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Developing TMDLs for Control of Excessive Bioaccumulation of Organochlorine Pesticides and PCBs

Previous issues of the Newsletter have discussed the occurrence and potential water quality significance of organophosphate pesticides such as diazinon and chlorpyrifos that are being widely used in urban and residential areas for structural and lawn and garden pest control. The organophosphate pesticides were developed a number of years ago as replacements for the organochlorine pesticides such as DDT, chlordane, toxaphene, dieldrin, etc. These pesticides were banned from further use because of their potential to cause cancer. Unlike the organophosphate pesticides, the organochlorine pesticides are extremely persistent and even though banned many years ago, are still present in soils where they have been used and aquatic sediments in waterbodies receiving runoff from areas where they were used.

The organochlorine pesticides are sometimes referred to as "legacy" pesticides because of their widespread continued persistence. In many areas, edible fish contain sufficient concentrations of these pesticides to be a threat to cause cancer for those who consume the fish as food. This situation has caused regulatory agencies to list waterbodies with fish with excessive concentrations on the Clean Water Act 303(d) list of impaired waterbodies which results in the need to develop a TMDL to control the excessive concentrations of the legacy pesticides in edible fish tissue.

Polychlorinated biphenyls (PCBs) were widely used as industrial chemicals until banned. They, like the organochlorine pesticides, are extremely persistent and have strong tendencies to bioaccumulate within fish tissue. They are also of concern because of their potential to cause cancer in those who consume the fish as food. Many areas where excessive concentrations of legacy pesticides found in fish tissue also contain excessive concentrations of PCBs. This situation has also led to the need to develop a TMDL to control the excessive bioaccumulation of PCBs.

Since legacy pesticides and PCBs were used in urban, residential, and commercial/industrial areas, soils in these areas can still contain sufficient concentrations so that stormwater runoff from the area is a source that continues to add these pollutants to waterbodies. Further, aquatic sediments in areas receiving urban/industrial stormwater runoff as well as municipal and industrial wastewater discharges can contain sufficient concentrations of legacy pesticides and PCBs in available forms to be a source for excessive bioaccumulation of these chemicals in edible fish. As a result, stormwater management agencies can become involved in an effort to control the excessive bioaccumulation of these chemicals in waterbodies receiving NPDES permitted stormwater runoff.

Dr. G. Fred Lee has become involved in developing TMDLs for the legacy pesticides and PCBs. Recently, Drs. G. F. Lee and Anne Jones-Lee have developed an extended abstract of a paper describing a suggested approach for developing and implementing TMDLs to control the excessive bioaccumulation of DDT, chlordane, toxaphene and other legacy pesticides, as well as PCBs. This paper will be presented at the American Chemical Society (ACS) national meeting that will be held in San Diego, California, in the first week of April 2001. Presented below is the extended abstract developed for the ACS Environmental Chemistry Division preprints of papers presented at the San Diego conference

DEVELOPING TMDLs FOR ORGANOCHLORINE PESTICIDES AND PCBs[1]

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Fish and other aquatic life in some agricultural and urban areas contain concentrations of organochlorine pesticides, such as DDT, dieldrin, chlordane, toxaphene and PCBs, which can be a human health threat to those who consume these organisms as food (Davis, *et al.*, 2000). Also in some urban industrial areas such as San Francisco Bay, edible fish have bioaccumulated dioxins to levels that are a threat to the use of the fish as food. Excessive bioaccumulation of organochlorines can lead to a 303(d) listing of the waterbody in which the fish with excessive edible tissue concentrations are located as an "impaired" waterbody. In 1998 California Regional Water Quality Control Boards listed 60 waterbodies as "impaired" by PCBs. In that same year, there were over 160 California waterbodies listed as "impaired" due to the organochlorine pesticides (DDT, aldrin, dieldrin, chlordane, endrin, heptachlor, heptachlor epoxide, hexachlorocyclohexane (including lindane), endosulfan and toxaphene). The 303(d) listing results in the need for the regulatory agency responsible for the waterbody to develop a total maximum daily load (TMDL) to control the concentrations of the organochlorine pesticides and PCBs (OCls) so that the concentrations in the edible fish tissue are less than those that are considered a threat to human health. The authors are involved in the review of several situations of this type. This paper presents an overview of the approach that we feel should be used to establish TMDLs and their implementation to control excessive bioaccumulation of OCls.

