

G. Fred Lee¹, Anne Jones-Lee¹, Scott Taylor², and Deborah Neiter²

EVALUATION OF THE WATER QUALITY SIGNIFICANCE OF OP PESTICIDE TOXICITY IN TRIBUTARIES OF THE UPPER NEWPORT BAY, ORANGE, COUNTY, CA

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ABSTRACT: Stormwater runoff in San Diego Creek, the primary tributary to Upper Newport Bay in Orange County, CA, has been found to be toxic to *Ceriodaphnia* and *Mysidopsis* with total acute 24 hr toxicities up to 16 TUa. About half of this toxicity has been found to be due to the organophosphate (OP) pesticides diazinon and chlorpyrifos used in urban areas for structural termite and ant control, and lawn and garden pest control. The other half is due to unknown causes likely associated with the use of pesticides in nurseries and agriculture. The non-stormwater flow into Upper Newport Bay is non-toxic. Stormwater runoff events cause short-term pulses of toxic waters to enter this marine Bay.

Studies on the fate of the toxic pulses of San Diego Creek water in Upper Newport Bay show that for many stormwater runoff events the Creek freshwater forms a lens above the marine waters that is diluted by tidal mixing with the Bay’s marine waters. The regulatory issue that should be assessed is the water quality and ecological significance of the pulses of aquatic life toxicity that exist in the waters at the bottom of the freshwater lens where the Creek waters mix with the marine waters. For some stormwater runoff events, potentially toxic waters are present to a limited areal and volumetric extent in the Bay for several days. It is unclear whether these toxic pulses of OP pesticides are significantly adverse to the beneficial uses of Upper Newport Bay because of their limited duration and the limited number/type of marine aquatic organisms that are exposed to toxic conditions associated with stormwater runoff events. Further studies need to be done to define the magnitude of the potential beneficial use impairment of Bay waters due to this toxicity.

KEYWORDS: aquatic life toxicity, *Ceriodaphnia*, *Mysidopsis*, diazinon, chlorpyrifos, water quality

Introduction

During the fall of 1996, the Evaluation Monitoring Demonstration Project (Lee and Taylor, 1997) found that stormwater runoff in San Diego Creek at Campus Drive as it enters Upper Newport Bay, Orange County, California was toxic to *Ceriodaphnia*. The stormwater runoff contained sufficient concentrations of diazinon and chlorpyrifos (organophosphate pesticides – OP pesticides), as well as some unidentified toxic constituents, to be highly toxic to *Ceriodaphnia* during

¹G. Fred Lee & Associates, 27298 East El Macero Drive, El Macero, CA 95618

²Robert Bein, William Frost & Associates, 14725 Alton Parkway, Irvine, CA 92618-2069

stormwater runoff events. A dry weather flow sample which was taken of San Diego Creek between the two stormwater runoff events sampled was found to be non-toxic. This paper summarizes some of the results of the aquatic life toxicity studies conducted from October, 1996 through August, 1998 on San Diego Creek and its tributaries. This paper is based on a comprehensive report (Lee *et al.*, 1999) devoted to these studies.

Background

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

Sample Collection and Analysis Procedures

The samples were collected in bottles furnished by the University of California Davis (UCD) Aquatic Toxicology Laboratory (Davis, CA), Pacific Eco-Risk Laboratory (Martinez, CA), and AQUAScience (Davis, CA) (Neiter and Lee, 1998). At each site, samples for toxicity testing were collected early in the stormwater runoff event, packed with blue ice in a cooler, and shipped overnight to the toxicity testing laboratories. Upon receipt at UCD or the other testing laboratories, the samples were stored in the dark under refrigeration at 4°C.

The samples were analyzed by the laboratory using the US EPA standard toxicity testing procedures described in the Quality Assurance Project Plan (Neiter and Lee, 1998). For freshwater samples, the procedures described by Lewis *et al.* (1994) were used, in which the fathead minnow larvae *Pimephales promelas*, the zooplankton *Ceriodaphnia dubia* and the alga *Selenastrum capricornutum* were used. For testing the potential toxicity to marine zooplankton, the salinity of the samples was increased to 20 ppt using Forty Fathoms® – bioassay grade and testing was done with *Mysidopsis bahia*. The mysid toxicity testing was done in accord with US EPA (1994) procedures. In order to determine whether the toxicity found was likely due to an organophosphate pesticide, piperonyl butoxide (PBO) was added to some of the duplicate tests. PBO interacts with organophosphate pesticides such as diazinon and chlorpyrifos to eliminate and/or reduce their toxicity (Bailey *et al.*, 1996).

