Water Quality Control TMDL Goals for Urban Stormwater Runoff OP Pesticide-Caused Aquatic Life Toxicity

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The finding of widespread urban stormwater runoff aquatic life toxicity and the listing of waterbodies experiencing this toxicity as 303(d) listed impaired waterbodies has established the total maximum daily load (TMDL) process to control this toxicity in several areas of California. Since the toxicity is typically associated with the organophosphate pesticides (OP pesticides) diazinon and chlorpyrifos, often these chemicals are targeted as the constituents that must be controlled in the TMDL process. However, considerable confusion exists today on the appropriate goal for the OP pesticide aquatic life toxicity control TMDL process. This paper reviews some of the issues that are pertinent to establishing TMDL goals for OP pesticide-caused aquatic life toxicity. A discussion is presented on some of the aspects of establishing appropriate TMDL goals that need to be considered in appropriately regulating OP pesticide-caused aquatic life toxicity in urban stormwater runoff. While the focus of this paper is urban stormwater runoff, the same issues apply to agricultural stormwater runoff where the toxicity is due to the use of OP pesticides.

Additional background information on the issues discussed in this paper are available from Lee and Jones-Lee (1999a,b).

Elimination of Pesticide Use

There are some, whose agenda is primarily that of controlling the use of chemicals and especially pesticides, who propose as a TMDL goal, termination of use of pesticides. Initially, this goal is manifested in the termination of use of diazinon and chlorpyrifos, but this goal is expected to be expanded to other pesticides. While this goal is sometimes advocated, it will not likely be accepted by the public, who encounter situations where pests are a significant threat to their health, welfare and interests.

Conflicting Regulatory Approaches for OP Pesticides

There are two different approaches used for regulating OP pesticide-caused aquatic life toxicity in NPDES-permitted wastewater discharges and stormwater runoff. OP pesticide-caused aquatic life toxicity in NPDES-permitted municipal and industrial wastewaters is not allowed. The public-owned treatment works (POTW) owner must control this toxicity so that it is not present in the wastewater effluent. The regulation of OP pesticide-caused toxicity in municipal wastewaters as discharged by a POTW has to meet the same toxicity control requirements as for other toxicants such as heavy metals, other organics, chlorine, ammonia, etc. However, NPDES-permitted urban stormwater runoff is regulated through the BMP ratcheting-down process where ultimately, under current regulations, it, too, could have to meet the requirement of no toxicity in the stormwater runoff at the point of discharge to public waters. Unless these regulatory requirements are changed, there will be a projected period of five to ten years where a BMP ratcheting-down process will control the violations of water quality standards - including the toxicity that is occurring in urban area stormwater runoff.

The possible TMDL goals for controlling aquatic life toxicity in urban stormwater runoff that are receiving the greatest attention at this time are those of "no toxics in toxic amounts" and "no significant toxicity that impairs water quality-beneficial uses." The no toxics in toxic amounts narrative standard is proposed to be implemented on the control of diazinon and chlorpyrifos to meet existing or proposed water quality standards and/or the control of toxicity in stormwater runoff so that no measurable toxicity using standard US EPA toxicity testing procedures is found in the ambient waters for the runoff.

Fox (1999), Assistant Administrator for Office of Water, US EPA, Washington, D.C. stated, "Since pesticides are also transported to receiving streams in sheet flow from agricultural and residential areas, non-point source control measures are expected to be an important component of water quality protection. This essentially relies on usage of best management practices by pesticide applicators.

Given the variable nature of non-point source pollution, these approaches are the most pragmatic way for the Office of Water to address toxicity from registered pesticides. Of course, the primary responsibility for pesticide control lies with OPP. Local water quality issues are typically addressed by the governing State or Tribe, with EPA support as needed."

No Toxics in Toxic Amounts

A likely TMDL aquatic life toxicity control goal is the reduction of diazinon and chlorpyrifos concentrations in urban area stormwater runoff so that the receiving waters for the runoff, including channelized urban creeks which are basically flood water conveyance structures, do not contain measurable aquatic life toxicity using US EPA standard toxicity testing procedures (Lewis *et al.*, 1994; US EPA, 1991). This approach for establishing TMDL goals to control the aquatic life toxicity associated with urban area stormwater runoff is based on the US EPA Clean Water Act and, in California, the Regional Water Quality Control Board Basin Plan objectives of "no toxics in toxic amounts." While several California Regional Water Quality Control Boards have a Basin Plan objective of no toxics in toxic amounts, the Santa Ana Regional Water Quality Control Board (SARWQCB, 1995) requirements for the control of toxicity include:

"Toxic Substances

Toxic substances shall not be discharged at levels that will bioaccumulate in aquatic resources to levels which are harmful to human health.