303(d) Listing

The first step in developing a TMDL for organochlorine pesticides and PCBs is a reliable assessment of excessive concentrations of these types of pesticides and PCBs within edible fish tissue. In order to make

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this assessment, it is necessary to assume a fish consumption rate for those in the area who use fish from the waterbodies of concern. While the US EPA uses 6.5 g of fish per person per day as the national average consumption rate (which translates to about one meal per month), it is generally agreed that that consumption rate is not normally appropriate for protecting some of those who utilize local fish as a source of food. More frequently, one meal per week or even several meals per week is the rate of consumption of fish that is used to evaluate potential hazards of bioaccumulation of organochlorine pesticides and PCBs. The US EPA (2000a, b) has provided guidance on a risk-based consumption rate which will be protective of those who consume fish with regulated hazardous chemicals in the edible tissue.

Table 1 presents a summary of the California Office of Environmental Health Hazard Assessment (OEHHA) 1999 fish tissue screening values for selected OCls. These values are based on a cancer risk of 1×10^{-5} and a fish consumption rate of 21 g/day.

The US EPA draft consumption criteria for DDT and other chlorinated pesticides provide a recommended risk-based consumption limit that is related to the fish tissue concentration. For example, if the fish tissue concentration of DDT is 0.2 mg/kg, the US EPA recommends that no more than twenty-three 8-oz. meals or eleven 16-oz. meals per month be consumed. These rates of consumption are significantly different from the Food and Drug Administration (FDA) DDT Action Level of 5 mg/kg.

Table 1
OEHHA Fish Tissue Contamination Screening Values

Chemical	OEHHA Screening Values (µg/kg)
Chlordane	30
Total DDT	100
Dieldrin	2
Endrin	1,000
Toxaphene	30
PCBs	20
Dioxin TEQ	0.3 picograms/kg

Source: SAWRCB (2000)

At that Action Level, the US EPA would recommend no more than one 4-oz. meal per month, six to eight 12-oz. meals per year, and no 16-oz. meals. It is evident that far greater attention needs to be given to the amount of fish consumed by those in a region who depend on local fish as a substantial part of their diet, where the concentrations of the chlorinated hydrocarbon pesticides and PCBs in the fish are above US EPA recommended risk-based levels.

Once the concentration of chlorinated hydrocarbon pesticides and PCBs in fish tissue that represents a threat to public health has been determined for a particular waterbody, considering local fish consumption rates, then detailed sampling of the fish is necessary to reliably assess whether the concentrations of OCls in each of the major types of edible fish exceed the critical concentrations. It has been found that various types of fish bioaccumulate hazardous chemicals to varying degrees. Also larger, higher trophic level fish tend to have higher concentrations of OCls than smaller fish. Further, fish with a higher body fat content tend to accumulate OCls to a greater degree. It is therefore, important to representatively sample the fish that are used as food in the region of concern. This may require a creel census. If the fish used as food contain OCls that exceed the critical concentrations, then the waterbody may be listed (if it is not already) as a 303(d) "impaired" waterbody, which requires that a TMDL be developed to control the excessive bioaccumulation of OCls in edible fish tissue.

While there are higher trophic level impacts of OCls, at this time, except for PCBs in the Great Lakes region, there are no national water quality criteria for protection of aquatic life. Generally, it is assumed that aquatic life will be protected if humans are protected, especially if the consumption rate is based on one meal per week. That assumption may not be protective for some situations.

In addition to concern about excessive bioaccumulation of the OCls as a human health threat, there is also increasing concern about the body burdens of these chemicals being adverse to the host organism. There are two publications (Jarvinen and Ankley, 1999, and US COE, 1987) which provide information on the concentrations of various chemicals, including several of the OCls, that have been found to be adverse to the host aquatic organism.

