Synopsis of the Upper Newport Bay Watershed 1999-2000 Aquatic Life Toxicity Results with Particular Reference to Assessing the Water Quality Significance of OP Pesticide-Caused Aquatic Life Toxicity[1]

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Introduction

In the early 1990s, several (Kuivila (1993), Foe and Sheipline (1993), Foe (1995a,b, 1998), Hansen & Associates (1995), Waller, *et al.* (1995)), reported finding aquatic life (*Ceriodaphnia*) toxicity in urban and agricultural stormwater runoff/drainage. In California, in accord with the Clean Water Act (CWA) and the Regional Water Quality Control Boards' Basin Plan requirements of "no toxics in toxic amounts," a number of waterbodies were listed as 303(d) "impaired" waterbodies because of this toxicity. This, in turn, has established the requirement that a Total Maximum Daily Load (TMDL) be developed to control this toxicity.

The toxicity has been found to be primarily due to the organophosphate pesticides diazinon and chlorpyrifos that are used in urban residential areas and in some agricultural areas. The toxicity has been generally found to be present in urban stormwater runoff that has been monitored in California. It is also associated with stormwater runoff and agricultural drainage from some types of crops. Of particular concern is the use of diazinon as a dormant spray in orchards. Kuivila and Foe (1995) found that the Sacramento River was toxic to *Ceriodaphnia* for several weeks associated with stormwater runoff from diazinon dormant sprayed orchards. This toxicity persisted for several weeks upstream of Sacramento in the Sacramento River all the way through the Delta into San Francisco Bay. Studies by Katznelson and Mumley (1997), Domagalski (1997), Larsen (1998), Lee and Taylor (1999), SRWP (2001) and Lee and Jones-Lee (2001), have confirmed that OP pesticide toxicity to *Ceriodaphnia* is a common occurrence in stormwater runoff in many urban areas and some agricultural areas in California. Larson, *et al.* (1999), as part of the USGS National Water Quality Assessment Program, have found concentrations of diazinon in urban and agricultural streams that are sufficient to be toxic to *Ceriodaphnia* in many parts of the U.S.

In the mid 1990s, as part of developing an Evaluation Monitoring approach (Jones-Lee and Lee, 1998) for developing best management practices (BMPs) for urban area and highway stormwater runoff water quality impacts, the authors initiated an aquatic life toxicity monitoring program in the Orange County, CA, Upper Newport Bay watershed. This watershed is highly urbanized and consists of urban, agricultural and open space land uses. The original impetus for the initiation of this toxicity monitoring program was the finding by the Orange County Public Facilities and Resources Department (OCPFRD, 1998, 1999) that stormwater runoff entering Upper Newport Bay contained several heavy metals, such as copper, zinc and cadmium, at concentrations above US EPA worst-case-based water quality criteria. This finding raised the issue as to whether the heavy metals present above the US EPA criteria were in toxic available forms. Similar studies for the same purpose were conducted by Hansen & Associates (1995) in the San Francisco Bay region.

The Hansen & Associates (1995) studies, as well as those of Lee and Taylor (1999) and Lee and Jones-Lee (2000a), found that although stormwater runoff from urban areas was toxic to *Ceriodaphnia*, the toxicity was due to organophosphate pesticides and not heavy metals. Lee and Jones-Lee (2000a) have

[1]Report of G. Fred Lee & Associates, El Macero, CA., March (2001).

recently summarized an approach that should be used to develop a TMDL to control heavy metal concentrations in urban area and highway stormwater runoff above US EPA water quality criteria and state standards based on these criteria.

In addition to being involved in the Upper Newport Bay watershed aquatic life toxicity studies, the senior author is also familiar with urban and agricultural stormwater runoff toxicity testing in the San Francisco Bay area and the Central Valley of California, as well as elsewhere. This paper presents a summary of the US EPA 319(h) grant 1999-2000 aquatic life toxicity test results and a discussion of issues that need to be evaluated with respect to assessing the water quality significance of OP pesticide-caused aquatic life toxicity, and is an update of Lee, *et al.* (2000).

Upper Newport Bay Watershed 1999-2000 Studies

During the past four years, the authors have conducted studies that have involved over 500 toxicity tests of stormwater runoff and baseline flow in the Upper Newport Bay tributaries. A major report covering the first three years of these studies was presented by Lee and Taylor (1999). During 1999 and 2000, Lee and Taylor conducted monitoring of the Upper Newport Bay watershed for the purpose of defining the sources of aquatic life toxicity as well as diazinon and chlorpyrifos that caused this toxicity. These studies were conducted as part of the Santa Ana Regional Water Quality Control Board's (SARWQCB, 2000) aquatic life toxicity diazinon and chlorpyrifos TMDL management efforts. They were supported by a US EPA 319(h) grant. The results of these studies have been recently reported by Lee and Taylor (2001). They represent one of the most comprehensive studies that have been conducted thus far on the occurrence, causes, sources, and impact evaluation for the OP pesticide-caused aquatic life toxicity.

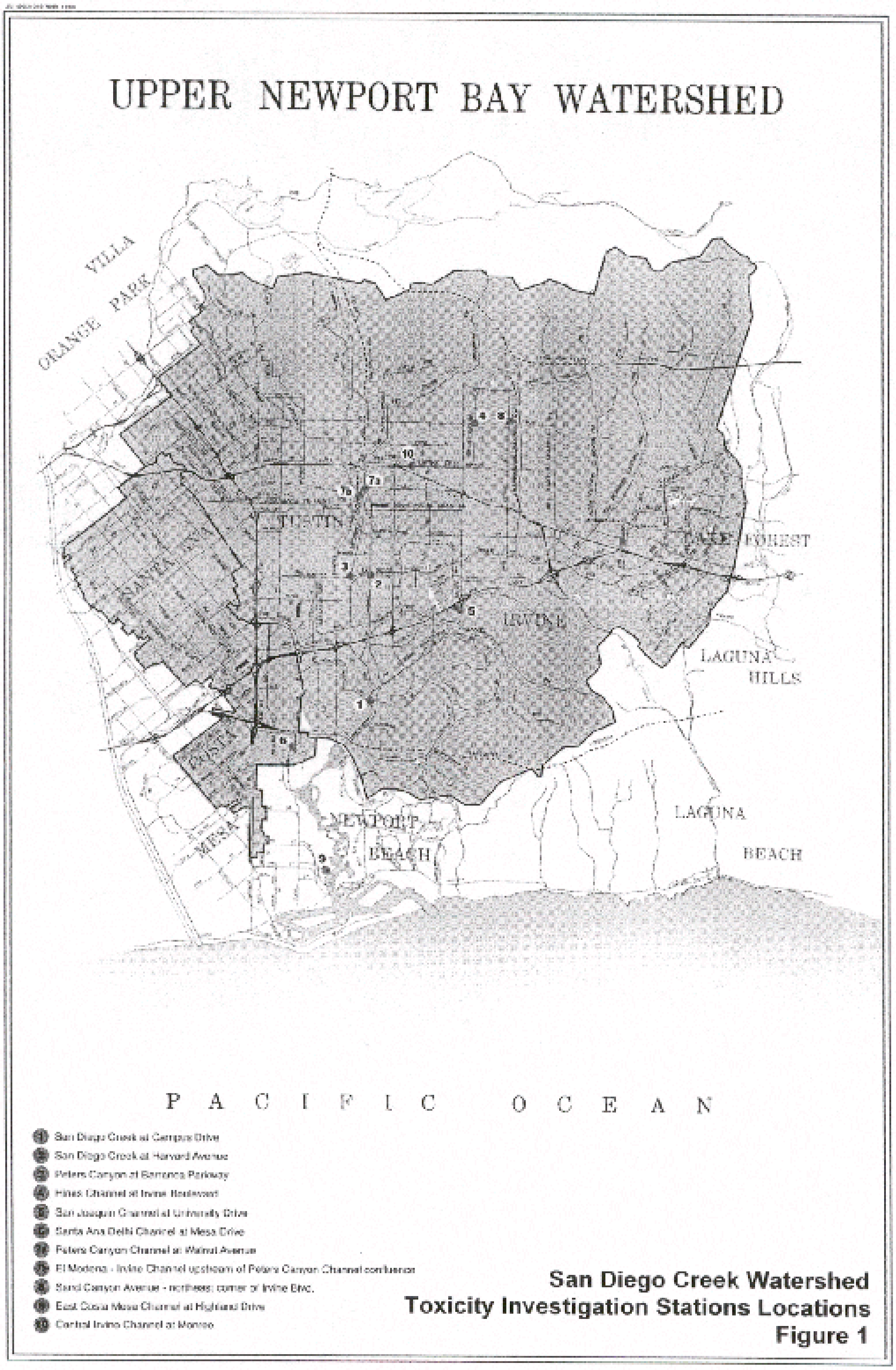
Overview of Ceriodaphnia Toxicity

The overall setting of this study and the locations of the sampling stations used in the 1999-2000 Upper Newport Bay watershed study are shown in Figures 1 and 2 with the sampling station numbers listed in Table 1. Table 2 presents a summary of the *Ceriodaphnia* toxicity testing results. The 1999-2000 water year was somewhat below normal in terms of total precipitation. Average annual precipitation in the Upper Newport Bay watershed ranges from about 12.9 inches in Tustin/Irvine Ranch to 11.5 inches at Newport Harbor (Source: Western Regional Climate Center). Precipitation during the 1999-2000 water year was about 8.1 inches in Santa Ana (Source: OCPFRD). The State Department of Water Resources lists precipitation as 59% of normal in the south coast area of California.

Table 1
319(h) Upper Newport Bay Watershed Sampling Locations

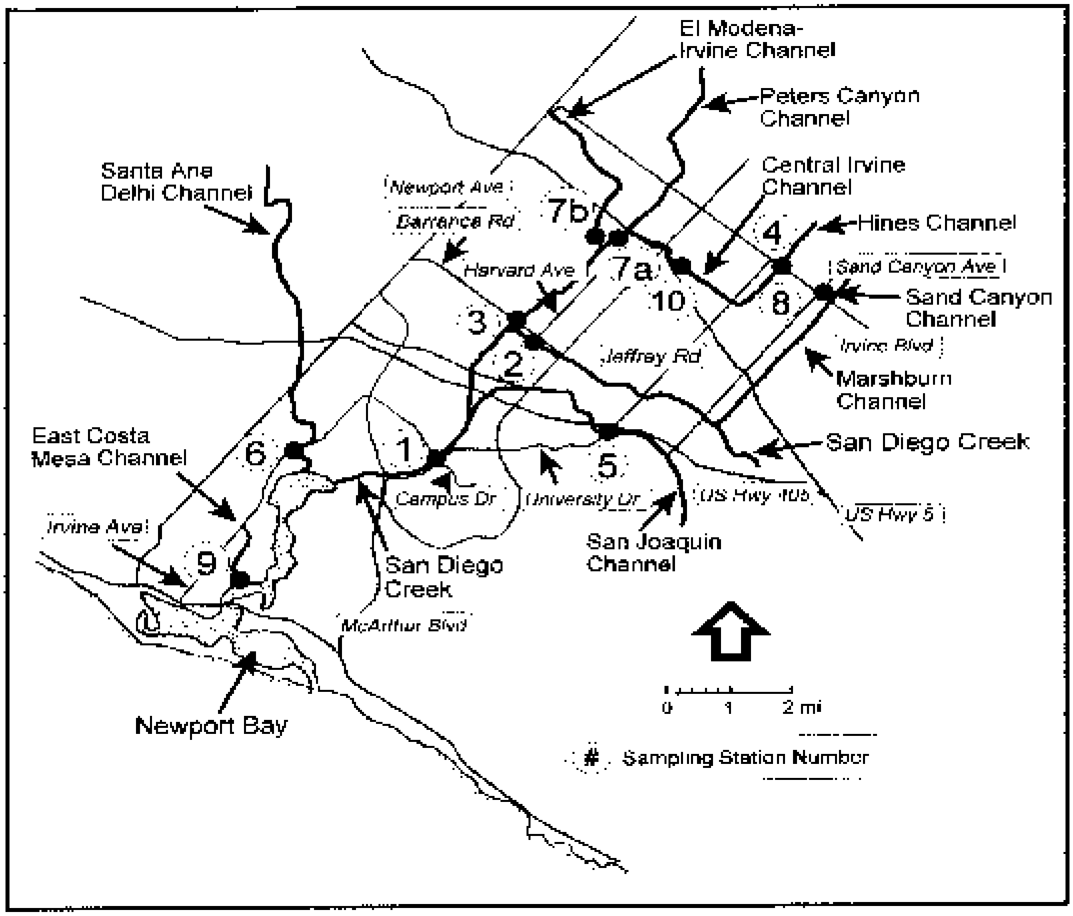
Station	Location
1	San Diego Creek at Campus Drive
2	San Diego Creek at Harvard Ave
3	Peters Canyon Channel at Barranca Pkwy
4	Hines Channel at Irvine Blvd
5	San Joaquin Channel at University Dr.
6	Santa Ana Delhi Channel at Mesa Dr.
7a	Peters Canyon Channel at Walnut Ave.
8	Sand Canyon Avenue-NE corner of Irvine Blvd
9	East Costa Mesa Channel at Highland Dr.
10	Central Irvine Channel at Monroe

