Stormwater Runoff Water Quality Science/Engineering Newsletter
Devoted to Urban Stormwater Runoff
Water Quality Management Issues

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Volume 3 Number 5
July 11, 2000

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Contents of this Newsletter

This issue of the Newsletter is devoted to discussion of **organophosphate pesticides (OP) caused aquatic life toxicity** in urban area stormwater runoff. This Newsletter updates information on this topic that was published in Newsletter Vol. 2 No. 1 which is available from www.gfredlee.com. That Newsletter was devoted to an introduction to OP pesticide aquatic life toxicity in urban stormwater runoff. The current Newsletter is also a companion to recently issued Newsletter Vol 3. No. 4 devoted to regulating heavy metal-caused aquatic life toxicity in urban area and highway stormwater runoff. These two Newsletters address regulatory issues associated with the two most common potential causes of aquatic life toxicity in urban stormwater runoff.

Recently, Drs. Anne Jones-Lee and G. Fred Lee have presented/published several papers and reports on issues that should be considered in appropriately regulating urban area stormwater runoff associated OP pesticide-caused aquatic life toxicity.. These papers include **Importance of Integrating Aquatic Chemistry with Toxicology in Regulating Urban Area Stormwater Runoff: OP Pesticide Aquatic Life Toxicity Management** that was published as an Extended Abstract of the American Chemical Society Division of Environmental Chemistry national meeting that was held in San Francisco, CA in March 2000. That paper provides an overview of heavy metal and OP pesticide aquatic life toxicity in urban stormwater runoff. A condensed version of that paper is presented in this Newsletter.

A paper entitled, **Development of TMDL Goals for Control of Organophosphate Pesticide-Caused Aquatic Life Toxicity in Urban Stormwater Runoff** is also attached. It is devoted to developing TMDL goals to control aquatic life toxicity caused by organophosphate pesticides in stormwater runoff. This paper will be presented at the Water Environment Federation's national meeting in Anaheim, CA in October 2000.

STORMWATER Journal
Forester Communications has announced the publication of STORMWATER The Journal of Surface Water Quality Professionals. The first issue will be published in September. To subscribe to STORMWATER go to www.stormh2o.com. Contributed articles to STORMWATER are being solicited.

Importance of Integrating Aquatic Chemistry with Toxicology in Regulating Urban Area Stormwater Runoff: OP Pesticide Aquatic Life Toxicity Management[1]

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Introduction

With the US EPA implementation of the 1987 revisions of the Clean Water Act section devoted to urban stormwater runoff impacts on receiving waters for the runoff, the US EPA (1990) established that urban stormwater runoff shall not cause or contribute to violations of water quality standards. This requirement is to be met through a best management practice (BMP) ratcheting down process where the urban stormwater management agencies that hold NPDES stormwater runoff water quality management permits shall implement BMPs to control the water quality standard violations. Stormwater runoff water quality monitoring programs in several areas of California and elsewhere have found that urban stormwater runoff contains several potentially toxic heavy metals, such as lead, copper, zinc, and sometimes cadmium, at concentrations that cause violations of worst case based US EPA water quality criteria/standards at the point of discharge of the stormwater runoff to ambient waters for both total and dissolved forms of the metals.

This is a technical violation of the NPDES permit that could require that the NPDES permit holder initiate BMPs to remove those heavy metals that are present in the stormwater runoff at concentrations above water quality standards at the point of discharge. The US EPA and states require that NPDES permitted discharges shall not contain regulated constituents in toxic amounts. This typically translates to no aquatic life toxicity in NPDES regulated sources. As discussed by Lee and Taylor (1999), urban stormwater runoff in several California cities, including Sacramento, Stockton, Los Angeles, San Diego, and communities in the San Francisco Bay region and Orange County, California, and elsewhere such as Fort Worth, Texas (Waller *et al.* 1995) has been found to be toxic to *Ceriodaphnia dubia*. While initially it was suggested that this toxicity was due to heavy metals in the stormwater runoff, it has been repeatedly found (Hansen & Associates 1995, and others, see Lee and Taylor 1999) that it is due to the organophosphate pesticides diazinon and chlorpyrifos (Dursban) that are used in urban areas for structural termite, ant, and lawn/garden pest control. In some areas, such as Orange County, California, over 100,000 pounds of active ingredient diazinon and chlorpyrifos are used each year on residential properties with most of the use for structural pest control (Lee and Taylor 1997). Based on pesticide use patterns it appears that aquatic life toxicity due to OP pesticides in urban stormwater runoff is a national problem that is not generally recognized. Lee