It should be noted that GC or GC/MS organochlorine pesticide and PCB scans of fish tissue from some areas show that there are unidentified, apparently anthropogenic chemicals in fish tissue that potentially could be a threat to those who use the fish as food. While this situation has been known for over 35 years, thus far, federal and state regulatory agencies and others, such as the USGS, are largely ignoring it. At this time, there is no effort to systematically investigate the chemicals responsible for the unidentified peaks in the GC or GC/MS scans for organochlorine pesticides and PCBs, as well as once they are identified, determine their hazard to human health and higher trophic level organisms.

Developing TMDL Goals for OCls

Normally the TMDL goal is the state water quality standard, which is based on the US EPA water quality criterion for the constituent of concern. These criteria are typically based on a worst case (greatest) bioaccumulation of the chemical in laboratory or field conditions. The US EPA, as part of promulgating the California Toxics Rule (US EPA, 2000c), has developed updated recommended water quality criteria for several organochlorine pesticides. Table 2 presents these criteria.

It is the authors' experience that, occasionally, the concentrations of total DDT in runoff from some agricultural areas, where DDT has not been used for many years, can exceed the drinking water maximum contaminant level (MCL) (Domagalski, 1997; Panshin, *et al.*, 1998). Generally, the MCL is much higher than the water quality criterion for prevention of bioaccumulation under worst-case conditions. Under those conditions, high levels of bioaccumulation would be expected.

The criteria presented in Table 2 could be used as TMDL goals to protect against excessive bioaccumulation ("organisms only" column in Table 2) or to protect against adverse impacts to aquatic life (the "CCC" columns in Table 2).

Table 2
Selected National Recommended Water Quality Criteria for Priority Toxic Pollutants-Pesticides

Priority Pollutant	Freshwater		Saltwater		Human Health For Consumption of:	
	CMC (µg/L)	CCC (µg/L)	CMC (µg/L)	CCC (µg/L)	Water + Organism (µg/L)	Organism Only (µg/L)
Chlordane	2.4	0.0043	0.09	0.004	0.0021	0.0022
4,4'-DDT	1.1	0.001	0.13	0.001	0.00059	0.00059
4,4'-DDE	–	–	–	–	0.00059	0.00059
4,4'-DDD	–	–	–	–	0.00083	0.00084
Dieldrin	0.24	0.056	0.71	0.0019	0.00014	0.00014
Endrin	0.086	0.036	0.037	0.0023	0.76	0.81
Polychlorinated Biphenyls PCBs	–	0.014	–	0.03	0.00017	0.00017
Toxaphene	0.73	0.0002	0.21	0.0002	0.00073	0.00075

Source: US EPA (1999)

Lee and Jones-Lee (1996) have discussed the problems of trying to use water column-based bioaccumulation water quality criteria to predict fish tissue concentrations. The basic problem is that the sediments of a waterbody act as an additional sink for the constituent of concern. Therefore, there is a partitioning between the organism tissue, the sediments and water. The distribution of a chemical like DDT into these compartments depends to a considerable extent on the characteristics (TOC content) and amounts of sediment. This situation frequently leads to a significant overestimation of the amount of bioaccumulation that will occur in a waterbody based on a measured concentration of the constituent in the water column relative to the US EPA worst case-based water quality criterion.

The US EPA senior staff (Pendergast, 2000) has indicated that the Agency is proceeding toward addressing the problem of not being able to reliably use US EPA water quality criteria to predict bioaccumulation of hazardous chemicals in fish tissue. Eventually, the US EPA may adopt a much more technically valid approach of basing TMDL goals on an allowable fish tissue residue, considering appropriate local fish consumption rates. For now, it appears that the Agency may allow this approach, provided that a site-specific water column constituent concentration be used to estimate the bioaccumulation that is occurring between the water column concentrations and the organisms. This site-specific bioaccumulation factor is a pseudo-bioaccumulation factor that ignores the role of the sediments in controlling tissue residues. While this approach will allow the Agency to continue to use a numeric chemical concentration as a TMDL goal, it should be understood that this pseudo-bioaccumulation factor has no predictive capabilities that can be used to estimate the amount of bioaccumulation that will occur if the magnitude of the sediment reservoir of the available forms of the constituent of concern is altered, such as through sediment remediation programs.

