrence of toxicity throughout the Upper Newport Bay Watershed and, to the extent that funds available would allow, identify primary sources of toxicity. Also, additional work was to be done in the 319(h) project on identifying the constituents responsible for the unknown-caused toxicity. As originally envisioned, the results of this 319(h) study would serve as the basis by which the SARWQCB would establish the TMDL and its allocation among sources.

The sampling station number/locations for this part of the study are as follows:

- 1 San Diego Creek at Campus Drive
- 2 San Diego Creek at Harvard Avenue
- 3 Peters Canyon Channel at Barranca Parkway
- 4 Hines Channel at Irvine Boulevard
- 5 San Joaquin Channel at University Drive
- 6 Santa Ana Delhi Channel at Mesa Drive
- 7a Peters Canyon Channel at Walnut Avenue
- 7b El Modena-Irvine Channel upstream of Peters Canyon Channel confluence
- 8 Sand Canyon Avenue – northeast corner of Irvine Boulevard
- 9 East Costa Mesa Channel at Highland Drive
- 10 Central Irvine Channel at Monroe

The locations of these sampling stations are shown in Figure 4.

Three wet weather sampling events (one additional event at some stations was included) and two dry weather sampling events were conducted for this 319(h) study. Wet weather sampling occurred during winter 2000. Dry weather sampling occurred during fall 1999 and spring 2000. Grab samples were collected on all occasions. All sample collection, handling and analysis were performed in accord with an approved Quality Assurance plan (Taylor and Lee, 2000). Samples were sent to the UC Davis Aquatic Toxicology Lab and/or *Aqua*Science, Davis, California, for toxicity measurements using US EPA *Ceriodaphnia* toxicity testing procedures with standard US EPA toxicity tests (Lewis, *et al*, 1994), as well as ELISA analyses for the OP pesticides diazinon and chlorpyrifos. Also, samples were sent to APPL Laboratories, Fresno, California, for 8141A special low-level OP pesticide analysis and US EPA 8321A carbamate pesticide analysis, using dual column gas chromatographic procedures.

Overview of *Ceriodaphnia* Toxicity

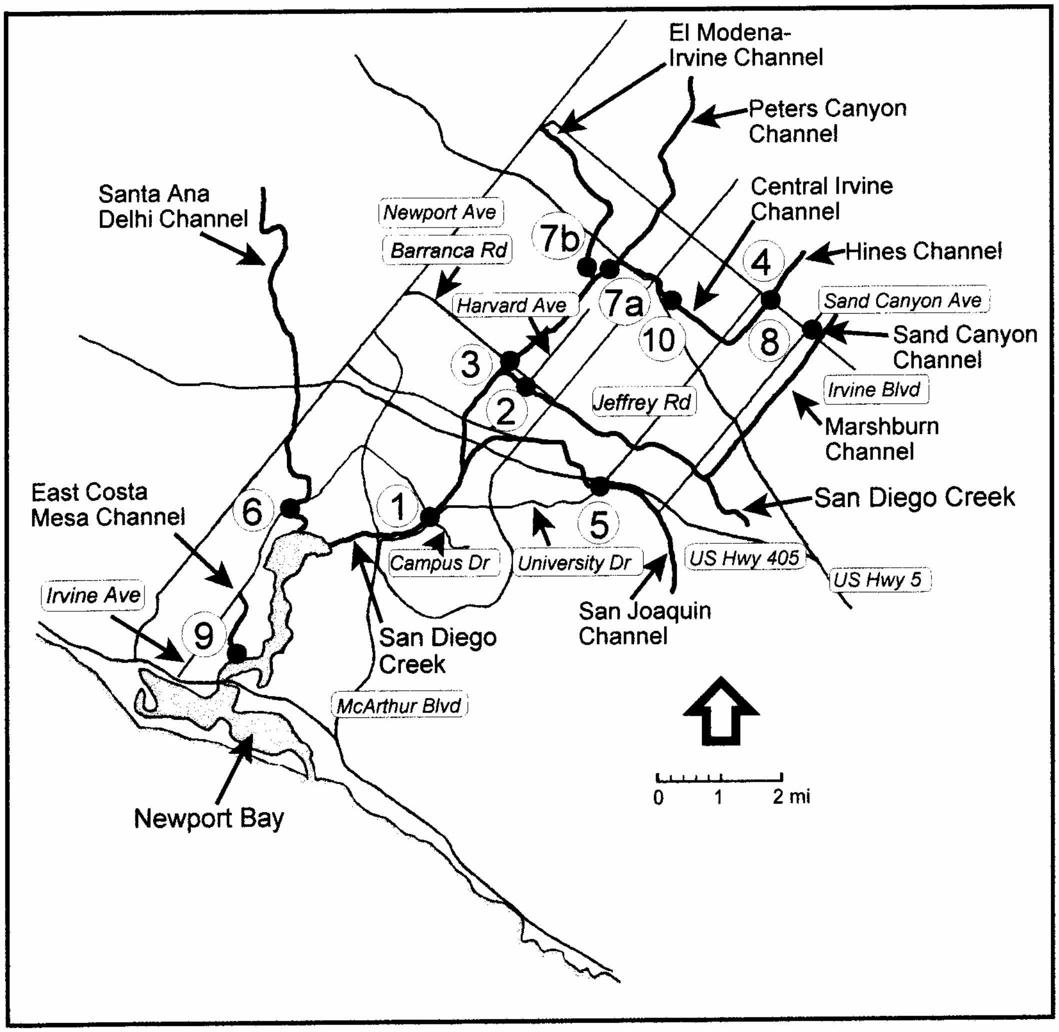
Table 7 presents a summary of the *Ceriodaphnia* toxicity testing conducted in this 319(h) Upper Newport Bay Watershed study. The information presented in this table shows that under stormwater runoff conditions that occurred on February 12 and February 21, 2000, there were high levels of *Ceriodaphnia* toxicity at all stations except Sand Canyon Avenue at the northeast corner of Irvine Blvd. Typically the total measured *Ceriodaphnia* TUa was 2 to 8. Some samples had a *Ceriodaphnia* toxicity of 16 and 32 TUa, with the latter occurring on February 12, 2000, for the San Joaquin Channel at University Drive sample. The 16 TUa sample occurred in the stormwater runoff collected at Peters Canyon Channel at Walnut Avenue on February 12, 2000.

The dry weather sampling that occurred on September 29, 1999, and May 31, 2000, generally showed low levels of *Ceriodaphnia* toxicity, with the exception of the September 29, 1999, sample obtained from Hines Channel at Irvine Blvd. This sample had a measured TUa of 16. The results for the Hines Channel at Irvine Blvd sample obtained on September 29, 1999, are similar to the results obtained for the same station in August 1997 and 1998. Both of those dry weather flow samples contained high levels of *Ceriodaphnia* toxicity. Since the expected primary source of water in the Hines Channel during dry weather flow conditions is runoff/seepage from the nurseries, it appears that the nurseries are releasing significant amounts of a variety of pesticides to the Hines Channel during dry weather and, for that matter, during stormwater runoff events.