[1] Condensed from a presentation at the American Chemical Society Division of Environmental Chemistry national meeting symposium, **Environmental Chemistry of Water:2000 and Beyond** held in San Francisco, CA March 2000. Published in the Extended Abstracts the ACS Environmental Division. The original version is available from www.gfredlee.com.

(1999) has recommended a monitoring approach for determining whether aquatic life toxicity is present in urban stormwater runoff and, if present, whether it is due to the OP pesticides.

Based on current information, the toxicity of the OP pesticides in urban stormwater runoff is largely restricted to certain cladacerans zooplankton (small animals) and the amphipod Gammarus. The concentrations of OP pesticides found in urban stormwater runoff are typically on the order of a few hundred nanograms/L (ng/L). The LC_{50} for diazinon to *Ceriodaphnia* is about 450 ng/L. The LC_{50} for chlorpyrifos to *Ceriodaphnia* is about 80 ng/L, while the LC_{50} for chlorpyrifos to *Mysidopsis* is about 35 ng/L. Neither pesticide is normally present in urban stormwater runoff at concentrations that are toxic to fish larva or algae. This means that in order for this toxicity to be adverse to fish and other higher trophic level forms of aquatic life, the OP pesticide sensitive zooplankton must be key components of the larva fish food at a critical period of the year.

In many urban areas where OP pesticide caused aquatic life toxicity is found, the total toxicity can largely be accounted for by the concentrations of diazinon and chlorpyrifos. In some areas, such as Orange County, California, stormwater runoff contains large amounts of unknown caused toxicity to *Ceriodaphnia* and *Mysidopsis*. Based on a three year study (Lee and Taylor 1999) of San Diego Creek as it enters Upper Newport Bay, Orange County, California, stormwater runoff contains from 8 to 30 24-hr acute toxic units of *Ceriodaphnia/Mysidopsis* toxicity where only about half of the toxicity can be accounted for based on the concentrations of diazinon and chlorpyrifos. The remainder of the toxicity is due to yet unidentified causes. This toxicity is not due to metals and does not appear to be due to other commonly measured OP and carbamate pesticides. Also, based on piperonyl butoxide (PBO) activation, it does not appear to be due to pyrithroid pesticides. The stormwater runoff in Orange County, as it enters Upper Newport Bay, is derived from urban, agricultural, and commercial nursery discharges. It appears that all three sources are responsible for some of the unknown caused toxicity (Lee and Taylor 1999).

Regulation of OP Pesticide Caused Aquatic Life Toxicity

As discussed by Lee *et al*. (1999), the finding of OP pesticide caused aquatic life toxicity associated with the use of these pesticides in agricultural and urban areas has caused regulatory agencies in California to list several waterbodies on the 303(d) list of impaired waterbodies. This in turn requires that TMDLs be developed to control the OP pesticides diazinon and chlorpyrifos and their associated aquatic life toxicity. Several California Regional Water Quality Control Boards are developing TMDLs for diazinon and chlorpyrifos and OP pesticide caused aquatic life toxicity to *Ceriodaphnia*. However, there is considerable controversy about the TMDL goal that should be used. This controversy stems from the fact that the US EPA Office of Pesticide Programs (US EPA OPP) requirements for control of the adverse impacts of pesticides to non target organisms allows toxicity to aquatic life, provided that this toxicity is not significantly adverse to the beneficial uses of the waterbody. While the Clean Water Act requires the control of all aquatic life toxicity, for pesticides before the registered use of a pesticide can be restricted, it must be shown to be significantly adverse to public health or the environment. Because of the conflict between Clean Water Act (no toxics in toxic amounts) and US EPA OPP (no toxicity that is significantly adverse to beneficial uses) it is not clear how the OP pesticide caused aquatic life toxicity in urban and agricultural stormwater runoff will be regulated.