In summary, there are a variety of approaches for establishing TMDL goals for OCls to prevent their excessive bioaccumulation. The most reliable approach is the development of an appropriate allowable fish tissue residue that will be protective of those who use fish from a waterbody as a source of food, considering the local fish consumption rate from the waterbody. The implementation of this TMDL goal should be based on a phased approach, in which readily-controllable sources of available forms of the constituent of concern are controlled to the extent technically and economically feasible during Phase I. After five years or so following sediment remediation to the extent possible during Phase I and it is found that the desirable fish tissue residue has not been achieved, then a Phase II sediment remediation program should be undertaken and the system be allowed to equilibrate for a number of years following the sediment remediation program. There is no need to invoke the technically invalid approach of establishing a TMDL goal of a single chemical water column concentration to appropriately implement a TMDL for controlling excessive bioaccumulation of OCls and, for that matter, other hazardous chemicals.

Defining the Source of Bioaccumulatable Chemicals

The next step in developing an appropriate TMDL-based control program for organochlorines that bioaccumulate to excessive levels in aquatic life is to define the location(s) where they occur to the greatest extent in the waterbody of concern. Ordinarily, in a TMDL, the focus of the control programs is on identified, currently-discharging sources of the constituents to be controlled. However, with the organochlorine pesticides and PCBs, since these chemicals have not been sold in the U.S. for many years and, therefore, should not ordinarily be present in wastewater discharges or runoff from current use, the TMDL must focus on identifying and controlling reservoirs of these chemicals associated with former use/discharge. The most likely reservoirs for these chemicals are terrestrial soils and/or aquatic sediments. The identification of the source(s) of the OCls that have bioaccumulated to excessive levels within edible organisms will require the use of techniques designed to assess bioavailable forms of the chemical(s) of concern within a waterbody and its watershed.

While some individuals attempt to make an assessment of the sources of OCls based on concentrations of organochlorines in sediments and water, usually today the concentrations in water are below analytical method detection limits. Water concentrations should be determined in various parts of the watershed to determine if, in fact, there are sufficient concentrations to be measured using highly sensitive, reliable analytical methods. The focus should be on both total and dissolved forms, with care exercised in determining the dissolved forms to insure that the separation process, such as filtration, does not bias the results through sorption on the filters. In some instances it is necessary to use high-speed, large-volume centrifugation to properly separate dissolved from particulate forms of pesticides and PCBs.

With respect to determining bioaccumulatable organochlorines in sediments, it is important not to equate concentrations in sediments to the sediments being a source of the OCls that are bioaccumulating to excessive levels in fish or other aquatic life. The bioaccumulation process is based on both a food web uptake and a partitioning between the sediments, the associated interstitial water and aquatic organisms. The availability of OCls for partitioning is dependent on the organic carbon content of the sediments. The OCls sorb onto organic carbon particles and thereby reduce their availability for partitioning with the interstitial water associated with the sediment particles. This partitioning, however, may not prevent uptake of the OCls by sediment-ingesting benthic organisms.

In order to assess where elevated concentrations of organochlorines present in sediments are a bioaccumulation source, it is necessary to do some forensic bioaccumulation evaluation using caged organisms. It may also be possible to use natural organisms to detect sources of bioaccumulatable chemicals. The key to reliably implementing this approach is the availability of aquatic life with limited mobility such as freshwater clams and, in marine waters, mussels, throughout the waterbody of concern and its tributaries. Through gradient analysis of aquatic organism tissue, it may be possible to identify toxic "hot spots" of the chemicals that are bioaccumulating to excessive levels in higher trophic level organisms.