Figure 1



San Diego Creek Watershed
Toxicity Investigation Stations Locations
Figure 1

Figure 2



Newport Bay Watershed Sampling Sites

The toxicity testing involved the use of the US EPA procedures described by Lewis, *et al.* (1994) and US EPA (1994). The information presented in Table 2 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, all 10 *Ceriodaphnia* test organisms were killed within 24 hours. The total measured *Ceriodaphnia* acute toxicity units (TUa) ranged from 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 (Lee and Taylor, 1999). Both of those dry weather flow samples contained high levels of *Ceriodaphnia* toxicity.

Table 2
Summary of *Ceriodaphnia* Toxicity in the 319(h)
Upper Newport Bay Watershed Studies

Date	Location	Mortality % (days)	Measured TUa	Expected TUa*	TUa Measured/ Expected
9/29/99	San Diego Cr. @ Campus Dr.	0	0	-	-
9/29/99	San Diego Cr. @ Harvard Ave.	0	0	-	-
9/29/99	Peters Cany Chann@ Barranca	100 (1)	2	2	1
9/29/99	Hines Channel @ Irvine Blvd.	100 (1)	16	4.5	3.5
9/29/99	Santa Ana Delhi @ Mesa Dr.	0	0	-	-
9/29/99	El Modena-Irvine Channel	0	0	-	-
1/25/00	San Diego Cr. @ Campus Dr.	100 (1)	8	3	2.7
2/12/00	San Diego Cr. @ Campus Dr.	100 (1)	8	5	1.6
2/12/00	San Diego Cr. @ Harvard Ave.	100 (1)	8	4.5	2
2/12/00	Peters Cany Chann @ Barranca	100 (1)	8	5	1.6
2/12/00	Hines Channel @ Irvine Blvd.	100 (1)	8	3	2.7
2/12/00	San Joaquin Chann @ Univ Dr.	100 (1)	32	29	1
2/12/00	Santa Ana Delhi @ Mesa Dr.	100 (3)	1	<1	1
2/12/00	Peters Cany Chan @ Walnut A	100 (1)	16	8.5	2
2/12/00	Sand Canyon Avenue-northeast corner of Irvine Blvd	22 (7)	0	0	-
2/12/00	E Costa Mesa @ Highland Dr.	100 (2)	ND	1.5	-
2/12/00	Cent Irvine Channel @ Monroe	100 (1)	8	4	2
2/21/00	San Diego Creek @ Campus	100 (1)	5	2.5	2
2/21/00	San Diego Cr. @ Harvard Ave.	100 (1)	3	3	1
2/21/00	Peters Cany Chann @ Barranca	100 (1)	3	2.5	1.2
2/21/00	Hines Channel @ Irvine Blvd	100 (1)	5	2.5	2
2/21/00	San Joaquin Chann @ Univ Dr.	100 (1)	6	8	1
2/21/00	Santa Ana Delhi @ Mesa Dr.	100 (7)	0	0.5	-
2/21/00	El Modena-Irvine Channel upstream of Peters Canyon	100 (6)	0	0.7	-
2/21/00	Sand Canyon Avenue-northeast corner of Irvine Blvd	30 (7)	0	0	0
2/21/00	E Costa Mesa @ Highland Dr.	100 (1)	2.5	1	2.5
2/21/00	Cent Irvine Chann @ Monroe	100 (1)	5.5	1.5	3.7
5/31/00	San Diego Cr. @ Campus Dr.	0	0	0.4	0
5/31/00	San Diego Cr. @ Harvard Ave.	0	0	0	-
5/31/00	Peters Cany Chann @ Barranca	0	0	0.4	-
5/31/00	Hines Channel @ Irvine Blvd.	44 (7)	-	0	-
5/31/00	Santa Ana Delhi @ Mesa Dr.	0	0	0.2	-
5/31/00	El Modena-Irvine Channel upstream of Peters Canyon	0	0	0.4	-
5/31/00	E Costa Mesa @ Highland Dr.	100 (5)	1	0.5	2
5/31/00	Cent Irvine Channel @ Monroe	NA	NA	0.2	NA

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

Since the expected primary source of water in the Hines Channel during dry weather flow conditions is runoff/seepage from two commercial nurseries located just upstream, 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 and urban dry weather flow to the downstream channels so that the toxicity and pesticides found at Peters Canyon at Barranca Parkway 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 2 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.

In order to estimate the total toxicity in the sample, a toxicity test dilution series was conducted. A comparison of the February 12 and 21, 2000, samples measured TUa at each of the sampling stations is of interest. In general, as shown in Table 2, 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 stormwater runoff events, it could be expected that the second event (February 21, 2000) might have lower concentrations than the first event (February 12, 2000).

Table 2 also 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, Fresno, CA. As discussed by Lee and Taylor (2001), duplicate data (see Table 3) obtained for the same sample by APPL, Pacific Eco-Risk, Martinez, CA and *Aqua*Science, Davis, CA, showed some major differences which would influence the magnitude of the TUa reported. Lee and Taylor (2001) discuss a systematic error that occurred between the APPL GC based diazinon and chlorpyrifos measurements and the *Aqua*Science ELISA based measurements on the same sample. There appears to be a calibration problem between these two laboratories.

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.

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% dilution is toxic and the 3.13% dilution is not toxic, then what is known is that the measured TUa is between 16 and 32. For the purposes of this study, it is reported as 16. It could be somewhat higher. Similarly, the estimated TUa based on normalized diazinon and chlorpyrifos concentrations could be significantly different from that reported, where there are major differences between the APPL GC measured concentration and the ELISA results obtained

Table 3
Summary of Results for Selected Analytes
Upper Newport Bay Watershed OP and Carbamate Pesticide Analysis

	Analyte (ng/L) [LC_{50}]							
Station	**Diazinon [960]**	**Chlorpyrifos [100]**	**Malathion [1,000]**	**Prowl [280,000]**	**Benomyl [80,000]**	**Carbaryl [13,000]**	**Diuron [21,000]**	**Methomyl [8,800]**
Sample Collection Date 9/29/99								
3	820	<50	<100	<100	<400	<70	<400	<70
4	220	310	<100	170	300J	70	<400	<70
Sample Collection Date: 2/12/00								
1	320 460-P	160 324-P	170	120	<400	200	<400	<100
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
10	810 965-A	150 310-A	390	700	2,200	420	<400	910
Sample Collection Date 2/21/00								
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
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
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 3 Continued

Station	Diazinon [960]	Chlorpyrifos [100]	Malathion [1,000]	Prowl [280,000]	Benomyl [80,000]	Carbaryl [13,000]	Diuron [21,000]	Methomyl [8,800]
Sample Collection Date 5/31/00								
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
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
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

by Pacific Eco-Risk and *Aqua*Science. In general, it is concluded that if the measured and estimated TUa are within about three units, the toxicity can be potentially accounted for by diazinon and chlorpyrifos. Using this approach, 10 of the 20 samples collected in the 319(h) study that were highly toxic to *Ceriodaphnia* had readily measurable unknown-caused toxicity.

Table 3 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) for all pesticides normally screened for in its US EPA GC low-level OP and carbamate pesticide tests. While some of the pesticides listed in Table 3 were found by Lee and Taylor (1999) to be present at sufficient concentrations to contribute to the *Ceriodaphnia* toxicity, except for carbaryl, none of them were present at sufficient concentrations in the 319(h) study to be considered a potential cause of *Ceriodaphnia* toxicity. As discussed by Lee and Taylor (1999) this conclusion is based on the LC_{50} data provided by the US EPA OPP Ecotoxicity Database where it is assumed that *Ceriodaphnia dubia* have a similar sensitivity to these pesticides as *Daphnia magn*a.

Table 4 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 paper, pyrethroid-type pesticides would be expected to be present in stormwater runoff in the Upper Newport Bay watershed, since about 20,000 lbs (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.

According to the SARWQCB (2000) report, the California Department of Pesticide Regulation (DPR) has reported dry weather flow toxicity to *Ceriodaphnia* on undiluted samples collected in the San

Diego Creek watershed. All of the dry weather flow samples reported in the 205(j) and in the 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 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.

Table 4
PBO Activation of *Ceriodaphnia* Toxicity

Date	Location	Activation	Sample %
9/29/99	Hines Channel at Irvine Blvd	Yes	3.13
2/12/00	Peters Canyon at Barranca Pkwy	Yes	12.5
2/12/00	Hines Channel at Irvine Blvd	Yes	12.5
2/12/00	Peters Canyon Channel at Walnut Ave.	Yes	6.25
2/12/00	Central Irvine Channel at Monroe	Yes	6.25
2/21/00	San Diego Creek at Campus Drive	Yes	6.25
2/21/00	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	E. Costa Mesa Channel at Highland Dr.	Yes	100

Overview of Mysidopsis Toxicity

Tables 5 and 6 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 study. The freshwater samples tested for *Mysidopsis* toxicity had sea salt added to them so that the test salinity was adjusted to 20 ppt (US EPA, 1994).

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.

Pesticide Use in the Upper Newport Bay Watershed

Lee and Taylor (1999) provided information on the 1995, 1996 and 1997 amounts of diazinon and chlorpyrifos and other pesticides used in Orange County, California, that have been detected in the 205(j) studies of stormwater runoff in this watershed. Recently, the California Department of Pesticide Regulation has made available the 1998 and provisional 1999 pesticide use data for Orange County. The 1999 data is under DPR review and is subject to revision. Lee and Taylor (2001) Appendices D-1 and D-2 present the amounts of selected pesticides used in Orange County in 1998 and 1999, respectively. Information is provided in these appendix tables on the monthly use for dominant types of use.

Table 5
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
9/29/99	San Diego Creek at Campus Drive	0 (7)	no	0	-	-
9/29/99	Santa Ana Delhi at Mesa Drive	0 (7)	yes	0	-	-
1/25/00	San Diego Creek at Campus Drive	100 (1)	yes	8	9	1
2/12/00	San Diego Creek at Campus Drive	100 (1)	yes	8	10	0.8
2/12/00	Santa Ana Delhi at Mesa Drive	40 (4)	-	1	1.5	1
2/21/00	San Diego Creek at Campus Drive	100 (1)	yes	6	6.5	1
2/21/00	Santa Ana Delhi at Mesa Drive	30 (7)	-	1	1.5	1
5/31/00	San Diego Creek at Campus Drive	30 (7)	-	1	-	-
5/31/00	Santa Ana Delhi at Mesa Drive	40 (7)	-	1	-	-

- = No analysis made.