As discussed by Lee *et al*. (1999), in order for the OP pesticide caused toxicity in the stormwater runoff to be significantly adverse to the Upper Newport Bay aquatic ecosystem, a marine zooplankton must migrate to the mixed non-toxic marine/toxic fresh water lens and stay in this water for a sufficient period of time to receive a critical exposure. Further the zooplankton that are killed must be an essential, non-replaceable component of the larva fish diet that are considered by the public to be important.

For urban streams, the travel time from the headwaters to the discharge to larger waterbodies is often short compared to the critical exposure that is needed to be adverse to the zooplankton which move with the water during a runoff event. At this time there are no guidelines on how regulatory agencies and others should evaluate what the killing of certain zooplankton by OP pesticides associated with stormwater runoff events means to higher trophic level organisms of concern to the public

The OP pesticide caused aquatic life toxicity associated with urban storm water runoff is typically associated with one to two units of acute *Ceriodaphnia* toxicity that last a day or so during the stormwater runoff event. Further, in many situations the toxic urban stormwater runoff is rapidly diluted below toxic levels in the receiving waterbody such as a river, lake, estuary, or marine waterbody. Therefore the potential area of impact for the OP pesticide caused toxicity is largely restricted to urban streams which in many cases are channelized to control flooding. While these waterbodies beneficial uses are often classified as aquatic life habitat, the quality of this habitat is often severely degraded. It is questionable whether the elimination of the OP pesticide caused aquatic life toxicity that is found when the US EPA standard *Ceriodaphnia* toxicity test is used will have a significant impact on the fisheries related beneficial uses of urban streams.

An aspect of the regulation of OP pesticide caused aquatic life toxicity that needs to be considered is that there are other pesticides available, such as the pyrithroids, that can provide about the same pest control as the diazinon and chlorpyrifos. These pesticides are also highly toxic to some forms of zooplankton. The current regulatory approach covering the registration and use of pesticides does not require that a potential environmental impact evaluation be made before substituting one pesticide for another. It is evident that there is need to significantly improve the pesticide registration process to screen pesticides for potential impact on lower trophic level organisms such as *Ceriodaphnia*.

Approach for Regulating Urban Stormwater Runoff Water Quality Impacts

The traditional, end of the pipe, compliance based water quality monitoring, where the monitoring results are compared to US EPA/state water quality criteria/standards is not an appropriate approach for regulating chemical constituents in urban area and highway stormwater runoff. The US EPA water quality criteria were not developed for urban stormwater runoff type situations where many of the constituents in the runoff are in non-toxic, non-available forms and the duration of exposure of receiving water aquatic life to the toxic available forms in runoff is short compared to critical exposure conditions. There is need to change the regulatory approach typically used for municipal and industrial wastewaters to an approach that involves site specific evaluations of the real, significant impairment of beneficial uses caused by regulated and unregulated constituents in urban stormwater runoff.

Jones-Lee and Lee (1999) have recommended that an Evaluation Monitoring approach be used where the emphasis is changed from regulating chemical concentrations to chemical impacts. This approach will require an integrated use of aquatic chemistry, toxicology, and water quality-beneficial use assessments. Rather than measuring a potentially toxic chemical such as copper in urban stormwater runoff, and then assuming it is toxic because it exceeds a US EPA worst case based water quality criterion/standard, the Evaluation Monitoring approach measures toxicity of the stormwater runoff and its persistence in the receiving waters for the runoff. If toxic for a sufficient period of time to be adverse to aquatic life in the receiving waters, then toxicity investigation evaluation studies (TIEs) are conducted to determine whether this toxicity is due to copper in the stormwater runoff.