The US EPA (2000d) has developed a procedure involving the use of *Lumbriculus variegatus* to assess bioaccumulation of constituents from sediments. The sediments are incubated in the presence of these organisms, and the tissue concentrations are assessed. The US EPA has recently expanded this testing procedure to include the testing of the sediments for aquatic life toxicity using *Hylella*, a freshwater amphipod. The toxicity of sediments would not likely be due to the organochlorines, but to other constituents in the sediments. Also, the US EPA and the Corps of Engineers (US EPA/COE 1991, 1998) present bioaccumulation testing procedures that can be used to assess bioaccumulatable chemicals in sediments.

Control of Bioaccumulatable Hazardous Chemicals

If the forensic studies identify areas where there are substantial concentrations of bioaccumulatable chemicals of concern in the waterbody sediments, then sediment remediation techniques can be used to remove the contaminated sediments from the waterbody. The approach that is followed in sediment remediation would, in general, be similar to that being used today at Superfund sites where contaminated sediments are part of the site. Through a phased approach, after remediation of contaminated sediments that are likely to be the most significant source of the bioaccumulatable chemicals that are leading to excessive edible tissue residues, it may be necessary to conduct a Phase II evaluation of potential sources if the remediation of the "hot spots" does not reduce the constituents of concern in the edible organism tissue to acceptable concentrations.

It should also be understood that if the source of the bioaccumulatable chemicals is widespread throughout the sediments, then it may not be possible to eliminate the exceedance of the tissue residue. Under these conditions, it may be necessary to change the designated beneficial uses of the waterbody through a Use Attainability Analysis to restrict consumption of fish or some types of fish from the waterbody with excessive tissue residues.

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The last issue of *Stormwater* contained an overview review article of the urban stormwater runoff aquatic life toxicity problem that is due to the organophosphate pesticides diazinon and chlorpyrifos. This article represented a synthesis of key issues that Drs. G. Fred Lee and Anne Jones-Lee have previously published on this topic. While *Stormwater* is available to those interested at no cost (www.stormh2o.com), there are some readers of the Newsletter who may not yet have subscribed to *Stormwater*. For those readers, the *Stormwater* article on pesticide-caused aquatic life toxicity in urban stormwater runoff is presented below.
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The Pesticide Problem[1]

ANTS/TERMITES

*Commonly used organophosphate pesticides are present in stormwater runoff and are responsible for toxicity to aquatic life in receiving waterbodies. But as OP pesticides are phased out and replaced with others, lack of thorough evaluation techniques leads to a "pesticide roulette"—**how do we know the substitutes aren't worse than the ones they're replacing?***

by G. Fred Lee

The organophosphate (OP) pesticides diazinon and chlorpyrifos are commonly used in residential areas to control termites, ants, and lawn and garden pests. In some counties in the US, more than 100,000 lb. of active ingredient diazinon and chlorpyrifos are used each year on residential properties (Lee and Taylor, 1997). The US Environmental Protection Agency estimates that nonagricultural use of OP pesticides totals 17 million lb. per year, and agricultural use accounts for another 60 million lb. (EPA 1999).

Urban stormwater runoff in several California cities and in Fort Worth, TX, (Waller, *et al.*, 1995) has been found to be toxic to zooplankton including *Ceriodaphnia dubia*. Although it was initially suggested that this toxicity was due to heavy metals in the stormwater runoff, it has been repeatedly demonstrated that the toxicity is caused instead by diazinon and chlorpyrifos (Hansen and Associates, 1995; Lee and Taylor, 1999). Based on pesticide use patterns, it appears that aquatic life toxicity caused by OP pesticides in urban stormwater is a national problem that is not generally recognized.

Toxicity in urban runoff is a violation of the narrative water quality standard, which requires that no toxics be present in toxic amounts, and it has caused some regulatory agencies to list some receiving waters for urban stormwater runoff as impaired waterbodies under section 303(d) of the Clean Water Act. This listing, in turn, requires that Total Maximum Daily Loads (TMDLs) be developed to control the concentrations of diazinon and chlorpyrifos. While TMDL development is an important—and sometimes controversial—issue, other health and safety issues are now beginning to overtake it. For example, the effect of chlorpyrifos (commonly sold under the brand name Dursban) on children's health is currently in question, and chlorpyrifos is now being phased out for most residential and commercial indoor and outdoor uses, including in homes, schools, parks, hospitals, retail stores, daycare centers, and other public buildings. The phase-out will occur over this year.