The information presented in Lee and Taylor (2001) Appendices D, E, and F is the most currently available information on pesticide use by commercial/licensed applicators in Orange County. In addition to the DPR reported use, there is also substantial use of diazinon, chlorpyrifos and pyrethroid pesticides by the public that are acquired through over-the-counter sales. The amount of the OP pesticides used by the public is estimated to be at least equal to the DPR reported use.

Table 6
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*
9/29/00	San Diego Cr@ Campus Dr	--	--	--
1/25/00	San Diego Cr@ Campus Dr	460	324	9
2/12/00	San Diego Cr@ Campus Dr	460	350	10
2/12/00	Santa Ana Delhi @ Mesa Dr.	325	50	1.5
2/21/00	San Diego Cr@ Campus Dr	300	230	6.5

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

Table 7 presents a summary of 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 1998 and 1999 backup data for Table 7 is included in Lee and Taylor (2001) Appendices D and F. Lee and Taylor (1999) presented the backup data for 1995 through 1997. The pesticides 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.

Examination of these 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 use have decreased while bifenthrin use has increased significantly. The bifenthrin increase may in part be related to the fact that this pesticide is being used for fire ant control in Orange County. A substantial part of the bifenthrin used, however, was due to new uses on agricultural crops that were initiated in 1999.

Table 7 also presents a summation of the total copper compounds that are used as a pesticide within Orange County for 1997 through 1999. Since the Orange County Public Facilities Resources Department (OCPFRD, 1998, 1999) and Lee and Taylor (2001) have found that the copper concentrations in stormwater runoff from various parts of the Upper Newport Bay watershed are significantly elevated, there is the issue of how much of this elevated copper is due to pesticide use versus vehicular traffic, such as release from wear of automobile break pads, etc.

With the phase-out of chlorpyrifos in 2001, there will likely be a significant shift to other pesticides as a replacement. It will be of interest to examine the changes in pesticide use that take place associated with this phase-out and the effects of the phase-out on aquatic life toxicity in stormwater runoff.

Table 7
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 Pesticides	-	-	15,635	23,883	16,389

- data not available

Apportionment of Pesticide Use in the Upper Newport Bay Watershed

Approximately 21,300 lb (ai) of diazinon and 68,103 lb (ai) of chlorpyrifos (average for data from 1995 to 1998 reported to the County Agriculture Commissioner) 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 (ai) of diazinon and 13,600 lb (ai) of chlorpyrifos are applied by commercial applicators in the Upper Newport Bay watershed, or approximately 3,200 lb (ai) 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. Therefore, it can be concluded that only a small part (less than 0.1%) of the diazinon and chlorpyrifos applied in the Upper

Newport Bay watershed is responsible for the stormwater runoff associated toxicity to aquatic life in San Diego Creek.

OP Pesticide Runoff Loads

One of the primary objectives of the 319(h) project was to gain insight into the potential significance of various types of land use in the Upper Newport Bay watershed as a source of the OP pesticides diazinon and chlorpyrifos as well as the unknown-caused toxicity. The Santa Ana Regional Water Quality Control Board staff selected 10 sampling stations in the Upper Newport Bay watershed. Then, based on the total funds made available through the Board in the 319(h) grant as well as the supplemental funding, it was determined that these 10 stations would be sampled for two major stormwater runoff events. This sampling took place on February 12, and February 21, 2000. Further, a set of samples was obtained during a limited stormwater runoff event on January 25, 2000, for San Diego Creek at Campus Drive. Also, a complete set of samples was to be obtained, if possible, from all 10 stations during dry weather flow conditions. This sampling took place on May 31, 2000. In addition, a more limited set of sampling locations (due to lack of flow) was taken during dry weather flow conditions on September 29, 1999.

It was understood at the initiation of the sampling program that there were insufficient funds available to fully define either the loads of pesticides or the total amount of *Ceriodaphnia* toxicity during a stormwater runoff event at the 10 stations selected for study. Of particular concern is whether the concentration of a pesticide found during a runoff event could be adequately characterized by a single grab sample taken at some time during the event. The 205(j) studies conducted by Lee and Taylor (1999) showed that the concentrations of diazinon and chlorpyrifos were essentially constant during a runoff event for several storms sampled at San Diego Creek at Campus Drive; however, there is no assurance that that same pattern of constant concentration during a runoff event would occur at all ten 319(h) sampling stations. While the San Diego Creek at Campus Drive sampling station is an integrator for most of the Upper Newport Bay watershed, it is possible/likely that as the San Diego Creek tributaries are sampled near the areas where the pesticides are used, there could be changes in concentration of the pesticides during a runoff event.

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. Lee and Taylor (2001) provide a summary of land use within each of the sampling station's watersheds. An issue of concern with respect to reliably estimating the potential significance of a particular type of land use as a source of diazinon and chlorpyrifos as well as unknown-caused toxicity, was that, of the 10 sampling stations selected, five had mixed land use in the watersheds upstream of the sampling location (see Table 8). 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% 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 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.

Constituent load calculations were completed for each of the two wet weather events for diazinon and chlorpyrifos at each of the 10 sampling stations. 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 for the May 31, 2000, dry weather sampling event were also made. The September 29, 1999, dry weather event did not provide a sufficient data set for load calculations since there was insufficient flow for measurements at several locations. The details of the load calculations are presented by Lee and Taylor (2001). A summary of the load calculations is presented herein.

Table 8
Summary of Sampling Station Watershed Dominant Land Uses

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

The 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. 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 to 0.8×10^{-5} lb/acre/storm. Export rates of chlorpyrifos are somewhat higher, ranging from 0.1×10^{-5} to about 2.3×10^{-5} lb/acre/storm. 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/storm. For chlorpyrifos, export rates for these same stations range from 0.2×10^{-5} to 1.2×10^{-5} lb/acre/storm, 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 tend 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.

Regulatory Requirements

The implementation of the CWA TMDL requirements has initiated a major effort in California to control diazinon- and chlorpyrifos-caused aquatic life toxicity. The no toxics in toxic amounts requirement is being used by the US EPA Region 9 and the California Water Quality Control Boards to initiate TMDL programs to control *Ceriodaphnia* toxicity that is due to diazinon and/or chlorpyrifos. There is, however, considerable discussion/controversy about the appropriate TMDL goal. Ordinarily, in a TMDL program, the TMDL goal is the water quality standard/objective for the constituent of concern. However, since the US EPA has not adopted a water quality criterion for diazinon, and is not requiring that states adopt the US EPA (1987a,b) "Goldbook" criteria for chlorpyrifos, and California and some other states have not voluntarily adopted the US EPA "Goldbook" criterion for chlorpyrifos into a state standard, states like California do not have water quality objectives (standards) for the OP pesticides like diazinon and chlorpyrifos.

The California Department of Fish and Game (DFG) (Siepmann and Findlayson, 2000) has developed recommended water quality criteria for diazinon and chlorpyrifos using US EPA guidance for criteria development. They recommend a freshwater diazinon acute criterion (CMC) of 80 ng/L and a chronic criterion (CCC) of 50 ng/L. No saltwater criteria were recommended for diazinon. They recommend a freshwater chlorpyrifos CMC of 20 ng/L and a CCC of 14 ng/L. The corresponding recommended chlorpyrifos saltwater CMC was 20 ng/L and CCC was 9 ng/L. They also indicate that the diazinon and chlorpyrifos toxicities are additive. The CA DFG criterion for chlorpyrifos is similar to the US EPA (1987a,b) criterion. According to current regulatory requirements, a concentration of a regulated constituent in ambient waters above a water quality standard by any amount more than once every three years represents a violation of the standard.

The LC_{50} for diazinon toxicity to *Ceriodaphnia* is about 450 ng/L. The concentrations of diazinon that can cause toxicity in the standard test (Lewis, *et al*., 1994) over an extended period of time are on the order of 100 to 200 ng/L. Therefore, the CA DFG criteria are considerably less than the concentrations of diazinon and chlorpyrifos that would cause aquatic life toxicity in a US EPA standard toxicity test. The US EPA Region 9 (Strauss, 2000) has indicated that the Region would accept CA DFG developed criteria as TMDL goals to eliminate aquatic life toxicity due to diazinon and chlorpyrifos.

Considering the small amounts of diazinon and chlorpyrifos that are needed to cause aquatic life toxicity to *Ceriodaphnia* (Lee and Taylor, 1999, 2001), establishing the TMDL goal as a concentration of diazinon and/or chlorpyrifos equal to the DFG criterion value effectively means that many, if not most, of the current uses where the pesticide is applied so that it is exposed to rainfall, runoff, and irrigation water releases, will need to be eliminated in order to eliminate violations of the DFG recommended water quality criteria.

Another complicating factor in regulating the OP pesticide-caused aquatic life toxicity is the different regulatory approaches that are used for controlling pesticide impacts on non-target organisms versus the control of toxicity to aquatic life by non-pesticides. The Clean Water Act, as being implemented by the US EPA, requires the control of toxics discharged in toxic amounts. If the OP pesticide-caused aquatic life toxicity were due to heavy metals in urban stormwater runoff, they would have to be controlled under Clean Water Act requirements. However, pesticides are regulated by the US EPA Office of Pesticide Programs (OPP). The US EPA OPP Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) regulations allow toxicity to non-target organisms, provided that this toxicity is not significantly adverse to the beneficial uses of the waterbody. FIFRA definitions include:

"x) Protect health and the environment.--The terms 'protect health and the environment' and 'protection of health and the environment' mean protection against any unreasonable adverse effects on the environment."

"(bb) Unreasonable Adverse Effects on the Environment.--The term 'unreasonable adverse effects on the environment' means (1) any unreasonable risk to man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of any pesticide, or (2) ..."

US EPA OPP has not determined whether diazinon- or chlorpyrifos-caused aquatic life toxicity represents an unreasonable adverse effect on the environment. Further, the US EPA OPP FIFRA regulations allow other factors (such as economics and social) than impairment of beneficial uses to determine whether a pesticide's registration or re-registration should be limited by adverse impacts to non-target organisms. The US EPA OPP FIFRA regulations point to the need to have a much better understanding of the role of specific types of zooplankton in influencing beneficial uses of waterbodies in regulating OP pesticides, such as diazinon and chlorpyrifos, that are toxic to only certain types of zooplankton. Basically the question becomes one of whether the numbers, types, and characteristics of aquatic life present in receiving waters for urban stormwater runoff containing OP pesticide-caused aquatic life toxicity are being significantly adversely impacted by this toxicity.

Toxicity Impact Evaluation

One of the most important components of developing an appropriate TMDL goal for control of OP pesticide-caused aquatic life toxicity is an evaluation of the potential water quality-beneficial use impacts of the stormwater runoff-associated toxic pulses of OP pesticide-caused aquatic life toxicity. The finding of toxicity in urban stormwater runoff should not be assumed to be significantly detrimental to the beneficial uses of the receiving waters for the runoff. The conditions of the US EPA standard toxicity text using *Ceriodaphnia* (zooplankton), fathead minnow larvae (fish) and *Selenastrum* (algae) can lead to laboratory-based toxicity that is not manifested in the field.

There are situations where OP pesticide-caused aquatic life toxicity in urban streams is rapidly lost through dilution in the receiving waters for the stream discharges. This situation appears to be occurring in Sacramento, California, where highly toxic urban streams that discharge to the Sacramento River do not cause this River to be toxic. It is essential, as part of a TMDL goal development program for OP pesticide-caused aquatic life toxicity, to determine if aquatic life in receiving waters for the stream discharge experience sufficient toxicity for a sufficient period of time to be toxic and adverse to aquatic organisms.

Further, it is important to assess whether toxicity in the urban stream as well as in the receiving waters to organisms with a sensitivity to OP pesticides, like *Ceriodaphnia*, is adverse to higher trophic level organisms that depend on zooplankton as food. Novartis (1997) and Giddings, *et al.* (2000) have developed a probabilistic ecological risk assessment (PERA) which shows that *Ceriodaphnia* is one of the most sensitive organisms known to OP pesticide toxicity. Novartis claims that killing zooplankton with an OP pesticide sensitivity, like *Ceriodaphnia*, will not be adverse to the beneficial uses of the ecosystem since there are other sources of larval or small fish food that are available that are not impacted by OP pesticide-caused toxicity. Hall and Giddings (2000) have discussed the need to use multiple lines of evidence in predicting site-specific ecological effects due to pesticides and other toxicants.