Similarly, for constituents in urban stormwater runoff that tend to bioaccumulate in receiving water aquatic life to excessive levels, the focus of the Evaluation Monitoring approach is directed to determining whether the aquatic life in the receiving waters contain excessive concentrations of a constituent of potential concern. If excessive concentrations are found, then studies are conducted to determine the source of the constituents responsible.

The Evaluation Monitoring approach will lead to more technically valid, cost effective regulation of real, significant water quality problems than the approach that is being used today.

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Importance of Integrating Aquatic Chemistry with Toxicology/Biology in Regulating Urban-Area Stormwater Runoff: OP Pesticide Aquatic Life Toxicity Management

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Chronology of Urban Stormwater Runoff Toxics Control

1960s Found Urban and Highway Stormwater Runoff Had High Concentrations of Several Potentially Toxic Heavy Metals

1987 Amendments to the Clean Water Act Required US EPA to Regulate Urban-Area, Industrial, & Highway Stormwater Runoff

1991 US EPA Developed Regulations That Require **Control of Pollution to Maximum Extent Practicable (MEP) Using Best Management Practices (BMPs)**

Neither "MEP" nor "BMP" Defined

1994 Monitoring Showed Urban Stormwater Runoff to Be Toxic

Thought to Be Due to Heavy Metals, Because of Exceedance of Heavy Metal Water Quality Criteria

Pollutant

Defined as *"Constituent That Impairs Beneficial Uses of a Waterbody"*

For Constituents That Are Potentially Toxic (Heavy Metals)

Pollutant Alters the Numbers, Types and/or Characteristics of Desirable Forms of Aquatic Life in the Waterbody

Exceedance of Water Quality Criteria ≠ Pollutant

Heavy Metal Toxicity in Urban Stormwater Runoff

Concentrations of Total and Soluble Cu, Pb, Zn and Sometimes Cd in Urban Street and Highway Stormwater Runoff above Worst-Case-Based Water Quality Criteria (WQC)

- Criteria Based on Toxicity to Aquatic Life
- Typically Assume That Exceedance of a WQC Leads to Toxicity
- Criteria Are Based on Worst-Case Conditions
  - Extended Exposure of Aquatic Organisms
  - 100% Available/Toxic Forms

    Ignores Aquatic Chemistry of Metals

  Can Be "Administrative" Exceedances of Worst-Case-Based Water Quality Criteria

  Need to Evaluate if Exceedance of WQC Represents "Pollution"

  Must Use Integrated Assessment of Aquatic Chemistry and Toxicology/Biology to Determine if Pollution Is Occurring

    Especially True for Urban Stormwater Runoff-Associated Constituents

Evaluation Monitoring

Conventional End-of-the-Pipe, Edge-of-the-Pavement "Water Quality" Monitoring Provides Unreliable Assessment of Water Quality Impacts

- Leads to Over-Regulation and Under-Regulation
- Need a Different Approach

Early 1980s Proposed Integrated Aquatic Chemistry-Toxicology/Biology Approach

Evolved from Work in 1970s on Screening New and Expanded-Use Chemicals for Environmental Impact – TSCA

1990s Had Opportunity to Demonstrate the Use of Evaluation Monitoring as Part of Developing the Eastern Transportation Corridor (ETC)

26-mi, $800 Million New Toll Road in Orange County, CA

Evaluation Monitoring Focuses on Defining the Real, Significant Water Quality Use-Impairments Caused by a Particular Discharge

Change Approach from Focus on Chemical Concentrations to Assessing Impacts of

Not *"How Much Copper Is Present in Runoff,"* but Rather, ***"What Is the Impact of the Copper Present on Aquatic Life?"***

Is It Toxic?

If Toxic, Is the Toxicity of Sufficient Magnitude and Duration to Impair Beneficial Uses of Waterbody?

Do Not Measure Copper Concentrations and Then Try to Estimate Whether Copper Is Toxic

Measure Toxicity

- If Toxic, Determine If It Is Significant to Beneficial Uses
- Also, Determine Cause of Toxicity through TIEs

Toxicity Identification Evaluation (TIE)

- Physical/Chemical Sample Fractionation Procedures to Determine Cause of Toxicity

  e.g., Add EDTA – Does Toxicity Disappear?

