



Commonly used organophosphate pesticides are present in urban stormwater runoff and are responsible for toxicity to aquatic life in receiving water bodies. But as these pesticides are phased out and replaced with others, the lack of thorough evaluation techniques leads to a "pesticide roulette."

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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 United States, more than 100,000 lb. of active ingredient diazinon and chlorpyrifos are used each year on residential properties (Lee and Taylor, 1997). USEPA estimates that nonagricultural use of OP pesticides totals 17 million lb. per year, and agricultural use accounts for another 60 million lb. (USEPA, 1999).

Urban stormwater runoff in several California cities and in

Fort Worth, TX, has been found to be toxic to zooplankton including *Ceriodaphnia dubia* (Waller et al., 1995). Although it was initially suggested that this toxicity was the result of heavy metals in the stormwater runoff, it has been repeatedly demonstrated that the toxicity is caused instead by diazinon and chlorpyrifos (Hansen & 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 not generally recognized.

Toxicity is a violation of the narrative water-quality standard, which requires that no toxics be present in toxic amounts. It has caused some regulatory agencies to list some receiving waters for urban stormwater runoff as impaired water bodies under section 303(d) of the Clean Water Act (CWA). 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 use, including in homes, schools, parks, hospitals, retail stores, daycare centers, and other public buildings. The phaseout will occur over several years.

Clearly, 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 to use as replacements. Many pesticides that are already registered can be used as substitutes. There is a substantial shift away from the use of both diazinon and chlorpyrifos toward pyrethroid pesticides (permethrin, cypermethrin, and others) by commercial pest control operators and the public. As discussed later in this article, however, the EPA Office of Pesticide Programs (OPP) registration of pesticides does not adequately evaluate the potential for them to cause aquaticlife 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/lit.). For comparison, the LC₅₀ (lethal concentration) for diazinon to *Ceriodaphnia* is about 450 ng/lit. The LC₅₀ for chlorpyrifos to *Ceriodaphnia* is about 80 ng/lit. (See sidebar.)

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, a guestion 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 are in fact not key components of the food chain, then in terms of beneficial use of the water body, current TMDL development goals might be considered too stringent and overprotective. However, the actual ecological role of the *Ceriodaphnia*-like organisms 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. In other areas such as Orange County, CA, however, 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 8 to 30, 24-hour acute units of Ceriodaphnia and *Mysidopsis* toxicity (Lee and Taylor, 1999). Only about half of the toxicity can be accounted for based on the concentrations of diazinon and chlorpyrifos. The remainder is the result of unidentified causes. Through the use of toxicity identification and evaluation, it has been determined that this toxicity is not caused by metals and does not appear to be

caused by other commonly measured OP and carbamate pesticides. Based on piperonyl butoxide (PBO) activation, it appears to possibly be caused at least in part by pyrethroid pesticides. Stormwater runoff entering Upper Newport Bay 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 EPA's OPP requirement for control of the adverse impacts of pesticides to nontarget organisms allows toxicity to aquatic life, provided that this toxicity is not significantly adverse to the beneficial uses of the water body. Although the CWA 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 CWA (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 EPA approach for establishing TMDL goals is to control the constituent that causes a water body 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 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.

An 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 EPA criteria-development approaches, has formulated recommended water-quality criteria for both diazinon and chlorpyrifos (Table 1). The recommended freshwater diazinon acute criterion (CMC) is 80 ng/lit., and the chronic criterion (CCC) is 50 ng/lit. (Siepmann and Finlayson, 2000). The recommended chlorpyrifos saltwater CMC is 20 ng/lit. and the CCC is 9 ng/lit. No saltwater criteria were recommended for diazinon. The same report indicates that both diazinon and chlorpyrifos toxicities are additive, raising the possibility that proposed TMDL goals might actually be underprotective if they do not take additivity into account.

	Acute (1-hr.) CMC (ng/lit.)	Chronic (4- day) CCC (ng/lit.)	Ceriodaphnia LC ₅₀
Diazinon	80	50	450
Chlorpyrifos	20	14	80

Table 1. Proposed Water-Quality Criteria for Diazinon and
Chlorpyrifos

Source: Siepmann and Finlayson, 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, Pimephales promelas (fathead minnow larvae), and Selenastrum *capricornutum* (algae) as the first three test species using the EPA standard testing protocol (Lewis et al., 1994). For marine waters, EPA's testing procedures are used with *Mysidopsis* bahia or other marine organisms as test organisms (EPA, 1991). 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 in the sample. For samples that are toxic to Ceriodaphnia, the dilution series should be tested with and without PBO. 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 cases. 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 gas chromatography (GC) or GC/mass spectrometry procedures. Further information on the use of these procedures is available (Lee, 1999).

When we find toxicity in urban stormwater runoff, however, we should not assume that the toxicity is significantly detrimental to the beneficial uses of the receiving water from the runoff. The conditions of the EPA standard toxicity test using *Ceriodaphnia*, *Pimephales promelas*, 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. The duration of the toxicity test can readily exceed the duration of exposure that aquatic life can receive in an urban stormwater runoff event. It is essential in developing TMDL goals to determine whether aquatic life in the receiving waters experiences 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 might 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. Propetamphos is not measured in the conventional dual-column GC scans using 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 OP pesticides are (Table 2).

Pesticide	LC ₅₀ (ng/lit.)	
	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

 Table 2. Toxicity of Selected Pyrethroid Pesticides to

 Daphnia magna and Mysidopsis bahia

Source: USEPA OPP Ecological Database, 1999

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 waterquality 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-life toxicity and aquatic organism assemblage information must be collected. The toxicity information should not be collected only at fixed

locations downstream from 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 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, 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 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 5 lb./yr. 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 aquaticlife toxicity. The more likely cause is the aboveground 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, it might be possible to continue using OP pesticides for belowground 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 might be enough to restrict the use of these pesticides for aboveground applications, allowing time for testing potential replacement pesticides for their effects on water quality.

Toxicity Terms

Ceriodaphnia and *Mysidopsis* are standard EPA test organisms used for evaluating the potential toxicity of NPDES-permitted wastewater discharges and stormwater runoff. Both organism are zooplankton that are representative of aquatic organism that serve as larval fish food in fresh and marine waters.

 LC_{50} indicates the degree of acute toxicity of a substance to aquatic organisms. Some 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 LC_{50} , the more toxic the substance is to that organism.

References

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