Lee and Jones-Lee (1999a) have pointed out that the single chemical PERA used by Novartis as an assessment of the ecological/water quality impacts of the OP pesticide-caused aquatic life toxicity may not be valid since the ecological role of the *Ceriodaphnia*-like organisms that are killed by OP pesticides in stormwater runoff is not known. It could be that the zooplankton that are sensitive to OP pesticide toxicity are essential components of the food web for important higher trophic level organisms. The loss of their food through OP pesticide-caused toxicity could be detrimental to the beneficial uses of the waterbody. Another problem with the single chemical PERA approach is that it does not consider additive and/or synergistic effects of other pesticides or chemicals which together could be adverse to the beneficial uses of a waterbody.

As discussed by Lee and Jones-Lee (1999a), a substantial site-specific research program is needed to substantiate that the PERA approach is a valid approach for protecting the beneficial uses of waterbodies that experience toxic pulses of OP pesticide-caused toxicity. Recently, Strauss (2000) of the US EPA Region 9 has indicated that the PERA approach is not acceptable for establishing a TMDL goal for OP pesticide-caused aquatic life toxicity. Strauss has indicated that the TMDL goal should be a chemical concentration that is based on the approach that the US EPA uses to develop a water quality criterion such as those used by CA DFG in developing their suggested criteria for diazinon and chlorpyrifos.

Since many urban streams have been converted to stormwater conveyance structures (some are concrete-lined) with severely limited aquatic life habitat, the elimination of OP pesticide toxicity will, in many cases, likely have little or no impact on the aquatic life-related beneficial uses of the urban stream. In conducting the studies for establishing the TMDL goal, it is important to determine if toxicity in an urban stream persists for a sufficient period of time in the stream and in the receiving waters for the stream discharge to be toxic to stream and/or receiving water zooplankton with OP pesticide toxicity sensitivity similar to *Ceriodaphnia*. Often the period of time that zooplankton can be exposed to toxic conditions in an urban stream associated with a stormwater runoff event is on the order of a few hours -- i.e., the time it takes for a zooplankton present in the headwaters of the stream to be carried from this location to the point where the stream mixes with nontoxic downstream waters. The results of a four-day toxicity test where the toxicity is only manifested on the third or fourth day have limited applicability to properly assessing significant urban stormwater runoff-associated toxicity.

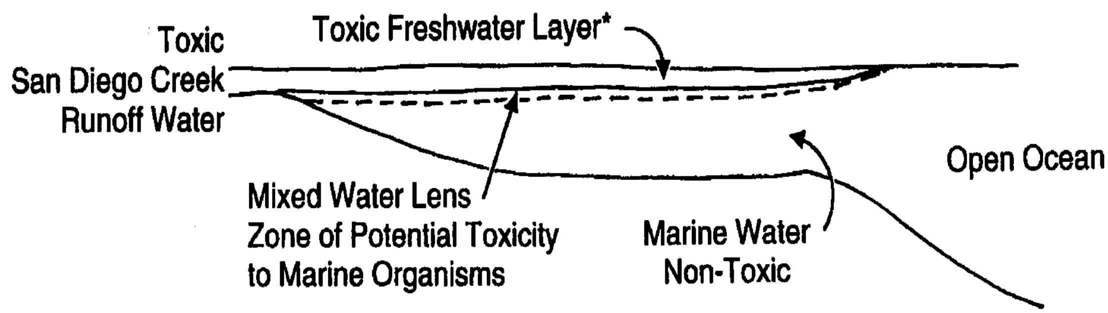
Urban stormwater runoff that enters marine waters creates a special situation for evaluating the impact of OP pesticide-caused aquatic life toxicity. The studies conducted by Lee and Taylor (1999) and Lee, *et al.* (2000) involve assessing the presence and impacts of OP pesticide-caused aquatic life toxicity in Upper Newport Bay, Orange County, CA. Based on a now four-year study of stormwater runoff, they have found that all stormwater runoff to Upper Newport Bay is highly toxic to *Ceriodaphnia* and *Mysidopsis* with typically 5 to 20 TUa. This toxicity is to *Ceriodaphnia* due to a combination of diazinon (LC_{50} of 450 ng/L) and chlorpyrifos (LC_{50} of 80 ng/L) as well as unknown constituents. This toxicity is typically manifested within 24 hours, where all *Ceriodaphnia* or *Mysidopsis* added to the undiluted test samples of stormwater runoff are killed within one day. Diazinon at the concentrations found in urban stormwater runoff in the Upper Newport Bay watershed is not toxic to *Mysidopsis* (LC_{50} of 4,500 ng/L). The toxicity found is due to chlorpyrifos (LC_{50} of 35 ng/L) and some as yet unidentified toxic constituents present in the runoff waters.

Upper Newport Bay is a marine bay with a typical salinity of 30 ppt. The stormwater runoff to the Bay is freshwater. Therefore, under most conditions, the stormwater runoff forms a freshwater lens on the underlying marine waters. Studies (Lee and Taylor, 1999) on the persistence of the OP pesticide-caused aquatic life toxicity in Upper Newport Bay show that it is present only in a relatively thin layer of freshwater stormwater runoff that has mixed to a limited extent with the marine waters of the Bay. Bay waters which have a salinity greater than about 5 ppt are nontoxic since the toxic freshwater has been diluted sufficiently to eliminate the toxicity to *Mysidopsis*.

Any freshwater organisms carried into the Bay in the stormwater runoff will be killed by the salinity of the Bay. Further, the impact of the toxicity to freshwater organisms in the tributary streams is restricted to a few hours of exposure during a stormwater runoff event since this is the maximum transport time from the tributary stream's headwaters to the Bay. Except for discharges apparently associated with nurseries, no toxicity has been found in the tributary streams during non-runoff events. Therefore, the focus of evaluating the impact of the OP pesticide-caused aquatic life toxicity should be on its impact to marine zooplankton and other marine organisms.

Lee, *et al.* (2000) have reviewed the conditions that need to be considered in reliably evaluating the OP pesticide-caused aquatic life toxicity in urban stormwater runoff to marine waters. They point out that in order for the OP pesticide-caused aquatic life toxicity in the stormwater runoff to Upper Newport Bay to be significantly adverse to the beneficial uses of the Bay, a marine zooplankton must migrate from the 30 ppt marine waters into the freshwater/marine water lens that has sufficient toxicity to kill the zooplankton in the period of time that this toxicity persists in the Bay. The stormwater runoff potential toxicity situation is shown in Figure 3. The studies of Lee and Taylor (1999) have shown that the toxic concentrations persist for a day or two in the upper part of the Bay within the freshwater/marine water lens. Upper Newport Bay is a tidal bay with a maximum 10-foot tidal range. This tidal action rapidly mixes any freshwater inputs to the Bay.

Figure 3. Stormwater Runoff Potential Toxicity



While significant toxicity to marine zooplankton in the Bay is possible, it appears to be unlikely. Studies need to be done to determine if marine zooplankton migrate into the freshwater/marine water lens during a runoff event and are exposed to toxic conditions within the lens water. If organisms of this type are found, then the ecological significance of these organisms to the Bay's beneficial uses needs to be evaluated.

Recommended Approach for Developing a TMDL to Control Aquatic Life Toxicity Caused by OP Pesticides

Harader (2001) has recently developed a proposed Arcade Creek Pesticide TMDL Process. Arcade Creek is an urban stream located in Sacramento, CA. It is on the CVRWQCB 303(d) list of impaired waterbodies due to the aquatic life toxicity caused by diazinon and chlorpyrifos. Harader's proposed approach for TMDL development is designed to meet US EPA national as well as Region 9 requirements for TMDLs. His approach includes developing the following information:

- Problem Statement
- Numeric Targets Report
- Source Analysis

- Linkage Analysis
- TMDL Report

Information on each of these areas is provided below.

Problem Statement. The problem statement should present the body of evidence pertinent to the current water quality/beneficial use impairment issues. It should review the database available at the time of the 303(d) listing for the waterbody and any additional data pertinent to TMDL formulation and implementation since the original listing. For OP pesticide-caused aquatic life toxicity, is any information available on the magnitude of the toxicity, the concentrations of diazinon and chlorpyrifos and other pesticides in the samples, the amount of the total toxicity that can be attributed to OP pesticides, the magnitude of unknown-caused toxicity, the duration of toxicity during stormwater runoff events, toxicity during dry weather flow and any information on the impact of the toxicity on the numbers, types and characteristics of desirable forms of aquatic life, including planktonic and benthic organisms as well as higher trophic level organisms, such as fish? In addition, an assessment should be made as to whether the conditions that led to the original 303(d) listing of the waterbody, exist today.

An issue of particular concern with urban streams is whether stream aquatic life habitat characteristics, such as armoring, are severely degraded because of flood control channelization and/or high stream flow erosion so as to preclude of alter the development of any significant aquatic life related beneficial uses of the stream.

Establishing Numeric Targets. In accord with the currently used approach in implementing Clean Water Act requirements, focusing on attainment of water quality standards based on chemical concentrations, the numeric targets for 303(d) listed waterbodies' TMDLs, where the listing is caused by OP pesticide-caused aquatic life toxicity, are the California Department of Fish and Game (Siepmann and Findlayson, 2000) recommended water quality criteria for diazinon and chlorpyrifos. These are discussed elsewhere in this paper. As indicated in that discussion, Strauss (2000) has stated that the DFG criterion values are considered appropriate TMDL goals for OP pesticide-caused 303(d) listing. Generally, if the concentrations of diazinon and chlorpyrifos above the criterion values is restricted to stormwater runoff events, the DFG acute (CMC) criteria should be used. However, if the elevated concentrations persist over a four- day period, then the chronic (CCC) criteria should be used. It is important in assessing the potential adverse impacts of the OP pesticides to aquatic life to incorporate the additive toxicity of these pesticides. There could readily be situations where the concentrations of diazinon and chlorpyrifos are below the criterion values, yet, because of their additive toxicity, there could be adverse impacts to some forms of aquatic life.

Since the overall goal of the water quality management program should be the control of aquatic life toxicity in the state's waters, the TMDL goal for OP pesticide-caused aquatic life toxicity should include elimination of toxicity to zooplankton and fish that adversely impacts the beneficial uses of the waterbody. The first step in assessing this requirement would be the determination of whether there is toxicity in the stream. Where toxicity is found, its cause(s) should be determined and an assessment should be made as to the water quality significance of the toxicity as it relates to the beneficial use impairment of the stream. It is important in interpreting the toxicity test results to consider the duration of exposure that aquatic organisms can experience in a stream compared to the duration of exposure necessary to cause toxicity under laboratory test conditions. For many urban streams the duration of exposure that planktonic organisms can experience during a stormwater runoff event is a few hours. Toxicity that is only manifested after several days of exposure has little relevance to toxicity in many urban streams.

While the US EPA recommends a three species toxicity test approach involving fish, zooplankton and algae, toxicity testing with algae is essentially impossible to interpret without a major site specific investigation of the potential consequences of this algal toxicity to the beneficial uses of the waterbody. Lee and Jones-Lee (1996) have discussed the issues that need to be considered in assessing whether laboratory measured algal toxicity translates to an adverse impact on the beneficial uses of waterbodies. For many waterbodies, excessive algal growth is an impairment of the beneficial uses of the waterbody.