  Screen for Most Heavy Metal Toxicity, Since Heavy Metal Complex Is Not Toxic

Current Regulatory Approach for Urban Stormwater Runoff Requires that Ultimately, Must Meet Water Quality Standards in the Runoff Waters at the Point of Discharge to Receiving Waters

Cannot Have Any Amount of a Regulated Constituent in Concentrations Greater Than a Standard More Than Once Every Three Years

Current Regulatory Approach Will Ultimately Cost the US Public Hundreds of Billions of Dollars to Meet Worst-Case-Based Water Quality Standards in Receiving Waters at the Point of Discharge

Obviously Need Different Regulatory Approach

Need to Reliably Evaluate the Real, Significant Adverse Impacts of Chemical Constituents such as Heavy Metals in Urban Stormwater Runoff as They May Impact the Beneficial Uses of Receiving Waters

Conclusions and Recommendations

- Urban Stormwater Runoff Contains Concentrations of **Potentia**l Pollutants That ***Could*** Impair Beneficial Uses
- Current Regulatory Approach for Urban Stormwater Runoff (Heavy Metal Concentrations Need to Meet Water Quality Standards in Runoff Water) Will Cost the Public Hundreds of Billions of Dollars and Will Likely Have Limited Impact on Beneficial Uses of the Receiving Waters for the Runoff
- Need to Change Regulatory Approach from Chemical-Concentration-Based Approach to Chemical Impact Assessment Approach
- Evaluation Monitoring Using an Integrated Assessment of Aquatic Chemistry & Toxicology/Biology Provides a Readily Implementable Approach to More Appropriately Regulate Water Quality Impacts of Chemical Constituents in Urban Stormwater Runoff and Other Sources of Potential Pollutants

DEVELOPMENT OF TMDL GOALS FOR CONTROL OF ORGANOPHOSPHATE PESTICIDE-CAUSED AQUATIC LIFE TOXICITY IN URBAN STORMWATER RUNOFF[1]

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ABSTRACT

Urban stormwater runoff in several municipalities in California has been found to be toxic to *Ceriodaphnia dubia*. This toxicity is due to residential use of the organophosphate (OP) pesticides, diazinon and chlorpyrifos, for termite, ant, lawn and garden pest control. This toxicity has caused regulatory agencies to list the receiving waters for the urban stormwater runoff as 303(d) "impaired" waterbodies. This listing requires that a TMDL be developed to control the concentrations of diazinon and chlorpyrifos so that they do not cause aquatic life toxicity in the runoff waters. This paper provides guidance on an approach that can be used to develop an appropriate TMDL goal to control aquatic life toxicity due to the OP pesticides used in residential areas. While the paper focuses on residential use of these pesticides, many of the same issues and approaches are applicable to runoff from agricultural areas where the pesticides are used.

KEYWORDS

Toxicity, pesticides, TMDL, urban stormwater runoff.

INTRODUCTION

The authors and their colleagues have recently completed a three-year study of aquatic life toxicity in stormwater runoff in the Upper Newport Bay, Orange County, CA watershed. Lee and Taylor (1999) have presented the results of this study. This study has found that stormwater runoff in this predominantly urban watershed contains from 5 to 20 units (TUa) of *Ceriodaphnia dubia* and *Mysidopsis bahia* acute toxicity. *Ceriodaphnia* and *Mysidopsis* are standard US EPA test organisms used for evaluating the potential toxicity of NPDES-permitted wastewater discharges and stormwater runoff. Both organisms are zooplankton that are representative of aquatic organisms that are used as larval fish food in fresh and marine waters. The Orange County study involved conducting over 140 toxicity tests and associated chemical measurements. These tests show that all stormwater runoff in the Upper Newport Bay watershed contains sufficient diazinon and chlorpyrifos, two organophosphate (OP) pesticides, to cause part of the toxicity found in the stormwater runoff. Over 100,000 pounds of diazinon and chlorpyrifos are used in Orange County each year on residential properties for termite,

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[1]Proceedings Water Environment Federation national 73rd Annual Conference, Anaheim, California, October 2000.

ant and lawn and garden pest control. Only about 5 pounds of the total amount applied per year is responsible for the aquatic life toxicity found in this study.