Measurements downstream of the Hines Channel sampling station during dry weather showed that the high levels of toxicity and measured pesticides released or present at the Hines Channel sampling station are diluted by groundwater inflow to the downstream channels so that the toxicity and pesticides found at Peters Canyon at Barranca Pkwy and San Diego Creek at Campus Drive are considerably reduced or do not exist. It is clear that the two nurseries and possibly other upstream sources of the Hines Channel sampling station are important sources of OP pesticides and known- and unknown-caused toxicity for parts of the Upper Newport Bay Watershed. The data in Table 7 also show that, while the nurseries are potential sources of OP pesticide-caused aquatic life toxicity and unknown-caused toxicity, there are many other sources of this toxicity in the Upper Newport Bay Watershed.

A comparison of the TUa at each of the sampling stations on February 12 and 21, 2000, is of interest. In general, the total amount of measured toxicities (TUa) in the February 21 samples was less than that found about a week earlier on February 12, 2000. Since it is unlikely that any significant amount of new pesticide application took place between the two

Figure 4



Newport Bay Watershed Sampling Sites

stormwater runoff events, it would be expected that the second event (February 21, 2000) might have lower concentrations than the first event (February 12, 2000).

Table 7 presents a summary of the expected *Ceriodaphnia* TUa found in the study. These expected TUa are based on the LC_{50} normalized sum of the diazinon and chlorpyrifos concentrations found in the sample by APPL Laboratory. A comparison of the measurements of the *Ceriodaphnia* toxicity test measured TUa with the estimated TUa based on the concentrations of diazinon and chlorpyrifos, shows that often there was a factor of two to three times more measured TUa than that estimated based on ELISA diazinon and chlorpyrifos concentrations. These results are similar to those reported by Lee and Taylor (1999) for the Upper Newport Bay Watershed. Therefore, there were, in general, about 3 to as much as 8 TUa of *Ceriodaphnia* toxicity found in these samples that was due to unknown causes. Table 8 presents the results of the dual column GC analysis of these samples.

As discussed by Lee and Taylor (1999), the nature of both the measured and estimated *Ceriodaphnia* TUa, as reported in studies of this type, is such that there can readily be errors of up to several TUa in each type of measurement. The toxicity test measured TUa, as reported herein, are based on the dilution of the sample that yields a measured acute toxic response (mortality). There is, however, an appreciable TUa difference between the dilutions used. For example, if the 6.25 percent dilution is toxic and the 3.13 percent dilution is not toxic, then what is known is that the measured TUa is somewhere between 16 and 32. For

Table 9 presents a summary of the toxicity test results, which showed PBO-enhanced toxicity, indicating that pyrethroid-type pesticides may be responsible for part of the unknown-caused toxicity. There were seven samples where PBO-enhanced toxicity was found. Failure to find PBO-enhanced toxicity does not mean that it was not present since, in order to see it, it was necessary to dilute out the OP pesticide-caused toxicity that was present in the sample. As discussed in a subsequent section of this report, pyrethroid-type pesticides would be expected to be present in stormwater runoff in the Upper Newport Bay Watershed, since about 25,000 lb (ai) of pyrethroid pesticides are used each year in Orange County by commercial applicators. In addition, a substantial amount of pyrethroid-type pesticides are being sold to the public for home or commercial use.

Table 8 also presents the results obtained by APPL Laboratories for the OP and carbamate pesticides that were found at measurable concentrations above the Practical Quantitation Limit (PQL).

According to the SARWQCB (2000) draft report, the California Department of Pesticide Regulation (DPR) has reported dry weather flow toxicity to *Ceriodaphnia* on undiluted samples. All of the dry weather flow samples reported in the 205(j) and in this 319(h) study which had electrical conductivities above about 2500 µmhos/cm were diluted (to reduce the salt content of the samples) to about 2000 µmhos/cm. This was necessary in order to eliminate the toxicity to *Ceriodaphnia* due to elevated TDS. Some of the toxicity being reported by DPR, based on California Department of Fish and Game laboratory results, for San Diego Creek and its

Table 7
Summary of *Ceriodaphnia* Toxicity in the 319(h)
Upper Newport Bay Watershed Studies

Date	Location	Mortality % (days)	Measured TUa	Expected Tua*	Tua Measured/ Expected
09/29/99	San Diego Creek @ Campus Dr.	0	0	-	-
09/29/99	San Diego Creek @ Harvard Ave.	0	0	-	-
09/29/99	Peters Canyon Channel @ Barranca	100 (1)	2	2	1
09/29/99	Hines Channel @ Irvine Blvd.	100 (1)	16	4.5	3.5
09/29/99	Santa Ana Delhi @ Mesa Dr.	0	0	-	-
09/29/99	El Modena-Irvine Channel	0	0	-	-
01/25/00	San Diego Creek @ Campus Dr.	100 (1)	8	3	2.7
02/12/00	San Diego Creek @ Campus Dr.	100 (1)	8	5	1.6
02/12/00	San Diego Creek @ Harvard Ave.	100 (1)	8	4.5	2
02/12/00	Peters Canyon Channel @ Barranca	100 (1)	8	5	1.6
02/12/00	Hines Channel @ Irvine Blvd.	100 (1)	8	3	2.7
02/12/00	San Joaquin Channel @ University Dr.	100 (1)	32	29	1
02/12/00	Santa Ana Delhi @ Mesa Dr.	100 (3)	1	<1	1
02/12/00	Peters Canyon Channel @ Walnut Ave.	100 (1)	16	8.5	2
02/12/00	Sand Canyon Avenue-northeast corner of Irvine Blvd	22 (7)	0	0	-
02/12/00	East Costa Mesa @ Highland Dr.	100 (2)	ND	1.5	-
02/12/00	Central Irvine Channel @ Monroe	100 (1)	8	4	2
02/21/00	San Diego Creek @ Campus	100 (1)	5	2.5	2
02/21/00	San Diego Creek @ Harvard Ave.	100 (1)	3	3	1
02/21/00	Peters Canyon Channel @ Barranca	100 (1)	3	2.5	1.2
02/21/00	Hines Channel @ Irvine Blvd	100 (1)	5	2.5	2
02/21/00	San Joaquin Channel @ University Dr.	100 (1)	6	8	1
02/21/00	Santa Ana Delhi @ Mesa Dr.	100 (7)	0	0.5	-
02/21/00	El Modena-Irvine Channel upstream of Peters Canyon	100 (6)	0	0.7	-
02/21/00	Sand Canyon Avenue-northeast corner of Irvine Blvd	30 (7)	0	0	0
02/21/00	East Costa Mesa @ Highland Dr.	100 (1)	2.5	1	2.5
02/21/00	Central Irvine Channel @ Monroe	100 (1)	5.5	1.5	3.7
05/31/00	San Diego Creek @ Campus Dr.	0	0	0.4	0
05/31/00	San Diego Creek @ Harvard Ave.	0	0	0	-
05/31/00	Peters Canyon Channel @ Barranca	0	0	0.4	-
05/31/00	Hines Channel @ Irvine Blvd.	44 (7)	-	0	-
05/31/00	Santa Ana Delhi @ Mesa Dr.	0	0	0.2	-
05/31/00	El Modena-Irvine Channel upstream of Peters Canyon	0	0	0.4	-
05/31/00	East Costa Mesa @ Highland Dr.	100 (5)	1	0.5	2
05/31/00	Central Irvine Channel @ Monroe	UCD?	UCD?	0.2	UCD?