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

series-measured toxicity, with and without PBO addition, it is possible to assess the amount of toxicity present in a sample that is not due to OP pesticides and/or diazinon and chlorpyrifos.

Characteristics of The Upper Newport Bay Watershed

The primary tributary of Upper Newport Bay is San Diego Creek. The watershed has been greatly altered due to residential and commercial development. The Newport Bay watershed includes an area of about 154 square miles. The San Diego Creek watershed contains about 119 square miles with a mix of residential (15%), commercial (8%), industrial (6%), recreational and open space (23%), agricultural (23%), and transportation/communication/roads (36%). Other major tributaries of Upper Newport Bay include the Santa Ana Delhi Channel with a watershed of about 17 square miles, Big Canyon Wash with a watershed of about 2 square miles, and 16 square miles from other smaller tributaries. Currently, it is estimated that less than 40 percent of the developed Upper Newport Bay watershed is impervious surface.

Physical and Hydrologic Characteristics of Newport Bay

The Coast Highway divides the Bay into upper and lower basins. The lower basin is heavily urbanized with numerous islands developed for residential use. The upper basin (about 1,000 acres) remains largely undeveloped within the nominal Bay boundaries with the exception of about the lower one-third, which contains boat docks and other commercial facilities. The remaining area (752 acres) is operated as a State Ecological Reserve by the California Department of Fish and Game. The Upper Bay is characterized by a semidiurnal tidal pattern of two unequal highs and lows occurring each day. The maximum tidal range is about 9 feet with little difference in absolute magnitude between the upper and lower Bays. The salinity during non-stormwater runoff events in the Upper Bay in 1959 (Gerstenberg, undated) and today is close to that of seawater (30 ppt).

Summary of Toxicity Testing Results

The results of the toxicity testing and chemical analysis have been presented by Lee et al. (1999). A brief summary is presented in this paper.

Toxicity to *Ceriodaphnia*. During 1996-98, nine stormwater runoff events were monitored. A total of 125 toxicity tests were conducted on San Diego Creek and its tributaries and other tributaries of Upper Newport Bay. With few exceptions, the undiluted sample of San Diego Creek water during a stormwater runoff event obtained at Campus Drive just before where the Creek enters Upper Newport Bay killed all *Ceriodaphnia* in the test system within one day. Many of the samples of San Diego Creek taken at Campus Drive had at least three, and often greater than eight, TUa to *Ceriodaphnia*. This means that up to a ten-fold dilution of San Diego Creek water at Campus Drive could occur, and the samples would still be toxic.

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

been diluted somewhat, reduced the amount of *Ceriodaphnia* toxicity. This is an indication that the toxicity found is due, at least in part, to OP pesticides.

Toxicity to *Mysidopsis*. Eleven toxicity tests were conducted of San Diego Creek water as it enters Upper Newport Bay. As shown in Table 1, diazinon is not highly toxic to *Mysidopsis*. Typically San Diego Creek samples contained sufficient chlorpyrifos to cause several acute toxic units to *Mysidopsis*. There was appreciable toxicity to *Mysidopsis* in the San Diego Creek water during a stormwater runoff event that cannot be potentially accounted for, based on the chlorpyrifos concentrations measured in the sample that was tested for toxicity. The cause of this toxicity to *Mysidopsis* is, at this time, unknown.

Estimated Toxicity of Diazinon and Chlorpyrifos. Table 1 presents a summary of information on the respective toxicities (LC₅₀) of diazinon and chlorpyrifos to *Ceriodaphnia* and *Mysidopsis*. These values are used to estimate the toxicity of the samples based on the concentrations of diazinon and chlorpyrifos measured in the samples.