The Orange County study results are similar to urban stormwater runoff studies conducted in the San Francisco Bay area, Stockton, Sacramento, Los Angeles, San Diego, CA, and Fort Worth, TX, in that this runoff is acutely toxic to *Ceriodaphnia dubia*. Further, the USGS (Larson, *et al*., 1999) has recently released a report covering the national pesticide monitoring program which shows that there are sufficient concentrations of diazinon and chlorpyrifos in urban streams located in several areas of the US to be toxic to *Ceriodaphnia*. It is now clear that the aquatic life toxicity problem associated with the use of OP pesticides on residential properties is a largely unrecognized national problem that needs attention.

This toxicity has caused several of the California Regional Water Quality Control Boards to list urban streams as 303(d) "impaired" waterbodies for which TMDLs must be developed to control the OP pesticide-caused aquatic life toxicity. This paper focuses on the issues that need to be considered in developing technically valid, cost-effective TMDL goals for appropriately managing the toxicity due to OP pesticides in urban stormwater runoff.

REGULATORY ISSUES

The regulation of OP pesticide-caused aquatic life toxicity in urban stormwater runoff is complicated by several factors. Lee, *et al*. (2000) have reviewed these issues, one of the most important of which is that the OP pesticides, while highly toxic to *Ceriodaphni*a and *Mysidopsis*, are not toxic to many other types of zooplankton and are nontoxic to fish and algae at the concentrations being found in urban stormwater runoff. An issue that immediately arises from this situation is whether killing *Ceriodaphnia*-type zooplankton in the short-term toxic pulses associated with stormwater runoff events is significantly detrimental to the beneficial uses of the receiving waters for the stormwater runoff. There are some advocates for the continued use of OP pesticides on residential properties who assert that the OP pesticide toxicity is highly selective to certain types of organisms which are not essential components of the aquatic food web that lead to desirable forms of aquatic life such as edible fish and shellfish.

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) ..."

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. 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.

It is important to note that OP pesticide-caused aquatic life toxicity in urban stormwater runoff is not a new problem. It has been occurring for 10 to 15 years. It was not until toxicity tests were conducted on urban stormwater runoff that this problem began to be identified. Another important issue is that under current pesticide regulations, restricting the use of OP pesticides will result in the use of other pesticides that may have at least the same or even greater adverse impacts to the beneficial uses of waterbodies as diazinon and chlorpyrifos. The current pesticide regulatory approach does not require adequate evaluation of potential toxicity to aquatic life in stormwater runoff as part of pesticide registration.

This paper summarizes these issues and presents recommended approaches for developing TMDL goals for the control of aquatic life toxicity in urban stormwater runoff that will protect the designated beneficial uses of receiving waters for urban stormwater runoff without unnecessarily restricting the use of OP pesticides for residential termite and ant control.

SUGGESTED APPROACH FOR TMDL GOAL DEVELOPMENT

Stormwater Runoff Monitoring Program

The first step in developing an appropriate TMDL goal and its implementation to control aquatic life toxicity in urban stormwater runoff is to establish a monitoring program that will define whether stormwater runoff and dry weather flow in urban streams and the receiving waters for the runoff are toxic to *Ceriodaphnia dubia*. The overall approach that should be used is the Evaluation Monitoring approach described by Jones-Lee and Lee (1998). This approach focuses on finding potential water quality use impairments in the receiving waters for the stormwater runoff. Where such use impairment potentially exists, the cause of the use impairment is determined and its significance is assessed. If it is determined to be significant to impairment of beneficial uses, then the constituents responsible are determined and their sources are defined through forensic studies.