ND = Not determined.
* = TUa estimated based on LC_{50} for diazinon, chlorpyrifos and carbaryl to *Ceriodaphnia*.

Table 8
Summary of Results for Selected Analytes

Station	Analyte (ng/L) [LC_{50}]								
	Diazinon [960]	**Chlorpyrifos [100]**	**Malathion [1,000]**	**Prowl [280,000]**	**Benomyl [80,000]**	**Carbaryl [13,000]**	**Diuron [21,000]**	**Methomyl [8,800]**	**Other**
Sample Collection Date: 09/29/00									
3	820	<50	<100	<100	<400	<70	<400	<70	-
4	220	310	<100	170	300J	70	<400	<70	Dimethoate 250
Sample Collection Date: 01/25/00									
1	320 460-P	160 324-P	170	120	<400	200	<400	<100	-
Sample Collection Date: 02/12/00									
1	460 460-P 506-A	260 350-P 438-A	230	320	1,100	4,200	1,100	240	-
2	280 466-A	310 507-A	150	140	500	730	500	<70	-
3	420 639-A	100 166-A	460	510	2,100	13,000	1,600	980	-
4	760 1,194-A	120 264-A	680	190	2,500	470	<400	320	-
5	<50 70-A	770 1,103-A	<100	280	9,900	78,000	<400	710	-
6	120 325-P 298-A	<50 50-P 30-A	120	200	<400	<70	1,100	<70	-
7	520 716-A	150 252-A	440	350	4,000	22,000	<400	810	-
8	110 138-A	<50 56-A	<100	<100	11,000	<70	<400	200	-
9	370 582-A	50 137-A	<100	430	<400	60 J	<400	<70	-

Table 8 (continued)
Upper Newport Bay Watershed OP and Carbamate Pesticide Analysis

Station	Analyte (ng/L) [LC_{50}]								
	Diazinon [960]	**Chlorpyrifos [100]**	**Malathion [1,000]**	**Prowl [280,000]**	**Benomyl [80,000]**	**Carbaryl [13,000]**	**Diuron [21,000]**	**Methomyl [8,800]**	**Other**
10	810 965-A	150 310-A	390	700	2,200	420	<400	910	Methiocarb 600
Sample Collection Date: 02/21/00									
1	220 300-P 98-A	170 230-P 122-A	<100	210	700	550	500	380	-
2	200 681-A	190 142-A	<100	<100	900	270	<400	<70	Dimethoate 580
3	330 450-A	80 42-A	<100	340	1,300	1,200	400	1,200	-
4	810 1704-A	50 38-A	<100	470	1,600	<70	<400	220	-
5	<50 62-A	470 265-A	<100	1,600	6,700	8,400	<400	1,200	Bromacil 400
6	200 160-P 185-A	<50 50-P <30-A	60 J	340	<1,000	<1,000	600 J	<1,000	-
7	330 309-A	<50 40-A	90 J	500	<400	<70	<400	<70	-
8	70 299-A	<50 38-A	90 J	<100	1,300	<70	<400	60 J	-
9	560 314-A	<50 38-A	170	830	<400	<70	<400	<70	-
10	280 434-A	70 67-A	<100	410	1,700	<70	<400	2,100	-

Table 8 (continued)
Upper Newport Bay Watershed OP and Carbamate Pesticide Analysis

Station	Analyte (ng/L) [LC_{50}]								
	Diazinon [960]	**Chlorpyrifos [100]**	**Malathion [1,000]**	**Prowl [280,000]**	**Benomyl [80,000]**	**Carbaryl [13,000]**	**Diuron [21,000]**	**Methomyl [8,800]**	**Other**
Sample Collection Date: 05/31/00									
1	160 104-A	<50 41-A	<100	<100	<400	<70	<400	<70	
2	<50 12-A	<50 42-A	<100	<100	<400	<70	<400	<70	
3	170 187-A	<50 41-A	<100	<100	<400	<70	<400	<70	Dimethoate 750
4	47 J 61-A	<50 36-A	83 J	330	<400	<70	<400	<70	
6	110 17-A	<50 27-A	<100	<100	<400	<70	<400	<70	
7	180 150-A	<50 45-A	<100	<100	<400	<70	<400	<70	Dimethoate 2,400
9	210 281-A	<50 54-A	<100	150	<400	<70	<400	<70	
10	90 95-A	<50 38-A	<90 J	<100	300 J	<70	<400	<70	

All samples analyzed by APPL Lab, Inc., using GC Procedures unless otherwise indicated
A = samples analyzed by *Aqua*Science using ELISA
P = Samples analyzed by Pacific Eco-Risk using ELISA
J = below the practical quantitation limit

Table 9
PBO Activation of *Ceriodaphnia* Toxicity

Date	Location	Activation	Sample %
09/29/99	Hines Channel at Irvine Blvd	Yes	3.13
02/12/00	Peters Canyon at Barranca Pkwy	Yes	12.5
02/12/00	Hines Channel at Irvine Blvd	Yes	12.5
02/12/00	Peters Canyon Channel at Walnut Avenue	Yes	6.25
02/12/00	Central Irvine Channel at Monroe	Yes	6.25
02/21/00	San Diego Creek at Campus Drive	Yes	6.25
02/21/00	San Diego Creek at Harvard Avenue	Yes	6.25
2/21/00	Hines Channel at Irvine Blvd	Yes	12.5
2/21/00	Central Irvine Channel at Monroe	Yes	6.25
5/31/00	Hines Channel at Irvine Blvd	Yes	100
5/31/00	East Costa Mesa Channel at Highland Dr.	Yes	100

tributaries is artifactual related to the high salt content of the dry weather flow in San Diego Creek and its tributaries. The issue of concern is not whether *Ceriodaphnia* could live in San Diego Creek in dry weather conditions (i.e., what is being evaluated by DPR-DFG), but rather whether Upper Newport Bay and its tributaries under dry weather flow conditions contain constituents which are toxic to *Ceriodaphnia,* where *Ceriodaphnia* is an indicator species for freshwater zooplankton. In order to make this assessment, it is necessary to dilute the samples to keep the total salinity below the concentrations that are toxic to *Ceriodaphnia*. In the Upper Newport Bay Watershed situation encountered in these studies, this dilution would not fail to detect potentially important OP pesticide-caused aquatic life toxicity.