Table 1
Toxicity of Diazinon and Chlorpyrifos to *Ceriodaphnia* and *Mysidopsis*

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

Diazinon and Chlorpyrifos Concentrations. The ELISA data for analysis of diazinon and chlorpyrifos show that frequently the concentrations of these OP pesticides in San Diego Creek waters as they enter Upper Newport Bay were sufficient, individually and/or when mixed, to be toxic to *Ceriodaphnia*. The expected acute toxicity units (TUa) based on the sum of the diazinon and chlorpyrifos concentrations, divided by the LC₅₀ for the respective compounds shows that the calculated expected TUa's, based on the sum of the diazinon and chlorpyrifos concentrations, should result in several acute toxic units for *Ceriodaphnia* in San Diego Creek water as it enters Upper Newport Bay. Further, when the expected toxicity was compared to the total toxicity measured in the toxicity testing dilution series, it was found that on the order of half of the toxicity present in the samples could not be accounted for by diazinon or chlorpyrifos.

Studies within the San Diego Creek watershed showed that a potentially significant part of this unknown-caused toxicity was apparently due to pesticides used in commercial nurseries and for agricultural crop production. Thus far, TIE studies on the cause of this toxicity have failed to identify the specific chemical constituents responsible for it. However, dual column GC analysis of water samples shows that there are a variety of OP and carbamate pesticides present in these waters, for which there is no information on their toxicity to *Ceriodaphnia* and *Mysidopsis*.

Water Quality Criteria/Standards for Diazinon and Chlorpyrifos.

Currently the US water pollution control programs are largely focused on the development of Total Maximum Daily Loads (TMDLs) for regulated constituents that are present at concentrations above water quality standards. In accord with current regulatory requirements, any waterbody that

shows aquatic life toxicity would be judged to be aquatic life-related beneficial use impaired and have to be placed on the state/US EPA 303(d) list of impaired waterbodies. This listing results in the need to develop a TMDL for control of this toxicity-impairment. One of the fundamental aspects of developing a Total Maximum Daily Load (TMDL) for diazinon and/or chlorpyrifos is the selection of a target value which can serve as the goal of the TMDL. Typically the TMDL goal is the elimination of the 303(d) impaired listing of a waterbody due to a particular chemical. The 303(d) listings arise out of the exceedance of numeric or narrative water quality standards. While, in the early 1980s, the US EPA (1986) developed a water quality criterion for chlorpyrifos, since chlorpyrifos is not listed as a toxic pollutant in the National Toxics Rule, the states are not required to adopt this criterion as a state standard. While the State of California Water Resources Control Board could have adopted this criterion as a state standard years ago, thus far it has chosen not to do so.

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

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

The US EPA has been developing a water quality criterion for diazinon since the late 1980s. While periodically announcing that this criterion would be promulgated in the near future, thus far the Agency has failed to do so, with the result that at this time there is no US EPA water quality criterion for diazinon. The California Department of Fish and Game (DFG), using US EPA water quality criteria development approaches (US EPA, 1987), has developed suggested water quality criteria for diazinon and chlorpyrifos (Menconi and Cox, 1994; Menconi and Paul, 1994). For chlorpyrifos, the DFG freshwater chronic suggested criterion is 20 ng/L, and salt water chronic suggested criterion is 10 ng/L. These values are similar to the US EPA water quality criteria for chlorpyrifos.

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

In accord with current US EPA guidance, the exceedance of these suggested criterion values in San Diego Creek waters throughout most of the watershed and as they enter Upper Newport Bay, by more than any amount once every three years represents a violation of a water quality standard that could result in the waterbody being listed as a 303(d) "impaired" waterbody. This listing sets

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

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

One of the issues that should be addressed in regulating the OP pesticide toxicity in San Diego Creek and its watershed is the water quality/ecological significance of *Ceriodaphnia* and other aquatic organism toxicity. While one of the beneficial uses of San Diego Creek waters is listed as aquatic life-related habitat by the Santa Ana Regional Water Quality Control Board in this Board's Basin Plan, the aquatic life-related resources of the waters in San Diego Creek and its tributaries are severely impacted by habitat characteristics. San Diego Creek and many of its tributaries have been channelized and armored in order to enhance flow and prevent flooding. Basically, these waterbodies are used as flood control channels. There is need to assess the potential improvement in the beneficial uses of these waters if the high levels of aquatic life toxicity that have been found under both low-flow and high-flow conditions were eliminated.