[1] Published in *Stormwater*, Forester Publications, www.stormh2o.com, January/February 2001

In December 2000 the US EPA announced that the residential indoor and outdoor use of diazinon will be phased out by 2004. This phase-out, like that for chlorpyrifos, is not based on consideration of aquatic life toxicity in stormwater runoff, but on an assessment that these OP pesticides represent a potential threat to children's health. The phase-out of these commonly used OP pesticides means that, in some areas, there will be widespread substitution of alternative pest control approaches and pesticides from the traditional approaches for pest control that have been used over the last decade or so.

As chlorpyrifos and other OP pesticides are phased out, the need to control termites and other pests will not disappear, and the important question is what we will use as replacements. Many pesticides that are already registered can be used as substitutes. Already there is a substantial shift away from the use of both diazinon and chlorpyrifos toward pyrethroid pesticides (permethrin, cypermethrin, bifenthrin and others) by commercial pest control operators and the public. As I discuss later in this article, however, the US EPA Office of Pesticide Programs (OPP) registration of pesticides does not adequately evaluate the potential for pesticides to cause aquatic life toxicity in urban and agricultural stormwater runoff, and a number of the pyrethroid pesticides are as toxic to certain zooplankton as the OP pesticides.

How Toxic Is Toxic?

Regulating OP pesticide-caused aquatic life toxicity in urban stormwater runoff is complicated by several factors. One of the most significant is that the toxicity of the OP pesticides in urban stormwater runoff is largely restricted to certain types of zooplankton such as *Ceriodaphnia* and *Mysidopsis* and the amphipod *Gammarus*. The concentrations of OP pesticides found in urban stormwater runoff are typically on the order of a few hundred nanograms per liter (ng/L). For comparison, the LC_{50} for diazinon to *Ceriodaphnia* is about 450 ng/L. The LC_{50} for chlorpyrifos to *Ceriodaphnia* is about 80 ng/L.

Toxicity Terms. 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 serve as larval fish food in fresh and marine waters.

LC50 indicates the degree of acute toxicity of a substance to aquatic organisms. Most toxicity tests measure the lethal concentration, or LC, of a substance in water that will kill 50% of the organisms in the sample in a single dose or exposure. The lower the LC50, the more toxic the substance is to that organism.

Although OP pesticides are highly toxic to *Ceriodaphnia* and *Mysidopsis*, they are not toxic to many other types of zooplankton. At the concentrations in which they are found in urban stormwater runoff, they are also nontoxic to fish and algae. Thus the question arises, Is killing *Ceriodaphnia*-type zooplankton in the short-term toxic pulses associated with stormwater runoff events significantly detrimental to the beneficial uses of the receiving waters? Some advocates for the continued use of OP pesticides on residential property assert that OP pesticide toxicity is highly selective to certain types of organisms, and these organisms are not essential components of the aquatic food web that lead to desirable forms of aquatic life such as edible fish and shellfish. For the toxicity to be adverse to these higher trophic level forms of aquatic life, the OP pesticide-sensitive zooplankton would have to be key components of the larva fish food at a critical period of the year. If the zooplankton that are killed by the OP pesticide stormwater-associated pulses are in fact not key components of the food chain, then in terms of beneficial use of the waterbody, current TMDL development goals may be considered too stringent and overprotective. However, the actual ecological role of the *Ceriodaphnia*-like organisms that are killed by OP pesticides is not known.