The phase-out of the OP pesticides due to US EPA and chemical manufacturers' agreements that arise out of the potential human health hazards to children, as well as any limitations on OP pesticide residential use due to TMDLs, will result in many instances in the use of other pesticides, such as the pyrethroid pesticides. It is important to not substitute one toxicity problem for another, i.e., "pesticide roulette." This is especially important for some of the pyrethroid pesticides since they are much more toxic to fish than the OP pesticides. This situation mandates that the TMDL goals for the OP pesticides include, as an integral component of the goal, the elimination of pesticide-caused aquatic life toxicity in the waterbody of concern. Simply focusing on diazinon and chlorpyrifos concentrations in an effort to achieve a chemically based TMDL goal without appropriately conducted toxicity measurements could readily lead to severe adverse impacts to the beneficial uses of the stream associated with the substitute pesticides that replace the OP pesticides. Toxicity testing, as part of the TMDL goal, is needed to ensure that associated with the decrease of diazinon and chlorpyrifos concentrations, is the elimination of the toxicity in the waterbody.

As discussed elsewhere in this paper and by Lee and Jones-Lee (1999a), the single chemical species probabilistic ecological risk assessment (PERA) approach is not a valid approach for establishing an OP pesticide-caused aquatic life toxicity TMDL goal unless it is demonstrated by the proponents of that approach that zooplankton and benthic organisms that are killed during a stormwater runoff event are not essential components of the food for higher trophic level organisms that are considered important components of the beneficial uses of a waterbody.

Source Analysis. Information on the specific sources of the OP pesticides that are causing significant aquatic life toxicity in the urban streams and their receiving waters should be compiled and if deficient, developed. Of particular importance, with respect to urban OP pesticide use, is whether the OP pesticides used for structural pest control contribute to stormwater runoff aquatic life toxicity. Information is needed on the specific role that various types of residential property OP pesticide use plays in leading to aquatic life toxicity in the urban streams and other waterbodies. It is highly likely that there will be residential pesticide uses that do not lead to stormwater runoff contamination. The TMDL restriction should be placed on those pesticide uses that impair the beneficial uses of waterbodies, and not all residential uses of pesticides.

Linkage Analysis. Typically, the linkage analysis component of a TMDL is a modeling effort which relates the sources of the constituents of concern to their impacts. Normally, impacts are translated into exceedances of water quality criteria/standards. However, often, as discussed by Jones-Lee and Lee (2000) and Lee and Jones-Lee (2000a) there is a poor correlation between exceedances of worst case based water quality criteria/standards and the impairment of the beneficial uses of waterbodies. This arises from the highly protective approach that the US EPA used in establishing national water quality criteria. This approach will likely apply to the use of the DFG recommended criteria for diazinon and chlorpyrifos. These criteria are well below the incipient toxic levels for these pesticides.

While, for some constituents such as nutrients, it is sometimes possible to establish a linkage analysis between the amounts of nutrients added to a waterbody and the water quality impacts of the nutrients, for the OP pesticides such a linkage analysis is not possible at this time. As discussed herein, only a very small part of the pesticides applied to residential properties is present in runoff from the property.

In order to establish a reliable linkage analysis in a TMDL based program, it is necessary to be able to gain an understanding of pollutant transport mechanisms from the source to the waters of concern. Obtaining this information for OP pesticide transport from some residential property uses will likely be difficult. An OP pesticide aquatic life toxicity/TMDL linkage analysis will have to be based on a phased adaptive management approach, where as part of phase 1, restrictions on certain types of residential uses will need to be imposed, such as the elimination of the use of diazinon on lawns and gardens. This issue is discussed further in the next section of this paper.

Since, in accord with the recent agreements reached between the US EPA and diazinon and chlorpyrifos registrants, both diazinon and chlorpyrifos will be phased out of residential use over the next few years, the development of a TMDL to control the use of these pesticides is moot. The currently required phase-out will almost certainly be implemented before any meaningful phased TMDL implementation approach is implemented. The phase-out of diazinon and chlorpyrifos use on residential properties could be an important situation for establishing residential use for certain purposes and the impacts of this use on aquatic life toxicity in the receiving waters for stormwater runoff from residential properties. This approach would require knowledge of the amounts of diazinon and chlorpyrifos used and the types of uses that occur on residential properties and the associated export of diazinon and chlorpyrifos from residential properties associated with each use during the phase-out process. Unfortunately, the amount of pesticides used on residential properties is poorly understood because of the over the counter sales of the pesticides to the public. There is no reliable information on the amounts of pesticides purchased by the public within an area and how the public uses these pesticides on their property. Without this information, the desired linkage analysis will not be achieved.

While not required in the US EPA TMDL development, the linkage analysis or some other section of the TMDL report should include an assessment of the improvements in the beneficial uses of the 303(d) listed waterbody expected to arise from the implementation of the TMDL. While often this is superficially addressed as reduced concentrations of regulated constituents, what should be assessed is not concentrations, but impacts of chemicals, i.e., will the restriction/elimination of the use of diazinon and chlorpyrifos lead to a discernible improvement in the beneficial uses.

TMDL Report. The TMDL report should present the results of the problem statement, and the assessment of target, source and linkage analysis. The TMDL report should also include a discussion of an implementation plan for achieving the TMDL. This plan should include definitive information on how pesticides that will be used as alternates to the OP pesticides will be evaluated with respect to protecting the beneficial uses of the waterbodies of concern. The overall approach that will likely need to be followed to control the aquatic life toxicity impacts of OP pesticides is to establish a goal of meeting the CA DFG recommended criteria in all waters having an unrestricted aquatic life designated beneficial use. In accord with current Clean Water Act implementation approaches, this approach is generally, but not always, protective of aquatic life resources. However since this worst case approach can be overprotective and thereby unnecessarily restrict the use of a useful pest control product, in accord with CWA implementation approaches those who want to manufacture, sell and use the OP pesticide under review should be provided the opportunity to fund and conduct the studies needed to determine whether a less restrictive approach can be followed for regulating the pesticide. Such studies should be conducted using a full public interactive stakeholder approach; those who want to continue to use a pesticide and allow its concentrations to occur in public waters at concentrations above DFG recommended criteria, should work with regulatory agencies, environmental groups, the public and others to formulate the studies, supervise their implementation, and participate in the interpretation and presentation of the results. A best professional judgement, triad weight of evidence approach of the type described herein should be used.

The tributary rule should apply to those waterbodies that do not have a formally designated beneficial use, including those intermittent streams that could during certain times of the year when water is present, serve as spawning areas for migratory fish such as steelhead trout. These criteria should be implemented as worst case values which are not to be exceeded by any amount more than once in three years. The implementation should be based on additive toxicity for the OP pesticides and other constituents that could enhance the toxicity of the OP pesticides.

The TMDL implementation plan must include a comprehensive monitoring program to determine whether the water quality goal, i.e., meeting the DFG criteria, is achieved. Since restricting the use of a pesticide could lead to the substitution of another pesticide that could cause at least equal, if not greater, environmental harm, it is essential that the TMDL program include a comprehensive toxicity testing program to detect aquatic life toxicity in ambient waters that may be due to the transport of the substitute pesticide(s) from the point of application to the waters of the state.

Suggested Approach for Implementing a Phase I TMDL Goal for Urban Stormwater Runoff OP Pesticide-Caused Aquatic Life Toxicity

In Orange County, California, about 100,000 lbs/yr (ai) of diazinon (25,000 lbs/yr) and chlorpyrifos (75,000 lbs/yr) are used by commercial applicators for residential structural purposes (termite and ant control). In addition, approximately the same amount that is purchased in the local hardware/garden store is projected to be used by the public on residential properties. The total amount of diazinon and chlorpyrifos that is needed to cause the toxicity found in stormwater runoff as it enters Upper Newport Bay is about 2 lbs per storm, with an average of about 11 storms per year (22 lbs/yr), out of the approximately 30,000 lbs/yr that are applied to the Upper Newport Bay watershed. It is evident that most of the diazinon and chlorpyrifos used on residential properties is not c1ontributing to the stormwater runoff toxicity problem.

There are two types of OP pesticide uses on residential properties. The typical structural use, which is often injected into the foundations of the structures below the ground surface, probably does not contribute significantly to OP pesticide-caused aquatic life toxicity. It is likely that the primary source of the diazinon and chlorpyrifos that causes the toxicity in urban stormwater runoff is due to the application of these pesticides above ground near structures and for lawn and garden pest control.

Studies are needed to determine how OP pesticides, and for that matter other pesticides used for various purposes on residential properties, contribute to stormwater runoff toxicity. It is suggested that it may be possible to continue to use the OP pesticides below ground and in other applications for structural pest control (termites and ants) that do not lead to water washoff/leaching, and thereby greatly reduce, if not eliminate, the OP pesticide aquatic life toxicity associated with stormwater runoff from residential areas.

An appropriate Phase I OP pesticide control program could involve restricting the use of OP pesticides for lawn and garden pest control as well as for aboveground near-structure applications where runoff waters could carry the pesticides from the residential properties to the nearby water courses. The implementation of this approach would require restrictions on the sale of the OP pesticides to the public. Such restrictions would have to be implemented through changing the registration governing the use of these pesticides at the federal or state level. Efforts are underway in California by municipal stormwater management agencies who face compliance with TMDLs designed to control OP pesticide-caused aquatic life toxicity in stormwater runoff to have the California Department of Pesticide Regulation change the registration of OP pesticides to restrict their use on residential properties to reduce aquatic life toxicity in stormwater runoff from these properties. This same approach needs to be followed for the pesticides that replace the OP pesticides for residential use.

Restricting the Sales/Use of OP Pesticides on Residential Properties

Recently the US EPA has announced that it will restrict the residential use of chlorpyrifos by the public under the Food Quality Protection Act because of its potential cumulative toxicity to humans. This restriction could potentially result in a significant reduction of the OP pesticide aquatic life toxicity that is found in the Upper Newport Bay watershed stormwater runoff. Placing similar restrictions on the public sales of diazinon for residential lawn and garden use, while still allowing the use of diazinon for below-ground structural control of termites and ants, could be an effective approach for implementing a Phase I TMDL OP pesticide aquatic life toxicity control program. If the restrictions on the sale of chlorpyrifos and diazinon for residential lawn and garden use do not control aquatic life toxicity in stormwater runoff, then a Phase II TMDL implementation program involving greater restrictions on the use of OP pesticides (diazinon and chlorpyrifos) would be needed.

Phase-Out of Chlorpyrifos Residential Use

The results of the 205(j) study (Lee and Taylor 1999) and the 1999-2000 319(h) study (Lee and Taylor, 2001) of the toxicity of San Diego Creek samples taken at Campus Drive and Santa Ana Delhi Channel samples taken at Mesa Drive lead to some interesting conclusions with respect to the future *Mysidopsis* toxicity of stormwater runoff from the Upper Newport Bay watershed. In June 2000, the US EPA and the chlorpyrifos registrants announced that they had reached an agreement to voluntarily withdraw the registration of chlorpyrifos for uses which could result in residential exposure of children to this pesticide. The final announcement on this action was published by the US EPA. A synopsis of this agreement developed by the US EPA is presented below.

> *"On September 20, 2000, US EPA announced receipt of requests by registrants to cancel registrations for chlorpyrifos intended for use to manufacture pesticide products. In addition, registrants are requesting US EPA to cancel or amend uses of certain pesticide products containing chlorpyrifos. These registration cancellations result from the memorandum of agreement signed by US EPA and certain registrants of chlorpyrifos products on June 7, 2000, and follow up agreements with other registrants. This agreement was designed to reduce risks to children and others from exposure to chlorpyrifos from dietary and non-dietary sources. The Federal Register notice (65 FR 56886) lists the products being canceled and describes uses that are being eliminated or changed."*

The phase-out of the manufacture and sale of chlorpyrifos-containing products will take place over a several-year period. All manufacture of chlorpyrifos for residential use associated with lawn application and similar outdoor uses was terminated on December 1, 2000. On February 1, 2001, the registrants terminated sale of chlorpyrifos products that could be used for outdoor residential purposes. The termination of retail sales of these types of products will occur on December 31, 2001. Some allowed residential uses will continue for several years after that date, such as for the control of termites.