OVERVIEW OF *MYSIDOPSIS* TOXICITY

Tables 10 and 11 present a summary of the toxicity testing results obtained using *Mysidopsis bahia* as a test organism for the San Diego Creek at Campus Drive and the Santa Ana Delhi Channel at Mesa Drive samples obtained in this 319(h) study. The freshwater samples tested for *Mysidopsis* toxicity had sea salt added to them so that the test salinity was adjusted to 20 ppt.

The San Diego Creek at Campus Drive and Santa Ana Delhi Channel at Mesa Drive dry weather flow samples showed no or very low levels of toxicity to *Mysidopsis*. However, the January 25, 2000; February 12, 2000, and February 21, 2000, stormwater runoff samples of San Diego Creek taken at Campus Drive all showed high levels of *Mysidopsis* toxicity, with 100 percent kill within one day. The magnitude of the toxicity was 6 to 8 TUa. Based on the concentrations of chlorpyrifos found, there was an expected total toxicity in the samples to *Mysidopsis* of about 9 TUa. The *Mysidopsis* toxicity results of the winter 2000 sampling for San Diego Creek at Campus Drive are similar to what was found in previous years' studies (Lee and Taylor, 1999).

The Santa Ana Delhi Channel stormwater runoff samples collected on February 12, 2000, and February 21, 2000, showed low levels of toxicity to *Mysidopsis*, which appeared to be related to the chlorpyrifos concentrations found.

Table 10
Summary of Results of *Mysidopsis* Testing on Samples Collected from San Diego Creek at Campus Drive and Santa Ana Delhi Channel at Mesa Drive

Date	Location	Acute % kill (days)	Chronic yes or no	TUa		
				Measured	Estimated	Ratio Meas:Est
09/29/99	San Diego Creek at Campus Drive	0 (7)	no	0	-	-
09/29/99	Santa Ana Delhi at Mesa Drive	0 (7)	yes	0	-	-
01/25/00	San Diego Creek at Campus Drive	100 (1)	yes	8	9	1
02/12/00	San Diego Creek at Campus Drive	100 (1)	yes	8	10	0.8
02/12/00	Santa Ana Delhi at Mesa Drive	40 (4)	-	1	1.5	1
02/21/00	San Diego Creek at Campus Drive	100 (1)	yes	6	6.5	1
02/21/00	Santa Ana Delhi at Mesa Drive	30 (7)	-	1	1.5	1
05/31/00	San Diego Creek at Campus Drive	30 (7)	-	1	-	-
05/31/00	Santa Ana Delhi at Mesa Drive	40 (7)	-	1	-	-

- = No analysis made.

Table 11
Diazinon and Chlorpyrifos Concentrations in San Diego Creek @ Campus Dr and Santa Ana Delhi Channel @Mesa Dr. Using ELISA Procedures

Date	Location	Diazinon ng/L	Chlorpyrifos ng/L	Estimated TUa*
09/29/00	San Diego Cr @ Campus Dr	-	--	--
01/25/00	San Diego Cr @ Campus Dr	460	324	9
02/12/00	San Diego Cr @ Campus Dr	460	350	10
02/12/00	Santa Ana Delhi @ Mesa Dr.	325	50	1.5
02/21/00	San Diego Cr @ Campus Dr	300	230	6.5

Analysis performed by Pacific Eco-Risk using ELISA procedures
-- no analysis conducted
* Based toxicity to *Mysidopsis bahia*

Estimated OP Pesticide Loads and Export Coefficients

One of the initial objectives of the 319(h) monitoring program was to determine if residential areas, agricultural activities or nurseries were the primary source of diazinon, chlorpyrifos or unknown-caused toxicity. Table 12 presents a summar of land use for the watersheds upstream of the sampling stations. Station 5 (San Joaquin Channel at University Drive) had a land use upstream of the sampling location of primarily open space with a secondary use of agriculture. Station 6 (Santa Ana Channel at Mesa Drive) watershed is 95 percent developed with commercial/residential uses. Station 7b is primarily devoted to residential use with some commercial area. Station 8 (Sand Canyon Avenue - northeast corner of Irvine Blvd) watershed is devoted to agricultural use. Station 9 (East Costa Mesa Channel at Highland Drive) watershed is devoted primarily to residential with a small amount of commercial use. All other sampling

Table 12
Summary of Sampling Station Watershed Dominant Land Uses

stations had a mixture of residential and agricultural uses, and Stations 1, 2, 3, 4, 7a and 10 also had nursery use within the sub-watershed.

Station	Location	Dominant Land Use
1	San Diego Creek at Campus Drive	Mixed residential, agricultural, nursery
2	San Diego Creek at Harvard Avenue	Mixed residential, agricultural, nursery
3	Peters Canyon Channel at Barranca Parkway	Mixed residential, agricultural, nursery
4	Hines Channel at Irvine Blvd	Nursery, agricultural
5	San Joaquin Channel at University Drive	Agricultural, open space
6	Santa Ana Delhi Channel at Mesa Drive	Residential, commercial
7a	Peters Canyon Channel at Walnut Avenue	Residential, agricultural, nursery
7b	El Modena Irvine Channel upstream of Peters Canyon Channel	Residential, some commercial
8	Sand Canyon Avenue-NE corner of Irvine Blvd.	Agricultural
9	East Costa Mesa Channel at Highland Dr.	Residential, commercial
10	Central Irvine Channel at Monroe	Agricultural, residential, nursery

Constituent load calculations were completed for each of the two wet weather events for diazinon, and chlorpyrifos. The purpose of the load calculations is to provide information to assist in allocating loads for toxics within the watershed by land use and discharger. Load calculations were also completed for the May 31, 2000, dry weather sampling event. The September 29, 1999, dry weather event did not provide a sufficient data set for load calculations since the objective at the time of sampling was to characterize the magnitude of the toxicity in the discharge.

FEBRUARY 12, 2000, STORM EVENT

The February 12, 2000, storm event resulted in 0.72 in. of rain at the Campus Drive rain gage with about 0.29 in. of runoff at this location. This storm could be viewed as “typical” for the season. Table 13 presents the runoff volumn and concentrations of diazinon and chlorpyrifos for this runoff event.