The concentrations of toxic substances in the water column, sediments or biota shall not adversely affect beneficial uses."

Further, the 1998 State Water Resources Control Board's proposed approach for implementation of the California Toxics Rule includes the control of significant toxicity, rather than an absolute control of all laboratory-measured toxicity.

The implementation of the no toxics in toxic amounts approach usually takes the form of a measurement of concentration of diazinon or chlorpyrifos that is either an established water quality criterion/standard, such as the US EPA criterion for chlorpyrifos (US EPA 1987) or the California Department of Fish and Game proposed water quality criterion for diazinon (Menconi and Cox, 1994). The US EPA has been developing a water quality criterion for diazinon for several years. University of Wisconsin, Superior and the Great Lakes Environmental Center (1998), under contract with the US EPA, developed a draft water quality criterion for diazinon. While they were able to develop a recommended acute criterion, they were unable to establish a recommended chronic criterion due to the wide range of acute/chronic ratio data that exists for this chemical in various organisms. This situation has delayed the promulgation of a national water quality criterion for diazinon using the US EPA established criteria development approach.

One of the issues that needs to be addressed in the interpretation of no toxics in toxic amounts is what is meant by "toxic." While it is often assumed that any measurement of toxicity in a US EPA standard toxicity test would be considered a measure of toxics, this is not necessarily the case. Toxicity under laboratory test conditions to a particular organism such as *Ceriodaphnia* may not be manifested as significant toxicity that impairs the beneficial uses of a waterbody.

There are some representing pesticide manufacturers and the regulated community who attempt to assert that the assessment of aquatic life toxicity due to OP pesticides is unreliable because of the inability of a variety of labs to conduct appropriate OP pesticide toxicity and analytical measurements. While there may be significant problems with OP pesticide toxicity measurements by some laboratories, there is substantial data that demonstrate that aquatic life toxicity can be reliably assessed using standard US EPA procedures in an experienced laboratory that carefully conducts the tests.

The approach of using US EPA water quality criteria as a TMDL goal for implementation of the no toxics in toxic amounts Clean Water Act and Basin Plan requirements is justified since the standard US EPA toxicity tests are acute tests and do not address chronic toxicity issues. While, in many urban stormwater runoff situations, because of the short duration of exposure of a few hours to a day or so, TMDLs based on acute toxicity may be appropriate, there are situations where OP pesticides persist for sufficient periods of time in waterbodies to potentially cause chronic toxicity to some forms of aquatic life. An example of this situation is that reported by Kuivila and Foe (1994), who found that toxic pulses of diazinonto *Ceriodaphnia* persisted in the San Joaquin and Sacramento Rivers through the Sacramento/San Joaquin River Delta of several weeks duration. This diazinon was found to be due to stormwater runoff from Central Valley orchard areas, where it had been used as a dormant spray during the winter. With the first major runoff event following application, high levels of *Ceriodaphnia* toxicity were found over considerable areas in the Central Valley rivers through the Delta, into upper San Francisco Bay. It is

important, therefore, in establishing appropriate TMDL goals, to evaluate, on a site-specific basis, the potential exposure to OP pesticide toxicity that zooplankton or benthic organisms could experience in a stormwater runoff event, to determine whether an acute or chronic water quality criterion should be used as the TMDL goal.

An issue of increasing concern is the approach that the US EPA uses to establish the acute and chronic criterion values involving an extrapolation of the four most sensitive species test results to the abscissa for a plot of percent exceedance of LC_{50}/EC_{50} cumulative concentration rank vs. diazinon concentration. Recently, several papers have been presented at national meetings showing that significantly different criterion values can be obtained dependent on the characteristics of the data set used in this extrapolation. In one case, the addition of a more sensitive aquatic organism data set in the data that is used to extrapolate to the abscissa has been found to cause the criterion value to increase significantly, since it causes the extrapolation line to be steeper than when it was based on a less sensitive organism data set.

No Significant Adverse Impact Toxicity

Another possible goal for the TMDL process is meeting the legal requirements for pesticide use as set forth in US EPA Office of Pesticide Programs (OPP) and the California Department of Pesticide Regulation (DPR) regulations of no significant water quality toxicity associated with pesticide use. Under these regulations, stormwater runoff from areas where pesticides are used in accord with the pesticide registration label can be toxic to test organisms such as *Ceriodaphnia*, provided that this toxicity is not significantly adverse to the designated beneficial uses of the receiving waters for the stormwater runoff.