Questions have been raised about several aspects of this action, one of the most important of which is the time period allowed for the elimination of future sales of chlorpyrifos that would become restricted under this voluntary reduction in the permitted uses. The immediate implementation of this restriction on residential use sales seems premature based on several factors, the most important of which is that, while causing aquatic life toxicity to a certain group of zooplankton, the significance of this toxicity to the beneficial uses of waters is appropriately questioned.

The Upper Newport Bay studies on the fate, persistence and toxicity, as well as chlorpyrifos concentrations in the Bay associated with stormwater runoff events indicate that the toxicity present in stormwater runoff entering the Bay is unlikely to be adverse to the beneficial uses of the Bay or its tributaries. In the Upper Newport Bay watershed and in most urban streams, there is a limited time from when the chlorpyrifos associated with stormwater runoff events enters the headwaters of the urban streams before it enters the Bay or is diluted in the receiving waters to nontoxic levels. Within Upper Newport Bay, there is a day or so from the time that the chlorpyrifos enters the Bay in a stormwater runoff event before it is diluted by mixing with marine waters to nontoxic concentrations.

In addition, there is substantial evidence that, because of the sorption tendencies of chlorpyrifos, its toxicity is significantly reduced in the sorbed form. As Lee and Taylor (1999) discussed, studies by the US EPA staff (Ankley, *et al.*, 1994) have shown that chlorpyrifos associated with sediments is in a nontoxic form. It may be concluded that, with respect to stormwater runoff impacts, there is considerable question about the water quality beneficial use significance of chlorpyrifos toxicity as a cause of beneficial use impairment of waterbodies.

Another argument has been made that this delayed voluntary restriction of the use of chlorpyrifos in residential areas could lead to additional 303(d) listings and the associated TMDLs, and thereby cause stormwater management agencies to have to initiate control programs. This is not a valid reason to immediately terminate the sale of chlorpyrifos to the public. The elimination of chlorpyrifos from residential use, while it may reduce, will not solve the aquatic life toxicity problem in urban stormwater runoff. This problem is due to both diazinon and chlorpyrifos, where most of the time the toxicity is due to diazinon. In some instances, chlorpyrifos adds to this toxicity. Any new 303(d) listings that occur during this period of phase-out of residential use of chlorpyrifos will likely occur due to diazinon's presence. It is highly doubtful that the elimination of the use of chlorpyrifos on residential properties will have any impact on the beneficial uses of urban streams that now show toxicity due to or in part to chlorpyrifos.

There is need for a program to determine which of the pesticides that are currently registered for residential use could be likely candidates to replace chlorpyrifos and their fate in stormwater runoff from residential properties. Are they transported in sufficient concentrations in the runoff waters to cause aquatic life toxicity or excessive bioaccumulation in aquatic life in the receiving waters for the runoff? Situations could develop where the questionable beneficial use impairment associated with chlorpyrifos aquatic life toxicity could be translated into a real significant water quality problem associated with the replacements for chlorpyrifos that will occur over the next year. These issues have recently been reviewed by Lee (2001).

An area of particular concern is that some of the replacements for chlorpyrifos, such as the pyrethroid pesticides, are highly toxic to fish. There are some who consider this limited toxicity to certain types of zooplankton, such as *Ceriodaphnia* and *Mysidopsis*, of lesser potential significance to aquatic ecosystems and water quality than direct toxicity to fish. While toxicity to *Ceriodaphnia*- and *Mysidopsis*-like organisms can be of potential significance to higher trophic level organisms if there are no other substitute zooplankton that can serve as larval fish food, direct toxicity to fish can be highly adverse to upper trophic level aquatic life.

The most likely candidates for chlorpyrifos replacement are the pyrethroid pesticides. There is a dearth of information at this time on the presence, fate and effects of pyrethroid pesticides associated with their use on residential and agricultural properties as they may impact the beneficial uses of receiving waters for stormwater runoff from these properties. There is an immediate need for US EPA and state pesticide regulatory agencies to require that this information be provided before there is a larger-scale use of pyrethroid pesticides arising from the phasing out of the residential use of chlorpyrifos.

Phase-Out of Diazinon Residential Use

On December 5, 2000, the US EPA (2000) announced an agreement to phase out diazinon for indoor uses beginning in March 2001, and for all lawn, garden and turf uses by December 2003. According to the US EPA, diazinon is the most widely-used pesticide ingredient for application around homes and in gardens. It is used to control insects and grub worms. The agreement reached with the manufacturers, Syngenta and Makhteshim Agan, will eliminate 75 percent of the use, which amounts to more than 11 million pounds of the pesticide used annually.

"Specifically, the terms of the agreement implement the following phase-out schedules:

- *For the indoor household use, the registration will be canceled on March 2001, and all retail sales will stop by December 2002.*
- *For all lawn, garden and turf uses, manufacturing stops in June 2003, all sales and distribution to retailers ends in August 2003. Further, the company will implement a product recovery program in 2004 to complete the phase out of the product.*
- *Additionally, as part of the phase out, for all lawn, garden, and turf uses, the agreement ratchets down the manufacturing amounts. Specifically, for 2002, there will be a 25 percent decrease in production; and for 2003, there will be a 50 percent decrease in production.*
- *Also, the agreement begins the process to cancel around 20 different uses on food crops."*

Syngenta (2000a,b) (formerly Novartis) and Fuelner (2000) are phasing out the registration of diazinon for many residential uses. Syngenta (2000a), in a media release stated:

> *"Diazinon has been marketed worldwide for more than 40 years. In the US it is sold mainly to control home lawn and garden insect pests, and many agricultural pests. While other manufacturers will continue to sell diazinon for agricultural uses after 2004, Syngenta will phase the product out completely.*
>
> *Many factors contributed to the company's decision to end diazinon sales, but the most compelling factors were economic."*
>
> * * *
>
> *"Earlier this year, Syngenta submitted a comprehensive response to EPA's Preliminary Risk Assessment of diazinon and has presented additional studies that show wide margins of safety. The EPA's agreement to a four-year market transition for lawn and garden use confirms the value and safety of this product, and reflects the agency's conclusion that no unreasonable risk to people or the environment exists."*

Based on a discussion of diazinon phase-out by G. Dugan (pers. comm 2001) of the US EPA Region 9 staff, the US EPA's action on the phase-out of diazinon effectively precludes another manufacturer from re-registering diazinon for residential property use. Therefore, by 2004 the sale of diazinon-containing products for residential use should significantly be decreased since diazinon-containing products will no longer be available for residential use. From an Orange County perspective, this means that on the order of 20,000 to 25,000 lbs (ai) of diazinon that is currently being used for residential purposes, will be replaced by some other pesticides or some other approach for pest management.

Evaluation of the Impact of Alternative Pesticide Use

At this time there are other OP pesticides, such as propetamphos, that are used on residential properties. Several thousand lbs/yr (ai) of propetamphos are used by commercial applicators on residential properties in Orange County, CA and in the Sacramento, CA area. Propetamphos is not measured in the conventional dual column GC scans using US EPA procedures. It could be a contributor to the unknown-caused toxicity that is found in Upper Newport Bay stormwater runoff. Also, and likely of greater concern, is the use of pyrethroid pesticides on residential properties. Through the late 1990's, approximately 25,000 lbs/yr (ai) of four pyrethroid pesticides (permethrin, cypermethrin, fenvalerate and bifenthrin) were used in Orange County, CA. The pyrethroid pesticides are as toxic, if not more toxic, to some zooplankton as the OP pesticides. Further, the pyrethroid pesticides are beginning to be sold over the counter in substantial amounts for residential use by the public. There is need to evaluate whether the use of pyrethroid pesticides on residential properties is now, or could in the future with increased use as the OP pesticides are phased out, be a cause of aquatic life toxicity in stormwater runoff.

Any TMDL for the control of OP pesticide-caused aquatic life toxicity should include funding to conduct studies to determine the aquatic life impacts of the alternative pesticides that are used as replacements for the OPs. Without this approach, the benefits of controlling the aquatic life toxicity in urban stormwater runoff associated with restricting the use of the OP pesticides may not occur. A key component of any TMDL program for control of OP pesticide-caused aquatic life toxicity should be an evaluation of the anticipated improvement of the beneficial uses of the receiving waters for the urban stormwater runoff.

Conclusions. The OP pesticides diazinon and chlorpyrifos are useful products for controlling pests on residential and agricultural properties. They are, however, causing substantial toxicity in urban stormwater runoff and in some receiving waters for agricultural runoff. Currently, their impacts on beneficial uses is poorly understood. It is possible that, through appropriately conducted studies, they can continue to be used for some purposes on residential properties. The development of a TMDL goal to control OP pesticide-caused aquatic life toxicity in urban stormwater runoff will require a substantial study/evaluation program to determine for the waterbodies receiving the urban runoff the beneficial use impairments that are likely occurring. The funding of these studies should be provided by pesticide manufacturers, formulators and users. Failure to provide adequate funding to demonstrate that the OP pesticides diazinon and chlorpyrifos can be used on residential properties without significant adverse impacts on the beneficial uses of receiving waters for the urban stormwater runoff will likely require restricting their use in residential settings.

Proactive Approach for Managing Pesticide-Caused Aquatic Life Toxicity

Over the past half a dozen years, several groups in California have been studying the aquatic life toxicity that is present in stormwater runoff from urban and some agricultural areas that is attributable to the use of the organophosphate (OP) pesticides diazinon and chlorpyrifos. These pesticides are sufficiently mobile from their point of application so that they cause aquatic life toxicity to certain forms of zooplankton (*Ceriodaphnia dubia* and *Mysidopsis bahia*) in the receiving waters for the runoff from the area of application. This toxicity was originally discovered in urban stormwater runoff associated with monitoring runoff from urban areas in the San Francisco Bay region for assessing the impacts of constituents such as heavy metals that are present in the runoff waters above water quality criteria/standards. It was also discovered in the early 1990s, through the work of Dr. Chris Foe of the California Central Valley Regional Water Quality Control Board in investigating aquatic life toxicity in the San Joaquin River and its watershed. It was found through the use of TIEs that the heavy metals present in urban stormwater runoff were not in toxic forms; however, there was appreciable toxicity due to the OP pesticides diazinon and chlorpyrifos. In agricultural areas, the toxicity is associated with the use of these pesticides on agricultural crops in the Central Valley. The Sacramento River, Feather River, San Joaquin River, Delta and Upper San Francisco Bay are toxic each winter/spring due to the use of diazinon as a dormant spray in orchards.

In recent years, in both urban and residential areas, increasing use of pyrethroid-type pesticides is being made as a substitute for the OP pesticides. According to Kuivila (2000), there are over 150 pesticides used in the Central Valley of California. Very few of these are being monitored for their potential impacts to aquatic organisms. Further, the information gathered by the US EPA Office of Pesticide

Programs, as well as the California Department of Pesticide Regulation for pesticide registration falls far short of providing the information necessary to evaluate whether the replacements for the OP pesticides (such as pyrethroids and other types of pesticides) will cause adverse impacts to the environment.

Basically, the situation today is one where pesticides are registered for use without adequate evaluation for potential environmental impacts. It is only when substantial problems are found that there is a potential for restriction on the use of the pesticides. As discussed by Lee and Jones-Lee (2000b), it is clear that there is need to significantly change from a passive to a proactive approach, in which pesticides that are in use today are evaluated by water quality management agencies for their impacts. This evaluation is not done as part of pesticide registration, because of the pressure on registration agencies at the federal and state level, which effectively precludes requiring that pesticide registrants conduct an adequate evaluation of the potential for pesticides in urban area and, for that matter, agricultural stormwater runoff and agricultural field discharges to cause aquatic life toxicity in the receiving waters for the runoff/discharges.