Basically, rather than measuring potentially toxic constituents, such as copper, in urban stormwater runoff and then trying to extrapolate the chemical concentration results to toxicity in the receiving waters for the runoff, toxicity is measured directly and its cause is determined through toxicity investigation evaluation procedures (TIEs). Evaluation Monitoring is a far more reliable, technically valid, cost-effective approach for developing water quality management programs for urban stormwater runoff than the traditional, conventional monitoring approach in which a suite of chemical parameters are measured and the results are compared to worst case- based US EPA water quality criteria/state standards based on these criteria.

It was through the use of toxicity measurements on urban stormwater runoff that it was found that the heavy metals that exceed US EPA water quality criteria in the urban street and highway stormwater runoff, such as copper, lead, and zinc, were in nontoxic forms. It was also determined through this approach that the OP pesticides, diazinon and chlorpyrifos, were responsible for aquatic life toxicity in urban stormwater runoff. These issues have been reviewed by Lee and Taylor (1999).

Lee (1999) has provided guidance on the characteristics of the stormwater runoff monitoring program that is designed to assess the magnitude of aquatic life toxicity, the cause of the toxicity, and the sources of the constituents responsible. This program focuses on using *Ceriodaphnia dubia*, fathead minnow larvae (*Pimephales promelas),* and *Selenastrum capricornutum* (algae) as the three test species using the US EPA standard testing protocol (Lewis, *et al.*, 1994). For marine waters, the US EPA 1994 testing procedures are used with *Mysidopsis bahia* or other marine organisms as a test organism.

In addition to measuring the toxicity to these organisms, toxicity measurements should be conducted on a dilution series of those samples of stormwater runoff and dry weather flow that show significant toxicity to the test organisms within a day or two. The dilution series testing should be designed to assess the magnitude of the toxicity (TUa) in the sample. For the samples which are toxic to *Ceriodaphnia*, the dilution series should be tested with and without PBO (piperonyl butoxide). The addition of PBO to a sample can remove the OP pesticide-caused toxicity and, therefore, if the toxicity of the sample is either eliminated or significantly reduced upon PBO addition, this is an indication that the toxicity was due to OP pesticides.

If toxicity is found, then chemical measurements on the samples should be conducted to determine the potential cause of the toxicity. The ELISA (enzyme linked immuno sorbent assay) procedures are highly specific for each of the OP pesticides. Further, the ELISA testing should be backed up by some dual column GC or GC-MS procedures. Further information on the use of these procedures is available from Lee (1999).

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 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*, fathead minnow larvae, and *Selenastrum*, 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. 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.

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) has 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. However, Lee and Jones-Lee (1999) have pointed out that the single chemical PERA used by Novartis 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 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 is 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 (1999), 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 IX has indicated that the PERA approach is not an acceptable approach 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.

Since many urban streams have been converted to stormwater conveyance structures (often 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.

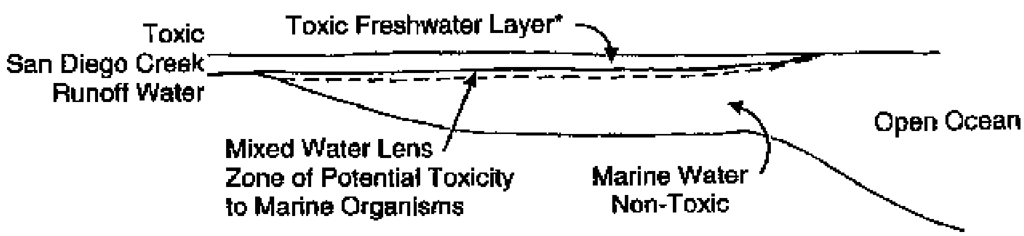
Urban stormwater runoff that enters marine waters creates a special situation for evaluating the impact of OP pesticide-caused aquatic life toxicity. The studies conducted by Lee and Taylor (1999) involve assessing the presence and impacts of OP pesticide-caused aquatic life toxicity in Upper Newport 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 10 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* in the undiluted 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 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. 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 1. 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 1



Not only must the marine zooplankton that migrate into the toxic freshwater/marine water lens be killed by the OP pesticide toxicity, but the loss of these zooplankton must represent an essential component of the food of marine organisms that are key components of the beneficial uses of the Bay. While this 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.