Another complicating factor is the difficulty in determining the cause of toxicity in some areas. In many 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. However, in other areas such as Orange County, CA, stormwater runoff contains large amounts of toxicity of unknown cause to *Ceriodaphnia* and *Mysidopsis*. A four-year study of San Diego Creek as it enters Upper Newport Bay in Orange County shows that stormwater runoff contains from 8 to30 24-hr. acute toxic units of *Ceriodaphnia* and *Mysidopsis* toxicity (Lee and Taylor, 1999). Only about half the toxicity can be accounted for based on the concentrations of diazinon and chlorpyrifos. The remainder is due to unidentified causes. This toxicity is not caused by metals and does not appear to be caused by other commonly measured OP and carbamate pesticides. Stormwater runoff entering Upper Newport Bay from Orange County derives from urban, agricultural, and commercial nursery discharges, and it appears that all three sources are responsible for some of the toxicity of unknown cause.

Determining TMDL Goals for OP Pesticides

Considerable controversy exists over the TMDL goal that should be used for diazinon and chlorpyrifos. Some of the controversy stems from the fact that US EPA's OPP requirement 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. Although the Clean Water Act requires the control of all aquatic life toxicity, 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 the Clean Water Act (no toxics in toxic amounts) and the OPP (no toxicity that is significantly adverse to beneficial uses), it is not clear how aquatic life toxicity in urban and agricultural stormwater runoff will be regulated.

The current US EPA approach for establishing TMDL goals is to control the constituent that cases a waterbody to be listed as "impaired" under section 303(d). Typically such a listing arises because worst-case-based water quality standards have been exceeded. Although the US EPA published a water quality criterion for chlorpyrifos in 1987, the Agency did not require states to adopt the criterion as a standard because chlorpyrifos was not considered a toxic pollutant.

A US EPA contractor has developed a proposed acute criterion for diazinon, but there have been problems in developing a chronic criterion. The California Department of Fish and Game, using US EPA criteria-development approaches, has developed recommended water quality criteria for both diazinon and chlorpyrifos (Table 1). The recommended freshwater diazinon acute criterion (CMC) is 80 ng/L, and the chronic criterion (CCC) is 50 ng/L (Siepmann and Finlayson, 2000). The recommended chlorpyrifos saltwater CMC is 20 ng/L and the CCC is 9 ng/L. No saltwater criteria were recommended for diazinon. Generally, diazinon is not expected to cause aquatic life toxicity in marine waters because of its low toxicity to marine organisms. The same report indicates that both diazinon and chlorpyrifos toxicities are additive, raising the possibility that proposed TMDL goals may actually be underprotective if they do not take additivity into account.

Table 1. Proposed Water Quality Criteria for Diazinon and Chlorpyrifos

	Acute (1-hr.) CMC (ng/L)	Chronic (4-day) CCC (ng/L)	Ceriodaphnia LC_{50}
Diazinon	80	50	450
Chlorpyrifos	20	14	80

Source: California Dept. of Fish and Game (2000)

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

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 samples that 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; therefore, if the toxicity of the sample is eliminated or significantly reduced when PBO is added, this is an indication that the toxicity was caused by OP pesticides.

If toxicity is found, chemical measurements on the samples should be conducted to determine the potential causes. The ELISA (enzyme linked immuno sorbent assay) procedures are highly specific for each of the OP pesticides. 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 (Lee, 1999).

However, when we find toxicity in urban stormwater runoff, we should not assume that the toxicity is significantly detrimental to the beneficial uses of the receiving water for the runoff. The conditions of the EPA standard toxicity test using *Ceriodaphnia*, fathead minnow larvae, and *Selenastrum* can lead to laboratory-based toxicity that is not manifested in the field. Situations occur in which aquatic life toxicity caused by OP pesticides in urban streams is rapidly lost through dilution in the receiving waters for the stream discharges. It is essential in developing TMDL goals to determine whether aquatic life in the receiving waters experience sufficient toxicity for a sufficient period of time to be toxic.

Testing Before Substitution

As other types of pesticides are used to replace OP pesticides, there is general agreement on the need to effectively screen the substitutes *before* large-scale substitution occurs. However, no formal mechanism exists to require comprehensive evaluation of the substitutes' potential to cause water quality problems. Legislative action is urgently needed that will empower and require regulatory agencies to properly evaluate the water quality impacts of all pesticides that have a potential to be present in stormwater runoff, either urban or agricultural. Without evaluation, the public and agricultural interests will be playing "pesticide roulette," substituting for one pesticide another that may cause even greater environmental problems than the first.