Table 13
Runoff Volume and Constituent Concentration – OP Pesticides
February 12, 2000, Storm Event

Station No.	Volume (ft^3)	GC Diazinon (ng/L)	ELISA Diazinon (ng/L)	GC Chlorpyrifos (ng/L)	ELISA Chlorpyrifos (ng/L)
1	74,553,372	460	506	260	438
2	19,436,220	280	466	310	507
3	7,961,166	420	639	100	166
4	203,104	760	1194	120	264
5	336,922	**50**	70	770	1103
6	13,710,060	120	298	50	30
7a	4,403,548	520	716	150	252
8	29,544	110	138	50	56
9	611,484	370	582	50	137
10	1,076,184	810	965	150	310

Note: Shaded value indicates volume is estimated, bold value indicates assumed as detection limit.

Table 14 presents the estimated loads of the diazinon and chlorpyrifos.

Table 14
Load in Pounds of Selected Constituents
February 12, 2000 Storm Event

Station No.	Diazinon		Chlorpyrifos	
	GC	ELISA	GC	ELISA
1	2.14	2.36	1.21	2.04
2	0.34	0.57	0.38	0.61
3	0.21	0.32	0.05	0.83
4	0.01	0.02	0.002	0.003
5	0.001	0.002	0.02	0.02
6	0.10	0.26	0.04	0.03
7a	0.14	0.20	0.04	0.07
8	0.00	0.00	0.00	0.00
9	0.01	0.02	0.002	0.01
10	0.05	0.06	0.01	0.02

Table 15 presents that data given in Table 14 in terms of pounds of constituent per acre of tributary drainage area to provide an estimate of the relative contributions of land uses that are represented at each sampling station.

Table 15
Pounds of Selected Constituents per Acre of Tributary Area
February 12, 2000, Storm Event
(All values lb/acre × 10^{-5})

Station No.	**Diazinon**		**Chlorpyrifos**	
	GC	**ELISA**	**GC**	**ELISA**
1	3.0	3.3	1.7	2.9
2	1.3	2.1	1.4	2.3
3	0.7	1.1	0.2	0.3
4	1.6	2.5	0.2	0.5
5	0.1	0.2	1.8	2.6
6	0.9	2.3	0.4	0.2
7a	1.1	1.5	0.3	0.5
8	0.2	0.3	0.1	0.1
9	1.6	2.6	0.2	0.6
10	2.5	3.0	0.5	1.0

The results generally indicate that, with respect to the OP pesticides, the entire Upper Newport Bay Watershed appears to be a contributor, with less contribution from certain specific land uses. The station at Campus Drive shows the highest unit load of OPs, followed by agricultural areas such as the Sand Canyon Channel and Central Irvine Channel. Residential areas (Stations 2, 6 and 9) also exhibit moderately high loadings.

FEBRUARY 21, 2000, STORM EVENT

The February 21, 2000, storm event resulted in 1.28 in. of rain at the Campus Drive rain gage with about 0.43 inches of runoff at this location. This storm could be viewed as on the high end of a "typical" storm for the season. Table 16 shows the volume of runoff that passed by each station as well as the reported constituent concentrations for diazinon and chlorpyrifos. Values are provided both for gas chromatographic (GC) as well as for the ELISA procedures.

Table 16
Runoff Volume and Constituent Concentration – OP Pesticides
February 21, 2000, Storm Event

Station No.	**Volume (ft^3)**	**GC Diazinon (ng/L)**	**ELISA Diazinon (ng/L)**	**GC Chlorpyrifos (ng/L)**	**ELISA Chlorpyrifos (ng/L)**
1	110,147,220	220	98	170	122
2	64,213,380	200	681	190	142
3	31,085,460	330	450	80	42
4	300,072	810	1704	50	38
5	497,778	**50**	62	470	265
6	20,487,834	200	185	50	30
7b	14,520,960	330	309	50	40
8	43,650	70	299	50	38
9	903,423	560	314	50	38
10	1,589,984	280	434	70	67

Note: Shaded value indicates volume is estimated, bold value indicates assumed as detection limit.

Table 17 provides loads for the specified constituents in pounds for the February 21, 2000, storm event.

Table 17
Load in Pounds of Selected Constituents
February 21, 2000, Storm Event

Sta. No.	GC Diazinon	ELISA Diazinon	GC Chlorpyrifos	ELISA Chlorpyrifos
1	1.51	0.67	1.17	0.84
2	0.80	2.73	0.76	0.57
3	0.64	0.87	0.16	0.08
4	0.02	0.03	0.001	0.001
5	0.002	0.002	0.02	0.008
6	0.26	0.24	0.06	0.04
7b	0.30	0.28	0.05	0.04
8	0.00	0.001	0.00	0.00
9	0.03	0.02	0.003	0.002
10	0.03	0.04	0.007	0.007

Table 18 presents the data given in Table 17 in terms of pounds of constituent per acre of tributary drainage area to provide an estimate of the relative contributions of land uses that are represented at each sampling station.

Table 18
Pounds of Selected Constituents per Acre of Tributary Area
February 21, 2000, Storm Event
(All values lb/acre × 10^{-5})

Station No.	GC Diazinon	ELISA Diazinon	GC Chlorpyrifos	ELISA Chlorpyrifos
1	2.1	0.9	1.6	1.2
2	3.0	10.1	2.8	2.1
3	2.2	3.0	0.5	0.3
4	2.5	5.2	0.2	0.1
5	0.2	0.2	1.6	0.9
6	2.3	2.1	0.6	0.3
7b	3.9	3.6	0.6	0.5
8	0.2	0.8	0.1	0.1
9	3.7	2.0	0.3	0.2
10	1.3	2.0	0.3	0.3

The results for the February 21, 2000, event generally indicate that, with respect to OP pesticides, the entire watershed appears to be a contributor, with less emphasis on certain land uses. The station at Campus Drive shows one of the higher unit loads of OPs, followed by agricultural areas such as the Sand Canyon Channel. Values of diazinon loading from residential areas are significantly greater than for the February 12, 2000, storm event, with Stations 6 (residential uses), 7b (urban commercial and residential uses) and 9 (residential uses) showing marked increases from the previous event. Note that Station 7a was sampled during the February 12 event, which is a different location with differing land use than Station 7b. Station 7b is highly urbanized with residential and some commercial use. Station 7a is a rapidly urbanizing area that retains significant agriculture and open space in addition to residential and commercial uses. Chlorpyrifos loadings do not differ significantly from the previous (February 12) event.

DRY WEATHER LOADS

Estimates were also made for annual dry weather loading using the data from the May 31, 2000, dry-weather sampling event. Total annual dry weather loads were computed for stations where gaged discharge data were available. Table 19 provides the results of this analysis. Gaged stream data is only available for Stations 1, 3, 6, and 9. The total annual load was estimated by averaging the dry weather flow data for a period of 4 yr (1991-94 flow data from OCFPRD). The computed dry weather volumes are shown in Table 19.