Water Quality Criteria/Standards as TMDL Goals

The current US EPA approach for establishing TMDL goals is to control the constituent that causes the 303(d) listing of the waterbody as being an "impaired" waterbody. Typically, the 303(d) listing arises out of an exceedance of a worst case-based water quality standard. While the US EPA (1987) published a water quality criterion for chlorpyrifos, the Agency did not require that this criterion be adopted by the states as a standard since chlorpyrifos is not considered a "toxic" pollutant.

While the US EPA has been developing the water quality criterion for diazinon for many years, it still has not developed a criterion. An Agency contractor has developed a proposed acute criterion, however, there are problems in developing the chronic criterion. The California Department of Fish and Game, however, using US EPA criteria development approaches, has developed recommended water quality criteria for diazinon and chlorpyrifos. Siepmann and Finlayson (2000) have recently completed an updated evaluation of the recommended water quality criteria of diazinon and chlorpyrifos. 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.

Implementation of these criteria as worst case water quality standards which are not to be exceeded by any amount more than once in three years would likely mean that neither diazinon nor chlorpyrifos could be used on residential properties where there is any possibility of runoff from the property that has either OP pesticide in the runoff waters.

Straus (2000) has indicated these criteria would be acceptable TMDL goals to the US EPA Region IX. However these criteria can readily over-regulate the use of OP pesticides dependent on how the criteria are applied. The application of these criteria to diazinon and chlorpyrifos concentrations at the point where the stormwater runoff enters the receiving waters on a worst case basis would effectively ban the use of these pesticides for many of the current homeowners' external outside uses. They may also under-regulate aquatic life toxicity if the criteria are applied as chemical concentrations without adequate aquatic life toxicity testing to be sure that toxicity is controlled to the degree needed to protect beneficial uses.

SUGGESTED APPROACH FOR IMPLEMENTING A PHASE I TMDL GOAL FOR URBAN STORMWATER RUNOFF

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 5 lbs/yr. It is evident that most of the diazinon and chlorpyrifos used on residential properties is not contributing 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 the 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. Thus far the authors have been unable to obtain funding from either governmental agencies or pesticide manufacturers to conduct the needed studies to determine how the use of OP pesticides on residential properties leads to toxic stormwater runoff from the properties.

It is suggested that it may be possible to continue to use the OP pesticides for below ground structural pest control (termites and ants) and 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.

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.

Evaluation of the Impact of Alternate 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. 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. 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 appropriately developed TMDL for the control of OP pesticide-caused aquatic life toxicity must include funding to conduct appropriate 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 properties. They are, however, causing substantial toxicity in urban stormwater runoff and in some receiving waters for this runoff. The current degree of understanding of 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 an appropriate 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.

ACKNOWLEDGMENTS

Many individuals have contributed to the information base upon which this paper has been developed. Of particular significance is the assistance of Scott Taylor, of Robert Bein, William Frost & Associates (RBF), Irvine, CA. Mr. Taylor and members of the RBF staff have been responsible for sample collection and have assisted in report preparation.

Drs. Valerie Connor and Chris Foe of the California Central Valley Regional Water Quality Control Board, Dr. Vic deVlaming of the California State Water Resources Control Board and Ms. Linda Deanovic and other staff members of the University of California, Davis, Aquatic Toxicology Laboratory have made significant contributions to the Orange County studies which serve as the basis for this paper.

Support for the background data upon which this paper is based has been provided by a US EPA 205(j) grant administered through the California Santa Ana Regional Water Quality Control Board and the Orange County Public Facilities and Resources Department. The assistance of Mr. Ken Theisen and Chris Crompton from these agencies in obtaining funding for these studies is greatly appreciated.

Dr. Jeff Miller of *Aqua*Science, Davis, CA, and Dr. Scott Ogle of Pacific EcoRisk, Martinez, CA, have also contributed background information upon which this paper is based.

We wish to acknowledge the editorial assistance of Debra Stevens, of G. Fred Lee & Associates.

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