Other OP pesticides such as propetamphos are being used by commercial applicators to treat residential properties in Orange County and elsewhere. Propetamphos is not measured in the conventional dual column GC scans using US EPA procedures, and this chemical could be a contributor to the toxicity of unknown cause found in Upper Newport Bay stormwater runoff. Of even greater concern is the use of pyrethroid pesticides, which are sold over the counter to the public in substantial amounts and which are as toxic, or more toxic, to aquatic life than are OP pesticides (Table 2).

Table 2. Toxicity of Selected Pyrethroid Pesticides to *Daphnia magna* and *Mysidopsis bahia*

Pesticide	LC_{50} (ng/L)	
	Daphnia magna	*Mysidopsis bahia*
Permethrin	320	46
Cypermethrin	1,000	5
Fenvalerate	50	8
Bifenthrin	1,600	4
Tau Fluvalinate	400	18
Esfenvalerate	150	Unknown

Under the current, passive approach, pesticides are registered for use without adequate evaluation for potential environmental impacts. Only when substantial problems are found is the use of a pesticide restricted. It is clear that we need to change from a passive to a proactive approach in which pesticides that are in use today are evaluated by water quality management agencies. This evaluation cannot be done as part of pesticide registration, because of the tremendous pressure on registration agencies at the federal and state levels, which effectively precludes requiring pesticide registrants to conduct adequate evaluation of the pesticides' potential to cause aquatic life toxicity in the receiving waters for urban and agricultural runoff.

A proactive approach to evaluating whether pesticide use in a particular region is adverse to the beneficial uses of the receiving waters for stormwater runoff, drainage, and discharges from areas where it is applied involves first determining which pesticides are applied in the region, as well as when and where. Each application area should have an associated monitoring program of the receiving waters for the area's runoff. Both chemical and biological monitoring should be conducted immediately following and for some time after pesticide application. Monitoring should use an event-based approach, specifically targeting stormwater runoff and discharge events when the pesticide is most likely to be present in the discharge. To assess potential biological impacts, a combination of aquatic toxicity and aquatic organism assemblage information must be collected. The toxicity information should not be collected only at fixed locations downstream of the runoff location; 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/purpose at a particular location. Eventually, if the formulation of the pesticide and its application remain the same, the monitoring program can be significantly curtailed. As we gain more experience, it should be possible to greatly reduce the amount of monitoring and evaluation needed for pesticides for which we have an adequate information base to determine that their use poses no environmental threat.

Immediate Implications

In Orange County, CA, about 25,000 lb. of diazinon and 75,000 lb. of chlorpyrifos are used every year by commercial applicators for controlling termites in residential structures (Lee and Taylor, 1999). Approximately the same amount of OP pesticide is estimated to be purchased by the public for use on residential properties. The total amount of diazinon and chlorpyrifos needed to cause the toxicity found in stormwater runoff as it enters Upper Newport Bay is only about 2 lb. per year. Therefore it is evident that most of the diazinon and chlorpyrifos used on residential properties is not contributing to the stormwater runoff toxicity problem.

It is important to distinguish between the two types of OP pesticide use. Typical structural use for termite control involves injecting the pesticide into the underground foundations of structures. This use probably does not contribute significantly to the OP pesticide-caused aquatic life toxicity. The more likely cause is the above-ground application of these pesticides for controlling lawn and garden pests.

Although studies are needed to determine how OP and other pesticides used for residential purposes contribute to stormwater runoff toxicity, I suggest that it may be possible to continue using OP pesticides for below-ground structural pest control for termites and ants and greatly reduce or eliminate the toxicity associated with stormwater runoff from residential areas. As a first-phase TMDL goal for urban stormwater runoff, it may be enough to restrict the use of these pesticides for above-ground applications, allowing time for testing potential replacement pesticides for their effects on water quality.

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