Associated with the US EPA, OPP and California DPR regulatory approaches is the potential use of a probabilistic risk assessment which purports to show that it is permissible to kill 10% of the types of organisms present in a waterbody through OP pesticide use and still protect the designated beneficial uses of a waterbody. As discussed below, however, the probabilistic risk assessment approach, as it is being put forthtoday, falls far short in adequately and reliably providing the information that is needed to conclude that the pulses of OP pesticide-associated toxicity present in urban stormwater runoff are not significantly adverse to key aquatic organisms of concern to the public or, for that matter, the overall ecosystem potentially impacted by the pesticides.

Inadequacies of the Single Chemical Probabilistic Risk Assessment Approach

Chemical companies, Superfund Principal Responsible Parties (PRPs) and others have been promoting probabilistic risk assessment as an approach that can be used to evaluate the potential water quality significance of hazardous chemicals in the aquatic environment. This approach is now being applied to the regulation of organophosphate pesticide aquatic life toxicity. Novartis (1997) and Giesy *et al.* (1999), on behalf of Dow AgroSciences have developed probabilistic risk assessments for assessing the water quality significance of *Ceriodaphnia* toxicity associated with the use of diazinon and chlorpyrifos. These risk assessments purport to show that based on the information available, there is a potential impact

of OP pesticide toxicity on aquatic life resources of a waterbody. However, this impact is within the promoted level of aquatic life toxicity that is claimed to be acceptable, i.e. 10% of the species within a waterbody can be killed without significant adverse impact on the ecosystem functioning. The OP pesticide ecological risk assessment work that has been done thus far confirms what was known from the exceedance of a water quality standard approach, that there are potentially significant water quality problems associated with the OP pesticide toxicity that need to be better understood before it can be concluded that this toxicity is not significantly detrimental to the designated beneficial uses of a waterbody.

Further, such issues as additive and synergistic effects of various toxicants, including other OP pesticides, are thus far ignored in the probabilistic risk assessments that have been conducted. Basically, the probabilistic risk assessment shows that the cladoceran *Ceriodaphnia* is highly sensitive to OP pesticide toxicity. It is not, however, the most sensitive organism known. The amphipod *Gammarus fasciatus* is about twice as sensitive to diazinon toxicity as *Ceriodaphnia dubia* (Novartis 1997). A similar situation exists with respect to chlorpyrifos, where the amphipod *Gammarus fasciatus* is about twice as sensitive to chlorpyrifos, where the amphipod *Gammarus fasciatus* is about twice as sensitive to chlorpyrifos as some cladocerans. There is a potential, through further study, that other organisms will be found to have even greater sensitivity to diazinon and chlorpyrifos toxicity than *Ceriodaphnia*. This points to the need to better understand the ecological role of cladocerans such as *Ceriodaphnia* and amphipods in providing food for key higher trophic-level aquatic organisms of concern to the public.

While an ecological risk assessment is an interesting initial step in an evaluation of the potential water quality significance of OP pesticide toxicity, at this time ecological risk assessment falls far short of providing the information needed to assert that the toxic pulses caused by OP pesticides that occur in receiving waters for urban area and some agricultural area stormwater runoff are not adverse to key aquatic organisms of concernt to the public. Further, and most importantly, the ecological risk assessment approach places a great demand for high quality data far beyond that available. The only possible way that ecological risk assessment can be an effective regulatory tool is for those who want to maintain the use of OP pesticides, such as the chemical manufacturers, agricultural interests, and the members of the public who wish to use these pesticides, fund the studies needed to reliably evaluate the potential ecological significance of toxic pulses of OP pesticide toxicity associated with urban stormwater runoff events.

Ecological risk assessment can be a reliable base for developing regulatory approaches for chemicals in the environment as they may impact public health and/or aquatic/terrestrial ecosystems. However, in order to use this approach, there must be a substantial database of reliable information which rarely, if ever, exists. It is inappropriate for chemical companies and pesticide users to expect that regulatory agencies and members of the public who do not use these chemicals will pay for the studies or wait for the studies to be done until regulatory decisions are made. The OP pesticide aquatic life toxicity problem has been known for many years. Little has been done, however, to obtain the necessary information to properly evaluate the ecological significance of the OP pesticide-caused toxicity associated with urban area stormwater runoff.