Table 19

Estimated Dry Weather Annual Runoff Volumes

Station No.	Estimated Annual Volume (ft^3)
1	408,916,800
3	282,772,800
6	763,723,080
9	5,150,880

Table 20 provides annual load data expressed in terms of pounds per tributary acre. Values are computed for those stations where data are available.

Table 20

Estimated Dry Weather Annual Load Data (lb)

Station No.	GC Diazinon	ELISA Diazinon	GC Chlorpyrifos	ELISA Chlorpyrifos
1	4.08	2.65	1.28	1.05
3	3.00	3.30	0.88	0.72
6	5.24	0.81	2.38	1.30
9	0.07	0.09	0.02	0.02

Table 21 provides annual load data expressed in terms of pounds per tributary acre. Values are computed for those stations where data are available.

Table 21
Dry Weather Annual Load per Acre of Tributary Area
(All values in. lb/acre × 10^{-5})

Station No.	GC Diazinon	ELISA Diazinon	GC Chlorpyrifos	ELISA Chlorpyrifos
1	5.7	3.7	1.8	1.5
3	10.4	11.4	3.1	2.5
6	47.6	7.3	21.5	11.7
9	**7.8**	**10.4**	**1.9**	**2.0**

Summary. The load data show that on average, about 1 to 2 lb of diazinon and 1 to 1.5 lb of chlorpyrifos are discharged to Upper Newport Bay during a "typical" storm event. Examining the information obtained this study shows that purely agricultural areas appear to be relatively low exporters of OP pesticides. These findings are in accord with the Department of Pesticide Regulation Orange County pesticide use information, which indicates that most of the reported uses of diazinon and chlorpyrifos are for structural purposes. In addition to the reported uses, there are considerable over-the-counter sales to the public for use on residential properties.

Stations 5 and 8 are either agricultural land use, or agriculture and open space. Each of these locations shows rates of diazinon export from about 0.1 to 0.8 × 10^{-5} lb/acre. Export rates of chlorpyrifos are somewhat higher, ranging from 0.1 × 10^{-5} to about 2.6 × 10^{-5} lb/acre. By comparison, for largely urban areas (residential, commercial, industrial), such as for stations 6, 7b and 9, diazinon export rates range from about 0.9 × 10^{-5} to 3.9 × 10^{-5} lb/acre. For chlorpyrifos, export rates for these same stations range from 0.2 × 10^{-5} to 0.6 × 10^{-5} lb/acre, somewhat lower than for agriculture. Export rates for diazinon and chlorpyrifos are generally largest at the Campus Drive station, incorporating all major land uses. An exception occurs for diazinon, which has the largest total export for Station 7b during the February 21, 2000, event. Station 7b serves a completely urbanized area consisting of commercial and residential uses.

The dry weather annual load data tends to support the trends for the wet weather data, with the Santa Ana Delhi watershed (Station 6 – residential, commercial and industrial uses) showing the highest export rates on an annual per acre basis for the OPs, and primarily agriculture and nursery areas showing the lowest export rates.

This limited study of OP pesticide loadings to Upper Newport Bay tributary streams during stormwater runoff events has provided some insight into potential sources of OP pesticides within the Upper Newport Bay Watershed. The results appear to follow the potential export from various types of land use based on reported pesticide use for various purposes. It is clear from this study that without a much more comprehensive study program, which would be based on a greatly expanded budget, it is not possible to define specific sources of OP pesticides using the mass transported per storm in a tributary stream approach to define specific pesticide sources.

PESTICIDE USE IN THE UPPER NEWPORT BAY WATERSHED

Table 22 presents a summary of the selected pesticide use in Orange County as reported by the Department of Pesticide Regulation (DPR) database for the period 1995 through 1999. The 1999 data presented in this table is provisional. The pesticide selected for inclusion in this table are those that have been identified in stormwater runoff in the Upper Newport Bay watershed or in the case of the pyrethroid pesticides, are pesticides that are highly toxic to certain zooplankton and are used in Orange County in amounts that could cause toxicity in stormwater runoff.

Table 22
Pesticide Use in Orange County (Based on DPR Database)

Pesticide	Pounds (ai) of Pesticide Used				
	1995	1996	1997	1998	1999
Diazinon	21,543	16,438	21,655	25,766	24,452
Chlorpyrifos	41,782	75,396	73,662	91,707	79,990
Carbaryl	5,648	3,199	5,636	6,506	2,835
Methomyl	4,174	3,163	3,059	2,413	3,181
Malathion	9,192	4,724	4,341	5,858	5,953
Permethrin	18,644	10,299	11,218	19,011	10,480
Bifenthrin	18	39	130	493	5,257
Cypermethrin	2,483	6,377	4,106	5,925	5,871
Esfenvalerate	396	436	278	227	113
Fenvalerate	4,129	8,125	8,492	428	18
Cyfluthrin	-	-	1,478	1,567	793
Deltamethrin	-	-	0.08	25	86
Piperonyl Butoxide, Technical, Other Related	-	-	461	547	387
Total Copper used as pesticide	-	-	15,635	23,883	16,389

- data not available

Examination of this data shows that about the same amounts of each of the OP and carbamate pesticides such as diazinon, chlorpyrifos, carbaryl, methomyl, and malathion, have been used since 1995. However, several of the pyrethroid pesticides have decreased in use since 1995 or increased. For example, permethrin and fenvalerate have decreased while bifenthrin has increased significantly. The bifenthrin increase may be related to the fact that this pesticide is being used for fire ant control in Orange County.

With the phase out of chlorpyrifos in 2001, there will likely be a significant shift to other pesticides as a replacement.

Apportionment of Pesticide Use in Upper Newport Bay Watershed

Approximately 21,300 lb of diazinon and 68,103 lb of chlorpyrifos (average for data from 1995 to 1998 reported to the County Agriculture Commissioner) (ai) are applied by commercial applicators in Orange County each year. In addition, the public, through over-the-counter purchases, applies at least an equal amount. The Upper Newport Bay Watershed represents approximately 20 percent of the land mass in Orange County. Assuming a proration by watershed area, approximately 4,300 lb of diazinon and 13,600 lb of chlorpyrifos are applied by commercial applicators in the Upper Newport Bay Watershed, or approximately 3,200 lb and 10,300 lb, (ai) respectively, in the San Diego Creek Watershed.

Over the 3-yr period of sampling in the San Diego Creek Watershed, the average storm depth of runoff is approximately 0.23 in. or 0.019 ft (excluding an ungaged 100-yr event). The average total rainfall depth per storm was approximately 1 in. Rainfall data for Newport Harbor indicate that approximately 11.5 in. of rainfall occurs per year. Therefore, on average, using the previous 3 yr of storm data developed during this study, approximately 11 storm events occur per year. The average concentration of diazinon per event is approximately 340 ng/L, and 126 ng/L for chlorpyrifos. Using the average event direct runoff depth of 0.019 ft, the average mass of diazinon and chlorpyrifos discharged via San Diego Creek to Upper Newport Bay per event is 1.34 lb and 0.5 lb, respectively. These average event values compare with the commercially applied load in the San Diego Creek Watershed (excludes residential applications by the public) of 3,200 lb of diazinon and 10,300 lb of chlorpyrifos (active ingredient). In addition, there is likely at least an equal amount of diazinon and chlorpyrifos applied in the Upper Newport Bay Watershed as a result of over-the-counter sales.