Associated with each stormwater runoff event to Upper Newport Bay is a pulse of toxic water that has a potential to kill certain zooplankton with a sensitivity to OP pesticides similar to *Ceriodaphnia* and mysids. Novartis (1997) has compiled information on the diazinon LC_{50s} for various freshwater and marine organisms. Based on the information available at this time, *Ceriodaphnia* is one of the most sensitive organisms to diazinon toxicity. Based on the review of Menconi and Paul (1994), there is no evidence from the literature that the organophosphate pesticides at the concentrations being found in this study in San Diego Creek waters as they enter Upper Newport Bay are toxic to adult or larval fish. There is need to determine if Upper Newport Bay has organisms that are key parts of the food web for the overall ecosystem that could be impacted by OP pesticide toxicity and/or the unknown-caused toxicity found in this study.

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

A fundamental issue that needs to be assessed is whether there is a significant amount of water present in Upper Newport Bay associated with stormwater runoff events with salinities less than 3 ppt that would persist for at least one to two days. Another issue is whether marine zooplankton could be mixed into, or migrate into the freshwater marine water lens with salinities less than 3 ppt

and stay in this lens. This assumes that the zooplankton persist in potentially toxic waters for a sufficient period of time to receive a toxic exposure to the toxic constituents in the San Diego Creek water that has been diluted by the Bay's marine waters. In order to review this situation an analysis of the currently available information on the mixing of San Diego Creek waters with Upper Newport Bay waters has been undertaken.

Mixing of San Diego Creek and Upper Newport Bay

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

Limno-Tech conducted an investigation of the quantity of water added to the Bay necessary to cause significant salinity stratification in the Bay (creation of a freshwater 'lens'). Their analysis

incorporated an estuarine stratification classification system using salinity stratification and water circulation patterns. Lee *et al.* (1999) have discussed application of the Limno-Tech mixing model for the Upper Newport Bay. Based on this review, the Upper Bay area appears to be well-mixed during low flow conditions, defined as 50 cfs and under, and partially stratified (and mixed) for San Diego Creek flows up to about 1,000 cfs. Above 1,000 cfs, the Upper Bay becomes fully stratified, depending on tide conditions. In reviewing County of Orange conductivity data, it also appears reasonable to assume that the Lower Bay is largely unaffected by flows of less than about 50 cfs from San Diego Creek and the Santa Ana Delhi Channel and is fully mixed. These conclusions are valid regardless of tidal stage. Between Creek discharges of 50 cfs and about 1,500 cfs, the influence of tide would appear to be important, and partial stratification (mixed condition) occurs in the Lower and Upper Bay, depending on tide conditions. Above about 1,500 cfs, the Bay would appear to be fully stratified at all locations and for all tide conditions.

Preliminary conclusions on the extent of stratification may be drawn relative to this project's 1997-98 sampled storm events using the Limno-Tech stratification analysis of the Bay. Table 2 provides a description of the estimated time that the Bay would be stratified vs. the time it would be mixed for selected storm events during the 1997-98 season.

Table 2
Estimated Time of Stratification during Sampled Storm Events

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

Upper Newport Bay marine waters typically exhibit a salinity of about 30 ppt. During a portion of a storm event there will be a zone in the Bay waters where the salinity drops significantly. The time this zone will exist depends on several variables. A salinity of about 3 ppt or less is considered critical with respect to mysid mortality based on the salinity threshold and an assumed toxicity of 10 TUa associated with the incoming stormwater discharge. The extent and time of mixed versus stratified flow in the Bay is highly variable, depending on the volume of stormwater entering the Bay versus the tide stage, the time of direct runoff of the stormwater hydrograph, the peak discharge of the stormwater hydrograph, and, to a lesser extent, the temperature differential of the Bay and stormwater, the amount of sediment in the stormwater, and the shape of the hydrograph. The results of this study have shown that it is possible that marine zooplankton could be exposed to toxic conditions in certain stormwater runoff events that would be adverse to the zooplankton. The water quality significance of this situation is an area that needs further study.

Recommendations For Future Studies

The results from this project have defined several areas that need additional studies to further define the magnitude of the aquatic life toxicity problem that exists in the Upper Newport Bay watershed and the Bay. Of particular importance is the need to conduct specific investigation of the fate/persistence of toxicity of the OP pesticides diazinon and chlorpyrifos within Bay waters. Also of concern is the persistence of the unknown toxicity in the Bay. Information on the persistence of the aquatic life toxicity in the Bay is the key to evaluating the potential water quality/ecological significance of the toxicity discharged to the Bay with each stormwater runoff event.

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