An aspect of the ecological risk assessment issue that needs to be understood is that environmental groups who are largely behind the current pressure to control the OP pesticide aquatic life toxicity will not likely accept the premise that OP pesticides can kill 10% of the species and not be adverse to the beneficial uses of a waterbody of concern to the public. In order to make a convincing argument for this position, it will be necessary to provide substantial, site-specific data. Simply stating, as is done in support of ecological risk assessment that some group somewhere stated that the appropriate approach for protecting ecosystems is to protect 90% of the organisms 90% of the time is not adequate. There is no justification for this approach that would be acceptable to the majority of the environmental groups, as well as many regulatory agencies and members of the public. While there is an attempt to shift the burden of showing that killing 10% of the species 10% of the time does not represent a significant adverse impact to the public or those who represent their interests, in fact, the burden of proof should be on the pesticides, to convincingly show that the pesticides can be used safely without significant adverse impacts to public health and the environment.

Anyone who is sufficiently naive to believe that environmental groups who have through litigation been able to force the US EPA and the state water pollution control agencies to finally conform to the regulatory process that has been in effect for many years of controlling exceedances of water quality standards through the 303(d) listing and the implementation of TMDLs to eliminate this listing, does not understand the current situation in the water pollution control field. Environmental groups have for years been trying to get the US EPA and states to implement the Clean Water Act in accord with regulatory requirements. While there is considerable justified concern about the appropriateness of some of the Clean Water Act requirements as set forth in the original Act and in various amendments to the Act, until the Clean Water Act is changed, the US EPA and the states have no choice but to fully implement its requirements for the control of exceedances of water quality standards, including the narrative standards of no toxics in toxic amounts. The special regulatory provisions provided to pesticides of requiring the control of pesticide-caused toxicity that is significantly adverse to the beneficial uses of the waterbodies will not likely prevail over long periods of time in the current regulatory situation.

Selecting Appropriate TMDL Goals for OP Pesticide-Caused Toxicity

The two goals that should be the focal point of TMDL development are the Clean Water Act requirements of no toxics in toxic amounts and the pesticide regulatory requirements of no toxicity that is significantly adverse to the beneficial uses of a waterbody. It is suggested that because of the uncertainty as to how pesticide toxicity is going to be regulated in the near-term, that those responsible for developing TMDL goals develop a set of TMDLs to achieve both of these goals. By covering the range from no toxicity as measured by laboratory tests and appropriate water quality criteria/standards to, where appropriate, address chronic toxicity through allowed laboratory-based toxicity that is judged to not cause significant water quality or ecological impacts, those responsible for developing TMDLs will have likely covered the range that will ultimately govern how OP pesticide aquatic life toxicity will be regulated. Ultimately, Congress and the state legislatures will have to resolve the conflict that exists now between

CleanWater Act and pesticide registration requirements. By adopting both goals and gathering information needed to implement either goal, those responsible for developing a TMDL will be in a position to appropriately implement a wasteload allocation for pesticide runoff in stormwater and fugitive irrigation waters to achieve the goal.

Implementation of the Wasteload Allocation

The database needed to appropriately implement a wasteload allocation for control of laboratorybased aquatic life toxicity using US EPA standard three species tests focuses on understanding the specific sources of OP pesticide toxicity that become part of stormwater runoff. For residential properties the key issues that have to be assessed are the amounts of stormwater and fugitive water runoff associated with aquatic life toxicity from various types of residential use. An important issue is the need to understand how diazinon and chlorpyrifos used for structural termite and ant control lead to stormwater runoff aquatic life toxicity. Similarly, there is need to understand the use conditions associated with pesticides applied to lawns and shrubbery that lead to toxic stormwater runoff from the property. One of the basic issues that needs to be resolved is whether diazinon and/or chlorpyrifos can be applied to lawns in accord with the label instructions and not have stormwater runoff and fugitive irrigation water transport sufficient OP pesticides to cause stormwater runoff to be toxic. These are areas that must receive a high priority for research support as part of TMDL development.

The implementation of the TMDL-based control program for OP pesticide aquatic life toxicity will likely be based on a phased approach, where the first phase will be based on a somewhat arbitrarily developed percentage control of OP pesticide application. It could readily be found that phase one of a TMDL program for urban pesticide aquatic life toxicity control could involve restricting the use of OP pesticides in residential areas that involves their application to lawns and shrubbery. Phase one could potentially continue to allow the use of the OP pesticides for structural termite and ant control. This approach would preserve most of the urban uses that are made of OP pesticides by commercial applicators. It would, however, likely greatly restrict the outdoor public use on residential properties.