IDENTIFICATION OF UNKNOWN-CAUSED TOXICITY

Samples of the waters with unknown-caused toxicity have been subjected to GC scans using US EPA standard low-level 8141 and 8321A analyses for the OP and carbamate pesticides. An evaluation of the pesticides found in these scans, compared to their toxicity (LC_{50} or EC_{50} values) has shown (see Table 23 that the cause of the unknown-caused toxicity is not due to the OP and carbamate pesticides typically detected in these scans.

In an effort to determine if other pesticides that are used in Orange County that are not measured in the OP and carbamate pesticide GC scans could be responsible for this toxicity, the DPR 1998 and draft 1999 Pesticide Use Report databases have been examined relative to the US EPA Office of Pesticide Programs (US EPA OPP) Pesticide Ecotoxicity Database. This database contains over 13,000 results of toxicity tests for pesticides. It includes toxicity test results for *Daphnia magna* and *Mysidopsis bahia.*

Generally, it is assumed, based on limited data, that the toxicity of pesticides to *Daphnia magna* is similar (within a factor of 2 or so) to the toxicity to *Ceriodaphnia dubia*. Tables 24 and 25 present the results of an evaluation of the pesticides used within Orange County in 1998 and 1999 that are applied by commercial applicators and/or are recorded in the DPR database. It was decided in the preparation of these tables, that the initial screening for pesticides that are toxic to *Daphnia magna* and *Mysidopsis bahia* would be for those pesticides that had an LC_{50} or EC_{50} for these organisms of 2,000 ng/L or less.

Table 23
OP and Carbamate Pesticides Found in Upper Newport Bay/San Diego Creek Watershed Samples During 1996-1999

(Concentrations are the highest value found by APPL Laboratory, Fresno, CA, using US EPA 8141 Special Low-Level List and US EPA 8321A procedures.)

Pesticide	Max Conc (ng/L)	Location	lbs Used 1998 (ai)	LC_{50} or EC_{50}	Dominant Use
Diazinon	12,000	H	25,800	960 D 4,200 M	90% S, 5%N, 3%A, 2% L
Chlorpyrifos	670	H	81,600	100 D 35 M	97% S, 1% N, 0.8% A, 1% L
Benomyl	2,000	H	2,500	80,000 D 180,000 M	0%S, tr N, 99.9% A, tr L
Carbaryl	11,000	H	5,330	13,000 D 10,000 M	5% S, 11% N, 83% A, tr L
Methomyl	14,000	SDC	2,420	8,800 D 230,000 M	tr S, tr N, 99.9% A, 0% L
Diuron	2,200	SADC	7,946	21,000 D 1,000,000 M	0% S, 0% N, 0.4%A, 5% L, 83% RW
Simazine	3,200	SDC	7,184	1,100,000 D ?? M[1]	0% S, 24% N, 52% A, 4% L, 20% RW
Dimethoate	7,100	H	1,860	?? D[1] 15,000,000 M	0% S, 31% N, 64% A, 5% L
Malathion	490	SDC	5,820	1,000 D 2,200 M	6% S, 27% N, 64% A, 2% L
Prowl (pendimethalin)	1,200	H	5,099	280,000 D ?? M[1]	0%S, 33% N, tr A, 70% L, 5% RW
Trifluralin	190	SDC	194	560,000 D ?? M[1]	0% S, tr N, 51% A, 48% L, tr RW
Methiocarb	2,500	H	575	19,000 D ?? M[1]	0% S, 95 %N, 0% A, 5% L,
Propoxur	500	Found in Yorba Linda residential stormwater runoff			

[1] ?? = No data available

Locations:
H - Hines Channel just downstream of two commercial nurseries
SDC - San Diego Creek at Campus Drive
SADC - Santa Ana Delhi Channel
D - *Daphnia magna*
M - *Mysidopsis bahia*
tr - trace

Dominant Use Categories:
S - Structural
N - Nursery
A - Agriculture
L - Landscape
RW - Right of Way

The most significant result from this evaluation is the finding that in 1998 and 1999 the pyrethroid pesticides were used in large amounts in Orange County. Over 25,000 lb (ai) were used during that year by commercial applicators. There were about the same amount of pyrethroid pesticides used in 1998 as diazinon. The most used pyrethroid pesticide was permethrin, with almost 19,000 lb used in 1998. Its use in 1999 decreased to about 10,500 lbs. As indicated in Table 23, permethrin is highly toxic to *Daphnia magna* and especially *Mysidopsis bahia*. Almost 6,000 lb of Cypermethrin were used in Orange County during 1998 and 1999. It is also highly toxic to these organisms. Bifenthrin, of which 493 lb were used during 1998 and over 5,200 lb in 1999 in Orange County, is also highly toxic to these organisms at the ng/L level. As discussed in another section, bifenthrin has been found in DPR monitoring to be present in the Upper Newport Bay Watershed tributaries at concentrations that are potentially toxic to certain zooplankton.

A review of Table 24 shows that, in general, *Mysidopsis bahia* has a lower LC_{50} than *Daphnia magna*. There is no information available on the toxicity of the pyrethroid pesticides to *Ceriodaphnia dubia.* There is need for information on the toxicity of the pyrethroid pesticides to this organism since it is widely used for ambient water toxicity testing.

Permethrin and cypermethrin were used in Orange County almost exclusively for structural pest control. Similarly, most of the use of bifenthrin was for structural pest control, although substantial amounts of the 1998 493 lb/yr were used in agriculture as well. In 1999, the amount of bifenthrin used for agricultural purposes (76 percent of the total use) was in excess of 4,000 lb (ai), while in 1998, only a 102 lb of bifenthrin was listed as being used in agriculture.

Bifenthrin is a pesticide that now is being sold over the counter in local hardware and garden stores for public use around the home. Its use in the Upper Newport Bay Watershed, therefore, could be considerably greater than that listed by DPR. There is need to determine the pyrethroid pesticides that are sold to the public, the amount sold, and the use of these pesticides by the public.

It was also of interest to find that 547 lbs. of PBO was used in Orange County during 1998, while 387 lb were used in 1999. PBO is used as a synergist to enhance the toxicity of pyrethroid pesticides.