In light of the current regulatory approaches toward controlling aquatic life toxicity associated with pesticide use, there is need to conduct studies associated with use to determine whether there is aquatic life toxicity in runoff from areas where the pesticide is applied. The proactive approach toward evaluating whether pesticide use in a particular region is adverse to the beneficial uses of the receiving waters for stormwater runoff/drainage/discharges from areas where it is applied involves determining what, when and where pesticides are applied in the region. Associated with each application area should be a monitoring program of the receiving waters for the runoff from the application area. A combination of chemical and biological monitoring should be conducted immediately following, and then for some time after the application(s) occurs. This monitoring should use an event-based approach, in which the monitoring specifically targets stormwater runoff/discharge events when the pesticide is most likely to be present in the discharge. A combination of aquatic toxicity and aquatic organism assemblage information should be collected to assess potential biological impacts. The toxicity information should be not only at fixed locations downstream of the runoff location, but sampling should also be done in the runoff plume matching the transport of the water receiving the pesticides from the point of application.

Studies of this type should be conducted for several years associated with the use of a particular pesticide on a particular crop at a particular location. Eventually, provided that the formulation of the pesticide and its application rate and method remain the same, the monitoring program for that particular pesticide use at the test application can be significantly curtailed. Further, as experience is gained with this proactive approach, it should be possible to greatly reduce the amount of monitoring/evaluation needed for pesticides for which there is an adequate information base to determine that their use does not pose a threat to the environment.

The funding of these types of studies should be provided by the pesticide manufacturers, where the costs are passed on to the users of the pesticides. Adoption of this proactive approach would significantly change the current after-the-fact definition of problems associated with pesticide use to detecting them when they first begin to be used. This approach should be considered part of the registration/re-registration process, where any registration would be provisional, subject to immediate revocation if it is found that the pesticides are adverse to ecologically/water quality important non-target organisms associated with the stormwater runoff/discharges.

Best Professional Judgment/Weight of Evidence Triad for Evaluation of Significant Pesticide Impacts on the Beneficial Uses of Waterbodies

It is becoming increasingly clear and accepted among the professional community that a best professional judgment/weight of evidence triad approach is the appropriate approach to evaluate potentially significant water quality impacts associated with chemical constituents in the environment. As described by Lee and Jones-Lee (1999b), the weight of evidence triad consists of:

- information on the toxicity/bioaccumulation of the constituents of concern to aquatic life or within aquatic organism tissue;
- information on the alteration of aquatic organism assemblages within the area of potential impact, relative to appropriate reference situations which are not impacted by the chemical(s) of concern; and
- chemical information on the concentrations and, in particular, toxic available chemical species present in the waters of concern associated with a stormwater runoff event discharge situation.

The toxicity and chemical concentration information should define the magnitude of toxicity and concentration as a function of time of exposure for organisms potentially impacted by the pesticide. A key component of the chemical information is toxicity identification evaluation studies to specifically determine the constituent(s) responsible for the toxicity. It should not be assumed that, because a constituent exists at elevated concentrations, it is in fact responsible for the toxicity. Incorporation of aqueous environmental chemistry information coupled with toxicity assessment can provide reliable assessments of the chemical species responsible for the toxicity.

Studies of pesticides focusing only on measuring chemical concentrations can provide highly misleading information on aquatic life toxicity and the impacts of the pesticides found on the beneficial uses of waterbodies. All pesticide water quality impact studies should include assessing total toxicity to a suite of different types of organisms. Further, and most importantly, where toxicity is found, a dilution series should be conducted to determine the magnitude of the toxicity and whether, through TIEs, all of the toxicity can be accounted for based on known toxicants in the samples.

The weight of evidence triad information should be presented to a panel of experts who would first critically review the information provided for its adequacy and reliability, and then define what, if any, additional studies are needed to make a proper adverse impact evaluation. This panel should conduct its review in a full public interactive peer review arena, where the panel's deliberations would be open to the public for review and comment. The public interactive peer review process (Lee, 1999a) that is recommended could, if properly implemented, significantly improve the quality and reliability of peer reviews of environmental issues.

The panel would present a preliminary assessment of its findings, with appropriate supporting information. Those who feel that the panel has not properly considered the information available would be provided the opportunity to comment on the panel's initial deliberations, providing any additional information that they feel is important. The panel then would issue a final determination, which would present their conclusions on the issue. Based on this information, the regulatory authorities would then determine whether the pesticide(s) or other constituents are significantly adverse to the beneficial uses of a waterbody. The adoption of this best professional judgment/weight of evidence triad, interactively peer-reviewed approach would lead to technically valid assessments of adverse impacts of pesticides and other constituents on the beneficial uses of waterbodies.

Identification of Unknown-Caused Toxicity

Aquatic life toxicity testing of stormwater runoff in the Upper Newport Bay watershed, Orange County, California, over the past four years has shown that this runoff is highly toxic to *Ceriodaphnia dubia* and *Mysidopsis bahia*. Typically, the stormwater runoff contains from 5 to 20 TUa of *Ceriodaphnia* and *Mysidopsis* toxicity. The stormwater runoff is not toxic to fathead minnow larvae or the alga *Selenastrum* in the US EPA standard short-term chronic toxicity tests. Through dilution series toxicity testing with and without PBO, it has been found that about half of this toxicity is apparently due to the

OP pesticides diazinon and chlorpyrifos. The remainder of the toxicity is due to unknown causes. TIEs have shown that the unknown-caused toxicity is not due to heavy metals.

As part of the 205(j) and 319(h) projects (Lee and Taylor, 1999, 2001), Dr. Jeff Miller of *Aqua*Science, Davis, California, has conducted a detailed TIE investigation of the unknown-caused toxicity and, thus far, has been unable to identify the constituents responsible for it (Miller, 2000). 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 9) 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*. Pertinent parts of this database were included in the Lee and Taylor (1999) 205(j) report.

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 9 and 10 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.

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 lbs (ai) were used during 1998 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 over 19,000 lbs (ai) used in 1998. Its use in 1999 decreased to about 10,500 lbs. As indicated in Table 10, permethrin is highly toxic to *Daphnia magna* and especially *Mysidopsis bahia*. Almost 6,000 lbs of cypermethrin were used in Orange County during both 1998 and 1999. It is also highly toxic to these organisms. Bifenthrin, of which 493 lbs were used during 1998 and over 5,200 lbs in 1999 in Orange County, is also highly toxic to these organisms at the ng/L level. Bifenthrin has been found in 1999 DPR monitoring to be present in the Upper Newport Bay watershed tributaries at concentrations that are potentially toxic to certain zooplankton (Siepmann and Holm, 2000).

A review of Tables 9 and 10 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, in 1998 much of the use of bifenthrin was for structural pest control, although substantial amounts of the 1998 493 lbs/yr were used in agriculture as well. In 1999, the amount of bifenthrin used for agricultural purposes (76 % of the total use) was in excess of 4,000 lbs (ai), while in 1998, only 102 lbs 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.

Table 9
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	0% S, 24% N, 52% A, 4% L, 20% RW
Dimethoate	7,100	H	1,860	?? D 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	0%S, 33% N, tr A, 70% L, 5% RW
Trifluralin	190	SDC	194	560,000 D ?? M	0% S, tr N, 51% A, 48% L, tr RW
Methiocarb	2,500	H	575	19,000 D ?? M	0% S, 95 %N, 0% A, 5% L,
Propoxur	500	Found in Yorba Linda residential stormwater runoff			

Locations: **Dominant Use Categories:**

H Hines Channel just downstream of two
S Structural
N Nursery commercial nurseries
SDC San Diego Creek at Campus Drive
A Agriculture
SADC Santa Ana Delhi Channel
L Landscape
RW Right-of-way
D Daphnia magna
M *Mysidopsis bahia*
tr trace
?? no data available

Table 10
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	Lbs Used (ai) 1998	Lbs 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
Fenvalerate	428	18	*Mysidopsis bahia*	8
			Daphnia magna	50
Bifenthrin	493	5,257	*Daphnia magna*	1,600
			Mysidopsis bahia	4
Piperonyl Butoxide	547	387	*Daphnia magna*	100,000
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

It was also of interest to find that 547 lbs of PBO were used in Orange County during 1998, while 387 lbs 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 four years that Lee and Taylor (2001) 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 the 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. Miller (2001) 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.

The results of the *Aqua*Science studies on the February 21, 2000 samples taken from the Upper Newport Bay watershed are presented in Lee and Taylor (2001) Appendix A. 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 A) states that the acute (48-hour) 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.

Recently, 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 (2000), 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.

The USGS as part of the National Water Quality Assessment Program (NAWQA) (Panshin, *et al*., 1998) reported on the results of monitoring of dissolved pesticides in the San Joaquin River basin runoff waters. They report that about 15,000 lbs (ai) of permethrin, cis were applied to agricultural crops in this basin in 1993. Panshin, *et al*., reported finding permethrin at 13 ng/L in the San Joaquin River at

Vernalis. The USGS used a GC/MS analytical procedure for permethrin that has a minimum detection level of 5 ng/L.

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, 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, and for that matter elsewhere, using analytical procedures that can determine their concentrations at levels that are less than one tenth the LC_{50} concentrations for procedures used. Another issue that needs to be considered is whether the toxicities of these various pyrethroid pesticides are additive among pyrethroid pesticides and with other pesticides/ constituents.

Recommendations for OP Pesticide Aquatic Life Toxicity Studies

It is recommended that all those in California who are involved in OP pesticide aquatic life toxicity management issues review the DPR 1999 pesticide use database to determine the types and amounts of pyrethroid pesticides used in their area. Also, it is essential that OP pesticide toxicity studies include measuring the total *Ceriodaphnia dubia* and, for marine waters as the receiving waters for stormwater runoff, *Mysidopsis bahia* toxicity. Further, it is essential that the toxicity dilution series include the use of PBO to check for pyrethroid pesticide activation. Lee (1999b) has described the toxicity testing program that should be used.

Request for Information on Pyrethroid Pesticide Fate and Effects

A request for information was submitted in the spring 2000 and again in December 2000 to the US EPA OPP, Washington, D.C., for information in the following areas:

- toxicity of the pyrethroid pesticides and their additive toxicity to *Ceriodaphnia dubia*,
- analytical methods for pyrethroid pesticides at the ng/L levels,
- pyrethroid pesticide mobility information from points of application, especially associated with residential structural use and lawn and garden use,
- pyrethroid pesticide persistence in aquatic systems,
- what other kinds of pesticides, besides pyrethroid pesticide toxicity, might be activated by PBO,
- the results of studies that have investigated the potential for pyrethroid pesticides to be a cause of aquatic life toxicity in ambient waters.

As of March 2001, the US EPA OPP has not responded to this request for information. With the phase-out of most of the residential use of chlorpyrifos within the next year, over 100,000 lbs (ai) of other pesticide(s) will likely be used as a replacement in Orange County, CA. The pyrethroids are the most likely candidates for this use. Therefore, there could be over 100,000 to as much as 200,000 lbs (ai) of pyrethroid pesticides used per year in Orange County, CA., with much of it being in the Upper

Newport Bay watershed, within a year or two. At this time, there is a very poor understanding of the risk that current pyrethroid pesticide use -- much less this greatly expanded use – would represent to aquatic ecosystems in fresh and marine waters. The current US EPA OPP registration of pyrethroid pesticides, as well as other pesticides, does not adequately screen for aquatic life toxicity in stormwater runoff of the type that is being found in the Upper Newport Bay watershed, as well as throughout California and elsewhere. There is an urgent need for information on the fate and effects of pyrethroid pesticides, especially related to urban residential use.

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References

Ankley, G. T., Call, D. J., Cox, J. S., Kahl, M. D., Hoke, R. A., and Kosian, P. A., "Organic Carbon Partitioning as a Basis for Predicting the Toxicity of Chlorpyrifos in Sediments," *Environmental Toxicology and Chemistry*, 13(4):621-626 (1994).

Domagalski, J. L., "Pesticides in Surface and Ground Water of the San Joaquin-Tulare Basins, California: Analysis of Available Data, 1966 through 1992," U.S. Geological Survey Water-Supply Paper 2468, Denver, CO (1997).