Toxicological Evidence for Pyrethroid Aquatic Life Toxicity

Over the past three years that Lee and Taylor have been monitoring Upper Newport Bay Watershed stormwater runoff toxicity, there has been some indication of PBO activation of the Upper Newport Bay stormwater runoff toxicity to *Ceriodaphnia dubia*, where in a toxicity dilution series, the higher dilutions were nontoxic to *Ceriodaphnia*. However, the same dilution with 100 µg/L of PBO was toxic to *Ceriodaphnia*. As part of this 319(h) project, Dr Jeff Miller of *Aqua*Science processed a set of stormwater runoff samples from the Upper Newport Bay Watershed collected on February 21, 2000. *Aqua*Science found that five of the 10 samples tested for *Ceriodaphnia* toxicity had PBO-enhanced toxicity. This is the strongest evidence yet that the pyrethroid pesticides are potentially responsible for at least part of the unknown-caused toxicity that is present in the Upper Newport Bay Watershed stormwater runoff.

Table 24
High Toxicity Pesticides Used in Orange County during 1998 and 1999
(Based on the California Department of Pesticide Regulation (DPR) and the

US EPA OPP Aquatic Life Ecotoxicity Database)

Pesticide	Lb Used (ai) 1998	Lb Used (ai) 1999*	Organism	Toxicity* (ng/L)
Chlorpyrifos	91,707	79,990	*Daphnia magna*	100
			Mysidopsis bahia	35
Diazinon	25,766	24,452	*Daphnia magna*	960
Permethrin	19,011	10,480	*Mysidopsis bahia*	46
			Daphnia magna	320
			Mysidopsis bahia	19
Cypermethrin	5,925	5,871	*Mysidopsis bahia*	5
			Daphnia magna	1,000
Malathion	5,858	5,953	*Daphnia magna*	1,000
Cyfluthrin	1,567	793	*Daphnia magna*	20
			Mysidopsis bahia	4
Piperonyl Butoxide	547	387	*Daphnia magna*	100,000
Bifenthrin	493	5,257	*Daphnia magna*	1,600
			Mysidopsis bahia	4
Fenvalerate	428	18	*Mysidopsis bahia*	8
			Daphnia magna	50
Tau-Fluvalinate	301	409	*Mysidopsis bahia*	18
			Daphnia magna	400
Naled	260	263	*Daphnia magna*	500
Esfenvalerate	227	113	*Daphnia magna*	150
Resmethrin	102	183	*Daphnia magna*	400
Fenpropathrin	82	28	*Mysidopsis bahia*	21
			Daphnia magna	530
Diflubenzuron	48	73	*Daphnia magna*	1,500
Lambda Cyhalothrin	30	716	*Daphnia magna*	68
			Mysidopsis bahia	4
Deltamethrin	25	86	*Mysidopsis bahia*	1.8
			Daphnia magna	110
Tralomethrin	8	6	*Daphnia magna*	39
Fenthion	6.5	9	*Mysidopsis bahia*	150
Pyridaben	1.9	13	*Mysidopsis bahia*	670
			Daphnia magna	530
Tetrachlorvinphos	0.3	0.06	*Daphnia magna*	1900
Fipronil	<0.1	0.05	*Mysidopsis bahia*	140
Hexaflamuron	<0.05	0.3	*Daphnia magna*	111

Dose type EC_{50} or LC_{50}

*provisional data

The results of the *Aqua*Science studies on the February 21, 2000, samples taken from the Upper Newport Bay Watershed are presented in Appendix C. This report presents the results of the *Aqua*Science TIE studies on the February 21, 2000, samples. The Executive Summary for the *Aqua*Science report (Appendix C) states that the acute (48-hr) toxicity to *Ceriodaphnia* measured in the February 21, 2000, samples ranged from <2.0 to 10.6 toxic units (TUa). The TIE revealed that diazinon and chlorpyrifos concentrations (62 to 1,704 ng/L and 42 to 265 ng/L, respectively) were sufficient to account for all or most of the TUa measured in four of the seven samples. Carbaryl was detected in four samples at concentrations ranging from 270 to 8,700 ng/L (0.08 to 2.5 TUa). Methomyl was detected in five samples at 380 to 2,100 ng/L (0.05 to 0.2 TUa).

Low levels (8 to 87 ng/L) of the pyrethroid insecticide esfenvalerate and/or permethrin were detected in filter extracts and/or raw water from five samples, and these results were consistent with the enhanced toxicity detected in the samples when treated with PBO. Several other pesticides were detected by GC in the samples at concentrations well below their toxicity to *Ceriodaphnia*. HPLC/MS/MS and ELISA analyses of toxic HPLC fractions confirmed the presence of diazinon and/or chlorpyrifos in specific HPLC fractions from all the toxic samples, but did not identify chemicals that were responsible for a substantial portion of the toxicity (3.0 and 4.6 TUa) detected in two of the samples. The *Aqua*Science study revealed that TIE procedures for identifying toxicity due to pyrethroid insecticides needs to be developed and validated. Analytical characterization of toxic HPLC fractions from the samples is continuing, and this report will be updated and reissued if these analyses identify additional candidate toxicants.

Data have been made available (Siepmann and Holm, 2000) from the California Department of Pesticide Regulation from the Upper Newport Bay Watershed, where bifenthrin has been used as part of the fire ant control program. DPR has found sufficient concentrations of bifenthrin in Upper Newport Bay Watershed tributary streams to be acutely toxic to *Daphnia magna*. It is important to note that the Lee and Taylor (1999) 205(j) studies finding of unknown-caused toxicity preceded the initiation of the fire ant control program, and, while bifenthrin could be contributing to some of the unknown-caused toxicity that was found this past year, it is unlikely to be the cause of the toxicity that has been found in parts of the watershed where it has not been used for fire ant control or prior to the initiation of the fire ant control program.

Need for Evaluation of Pyrethroid Pesticides as a Cause of Ambient Water Aquatic Life Toxicity

It is commonly stated that the pyrethroid pesticides, while highly toxic to some forms of aquatic life, are "non mobile" and therefore are not a cause of ambient water aquatic life toxicity. It is now clear from the Upper Newport Bay Watershed, Orange County, CA, studies as well as those conducted in the San Joaquin River watershed, that there is need to more critically evaluate the mobility of pyrethroid pesticides where stormwater runoff or fugitive/drain irrigation waters could transport the pesticides from the point of application to surface waters. With an increased use projected for the pyrethroid pesticides as replacement for the OP pesticides (see discussion presented below), there is need to evaluate whether the replacement of the OP pesticides by pyrethroid pesticides leads to another source of aquatic life toxicity. Of particular concern is the fact that this toxicity could be broadened to include fish.

There is need to measure the concentrations of the most commonly used pyrethroid pesticides in Orange County using analytical procedures that can determine their concentrations at levels that are less the LC_{50} concentrations for procedures. Another issue that needs to be considered is whether the toxicities of these various pyrethroid pesticides are additive.

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