Foe, C., "Evaluation of the Potential Impact of Contaminants on Aquatic Resources in the Central Valley and Sacramento-San Joaquin Delta Estuary," Central Valley Regional Water Quality Control Board, Sacramento, CA, June (1995a).

Foe, C., "Insecticide Concentrations and Invertebrate Bioassay Mortality in Agricultural Return Water From the San Joaquin Basin," Central Valley Regional Water Quality Control Board, Sacramento, CA., December (1995b).

Foe, C., "Toxicity Identification Evaluation of Orchard Dormant Spray Storm Runoff," California Regional Water Quality Control Board, Central Valley Region, Sacramento, CA, November (1998).

Foe, C. and Sheipline, R., "Pesticides in surface water from applications on orchards and alfalfa during the winter and spring of 1991-92," Central Valley Regional Water Quality Control Board, February (1993).

Fuelner, R. L., "Request for Cancellation or Amendment of Existing Diazinon Product Registrations to Terminate all Indoor Uses and Certain Agricultural Uses," Letter to L. Rossi-US EPA, from Syngenta Crop Protection, Greensboro, NC., December 1, (2000).

Giddings, J. M., Hall Jr., L. W., and Solomon, K. R., "Ecological Risks of Diazinon from Agricultural Use in the Sacramento-San Joaquin River Basins, California," *Risk Analysis*, Vol. 20, No. 5, pp. 545-572 (2000).

Hall Jr., L. W. and Giddings, J. M., "The Need for Multiple Lines of Evidence for Predicting Site-Specific Ecological Effects," *Human and Ecological Risk Assessment*, Vol. 6, No. 4, pp. 679-710 (2000).

Hansen & Associates, "Identification and Control of Toxicity in Storm Water Discharges to Urban Creeks, Final Report," Prepared for Alameda County Urban Runoff Clean Water Program, Hayward, CA, March (1995).

Harader, S., "Proposed Arcade Creek Pesticide TMDL Process," California Regional Water Quality Control Board, Central Valley Region, Sacramento, CA., February 23 (2001).

Jones-Lee, A. and Lee, G. F., "Evaluation Monitoring as an Alternative to Conventional Water Quality Monitoring for Water Quality Characterization/Management," Proc. of the NWQMC National Conference Monitoring: Critical Foundations to Protect Our Waters, US Environmental Protection Agency, Washington, D.C., pp. 499-512 (1998).

Jones-Lee, A. and Lee, G. F., "Development of TMDLs for Control of Organophosphate Pesticide Caused Aquatic Life Toxicity in Urban Stormwater Runoff," Proceedings WEFTECH 2000 Water Environment Federation annual meeting, Anaheim, CA, October (2000).

Katznelson, R. and Mumley, T., "Diazinon in Surface Waters in the San Francisco Bay Area: Occurrence and Potential Impact," Report to California State Water Resources Control Board and Alameda Countywide Clean Water Program, Oakland, CA, June (1997).

Kuivila, K. M. "Diazinon Concentrations in the Sacramento and San Joaquin Rivers and San Francisco Bay, California, February 1993," Open-File Report 93-440, Water Facts Sheet, U.S. Geological Survey, Sacramento, CA (1993).

Kuivila, K. M. and Foe, C. G. "Concentrations, Transport and Biological Effects of Dormant Spray Pesticides in the San Francisco Estuary, California," *Env. Tox. and Chemistry*, 14:1141-1150 (1995).

Kuivila, K. M., "Pesticides in the Sacramento-San Joaquin Delta: State of Knowledge," CALFED Bay-Delta Program Science Conference 2000, Sacramento, CA, October (2000).

Larsen, K., "Sacramento River Watershed Project Toxicity Monitoring Results: 1996-97," Regional Water Quality Control Board, Sacramento, CA (1998).

Larson, S. J., Gilliom, R. J., and Capel, P. D., "Pesticides in Streams of the United States-Initial Results from the National Water-Quality Assessment Program," US Geological Survey: Water Resources Investigations Report 98-4222, Sacramento, California (1999).

Lee, G. F., “Public Interactive Peer Review Process for Water Quality Technical Dispute Resolution: A Guide For Implementation of H&S Code Section 57004 for Conducting Peer Review of Proposed Policy,” Report of G. Fred Lee & Associates, El Macero CA, October (1999a).

Lee, G. F., “Recommended Aquatic Life Toxicity Testing Program for Urban Stormwater Runoff,” Comments submitted to E. Bromley, US EPA Region IX, San Francisco, CA (1999b).

Lee, G. F., “The Urban Pesticide Problem,” *Stormwater*, January/February, pp. 68-71, (2001).

Lee, G. F. and Jones-Lee, A., “Planktonic Algal Toxicity Testing in Regulating Point and Non-Point Discharges and Its Implications for Use of Dissolved Metal Criteria/Standards,” Report of G. Fred Lee & Associates, El Macero, CA (1996).

Lee, G. F. and Jones-Lee, A., “The Single Chemical Probabilistic Risk Assessment Approach is Inadequate-For OP Pesticide Aquatic Life Toxicity,” Published in Learned Discourses, *SETAC News*, 20-21 November (1999a).

Lee, G. F., and Jones-Lee, A., “Appropriate Use of Chemical Information in a Best Professional Judgment Water Quality Weight of Evidence Evaluation,” Report of G. Fred Lee & Associates, El Macero, CA (1999b).

Lee, G. F. and Jones-Lee, A., “Development of TMDLs and Wet Weather Standards for the Control of Heavy Metals in Urban Stormwater Runoff,” Proceedings WEFTECH 2000 Water Environment Federation annual meeting, Anaheim, CA, October (2000a).

Lee, G. F., and Jones-Lee, A., “Proactive Approach for Managing Pesticide Caused Aquatic Life Toxicity,” Report of G. Fred Lee & Associates, El Macero, CA (2000b).

Lee, G. F. and Jones-Lee, A., “Conclusions from Review of the City of Stockton’s Urban Stormwater Runoff Aquatic Life Toxicity Studies Conducted by the CVRWQCB, DeltaKeeper and the University of California, Davis Aquatic Toxicology Laboratory between 1994 and 1999,” Report of G. Fred Lee & Associates, El Macero, CA, Submitted to the Central Valley Regional Water Quality Control Board, April (2001).

Lee, G. F., Jones-Lee, A., and Taylor, S., “Evaluation of the Water Quality Significance of OP Pesticide Toxicity in Tributaries of Upper Newport Bay, Orange County, CA,” Ninth Symposium on Environmental Toxicology and Risk Assessment: Recent Achievements in Environmental Fate and Transport, ASTM STP 1381, pp 35-51 (2000).

Lee, G. F., and Taylor, S., “Results of Aquatic Life Toxicity Studies Conducted During 1997-99 in the Upper Newport Bay Watershed, and Review of Existing Water Quality Characteristics of Upper Newport Bay, Orange County CA and its Watershed,” Submitted to State Water Resources Control Board, Santa Ana Regional Water Quality Control Board, and Orange County Public Facilities and Resources Department, to meet the requirements of the US EPA 205(j) project, Report of G. Fred Lee & Associates, El Macero, California October (1999). (The aquatic toxicity part of this report is available from www.gfredlee.com.).

Lee, G. F., and Taylor, S., “Results of Aquatic Toxicity Testing Conducted During 1999-2000 withn the Upper Newport Bay Watershed,” Report to the State Water Resources Control Board, Santa Ana Regional Water Quality Control Board, and the Orange County Public Facilities and Resources

Department to meet the requirements of the US EPA 319(h) Project, G. Fred Lee & Associates, El Macero, CA and RBF Consulting, Irvine, CA, January (2001).

Lewis, P. A., Klemm, D. J., Lazorchack, J. M., Norberg-King, T., Peltier, W. H. and Heber, M. A., "Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms," Environmental Monitoring Systems Laboratory, Cincinnati, OH; Environmental Research Laboratory, Duluth, MN; Region 4, Environmental Services Division, Athens, GA; Office of Water, Washington, D.C.; Environmental Monitoring Systems Laboratory, Cincinnati, OH; Office of Research and Development, US Environmental Protection Agency, Cincinnati, OH (1994).

Miller, J., "Toxicity Identification Evaluation with Upper Newport Bay Watershed Samples, February 21, 2000 Sample Set," Report to RBF Consulting, Submitted by *Aqua*Science, Davis, CA., December, (2000).

Novartis, "An Ecological Risk Assessment of Diazinon in the Sacramento and San Joaquin River Basins," Novartis Crop Protection, Inc., Technical Report: 11/97, Greensboro, NC (1997).

OCPFRD, "NPDES Annual Progress Report," Orange County NPDES Stormwater Program, County of Orange and the Orange County Flood Control District, Santa Ana, CA, November 15 (1998, 1999).

Panshin, S. Y., Dubrovsky, N. M., Gronberg, J. M., and Domagalski, J. L., "Occurrence and Distribution of Dissolved Pesticides in the San Joaquin River Basin, California," US Geological Survey, Water-Resources Investigations Report 98-4032, USGS, Sacramento, CA (1998).

SARWQCB, "Final Problem Statement for the Total Maximum Daily Load for Toxic Substances in Newport Bay and San Diego Creek," California Regional Water Quality Control Board Santa Ana Region, Riverside, CA., December 15 (2000).

Siepmann, S. and Findlayson, B., "Water Quality Criteria for Diazinon and Chorpyrifos," California Department of Fish and Game, Administrative Report 00-3, Rancho Cordova, CA (2000).

Siepmann, S. and Holm, S., "Hazard Assessment of the Synthetic Pyrethroid Insecticides Bifenthrin, Cypermethrin, Esfenvalerate, and Permethrin to Aquatic Organisms in the Sacramento-San Joaquin River System," Resources Agency, California Department of Fish and Game, Office of Spill Prevention and Response, Administrative Report 00-6 (2000).

SRWP, "Sacramento River Watershed Program Annual Monitoring Report: 1999-2000," Prepared for Sacramento River Watershed Program by Larry Walker Associates, Davis, CA., January, (2001).

Strauss, A., "Comments on the Use of Probabilistic Ecological Risk Assessment to Establish Organophosphate Pesticide Aquatic Life Toxicity TMDL Goal," Letter to G. Carlton, Executive Officer, Central Valley Regional Water Quality Control Board, Sacramento, CA, from US EPA Region IX, San Francisco, CA, April (2000).

Syngenta, "Transition from Its Diazinon Business," Media Release, Syngenta Crop Protection, Greensboro, NC, December (2000a).

Syngenta, “Memorandum of Agreement between the Environmental Protection Agency and Syngenta Crop Protection, Inc. and Makhteshim Chemical Works, Ltd., Regarding the Registration of Pesticide Products Containing Diazinon,” Draft Agreement-Syngenta and US EPA, December (2000b).

US EPA, “Water Quality Criterion for Chlorpyrifos,” in Quality Criteria for Water 1986, EPA 440/5-86-001, US Environmental Protection Agency, Office of Water Regulations and Standards, Washington, D.C. (1987a).

US EPA, “Quality Criteria for Water 1986,” EPA 440/5-86-001, US Environmental Protection Agency, Office of Water Regulations and Standards, Washington, DC (1987b).

US EPA, “Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, Second Edition,” EPA-600-4-91-003, US Environmental Protection Agency, Cincinnati, OH (1994).

US EPA, “EPA Announces Elimination of All Indoor Uses of Widely-Used Pesticide Diazinon; Begins Phase-Out of Lawn and Garden Uses,” US Environmental Protection Agency, Washington DC (2000).

Waller, W. T., Acevedo, M. F., Morgan, E. L., Dickson, K. L., Kennedy, J. H., Ammann, L. P., Allen, H. J. and Keating, P. R., “Biological and Chemical Testing in Storm Water,” In: Stormwater NPDES Related Monitoring Needs, H. C. Torno (ed.), Proc. Engineering Foundation Conference, August 1994, ASCE, New York (1995).