Factors Influencing the Toxicity of OP Pesticides

The approach that is frequently being used today of establishing TMDL goals based on the total concentration of a constituent of concern, ignoring its aqueous environmental chemistry and toxicology, is obviously technically invalid and can be highly wasteful of public and private funds. Further, it can force the substitution of other pesticides, which may cause as much or even greater harm to the environment than the constituents that are being controlled. Lee and Jones-Lee (1997) have discussed the importance of basing TMDL goals on toxic/available forms of constituents, rather than total concentrations. As they discuss, this is especially important in such areas as "pollutant trading." Frequently those developing TMDLs ignore the well-established fact that many of the constituents of concern exist in a variety of forms, only some of which are toxic/available. Lee and Jones-Lee (1996a,b) have discussed the importance of

incorporating at least mid-1990s-level science into developing TMDLs, where appropriate incorporation of aquatic chemistry and toxicology are an integral part of the TMDL process.

With respect to the OP pesticides diazinon and chlorpyrifos, diazinon is well-known to have limited sorption tendencies. While Woodward-Clyde (1996) reported finding diazinon in Alameda County/San Francisco Bay, California area stream sediment samples, it is unclear whether this diazinon is present there through a sorption process or simply a diffusion control process from the overlying waters. The Woodward-Clyde studies reported the diazinon concentration in sediments on a ng/kg sediment basis. What is needed to evaluate this situation is the concentration of diazinon in the interstitial/pore water.

From the limited information available, it appears that while diazinon can be found in stream sediments, its concentrations appear to be below those that have been found to be toxic to benthic organisms such as the amphipod *Gammarus fasciatus*. This organism has been found to be the most sensitive to diazinon and chlorpyrifos toxicity of all freshwater organisms tested.. Since it is possible that aquatic life in urban area stream and other waterbodies could be adversely impacted through diazinon toxicity to benthic organisms, there is need to do studies at various locations in which the interstitial waters of sediments underlying a watercolumn with high concentrations of diazinon are assessed with respect to their toxicity to *Gammarus* and possibly other benthic invertebrates.

Chlorpyrifos is well-known to have substantial sorption tendencies with a log K_{ow} of 5.25 (Ankley *et al.*, 1994). This magnitude of K_{ow} indicates that chlorpyrifos would tend to partition between water and particulate organic carbon. Anderson, *et al.* (1997) reported finding chlorpyrifos in the uppermost reaches of Upper Newport Bay, Orange County, California sediments. This is to be expected, based on the results of the Lee *et al.* (1999b) study of aquatic life toxicity and OP pesticides in the primary tributaries of Upper Newport Bay. They found that chlorpyrifos and a variety of other OP pesticides are consistently present in stormwater runoff to Upper Newport Bay at concentrations that, based on LC₅₀s for *Americamysis bahia (Mysidopsis bahia)*, potentially represent several TUa (acute toxicity units). It appears that the chlorpyrifos present in the tributary waters during stormwater runoff events is sorbed onto particulates in the runoff waters that settle in the upper parts of the Bay.

Ankley *et al.* (1994) have reported that, as expected, chlorpyrifos partitions with particulate organic carbon (TOC) in sediments. This partitioning detoxifies the chlorpyrifos. Ankley *et al.* stated, "Overall, these results suggest that within the range of organic carbon tested in the present study, an equilibrium partitioning model based on organic carbon is appropriate for predicting the bioavailability of sediment-associated chlorpyrifos to benthic invertebrates." While their work was concerned with bedded (deposited) sediment situations, this partitioning would also occur with particulate organic carbon in the watercolumn. The net result is that the total measured concentration in a water sample may be a poor measure of the toxicity of the chlorpyrifos due to sorption reactions, which detoxify chlorpyrifos.

Addressing this issue may not be as simple as using dissolved chlorpyrifos for the chemical measurements, since the particulate organic carbon - TOC can be present in small particles that will pass through a 0.45 : pore-size filter, and therefore appear as "dissolved" chlorpyrifos. This so-called dissolved chlorpyrifos may be appreciably detoxified by colloidal TOC particles. In order to properly evaluate whether chlorpyrifos in a water sample is toxic, it will be necessary to use high-speed centrifugation to pretreat the water sample to remove particulate, including colloidal, forms of TOC.

Another area of concern is whether constituents or characteristics of a water, such as low DO, ammonia, and other non-pesticide toxicants, could significantly influence the toxicity of the OP pesticides. Stressing a sensitive organism through other toxicants could exacerbate the OP pesticide-caused toxicity due to diazinon and chlorpyrifos.

An additional issue of concern is enhanced OP pesticide toxicity due to unknown causes. Dr. Jeff Miller of *Aqua* Science (personal communication, 1998) has indicated that he has found enhanced toxicity of diazinon to *Ceriodaphnia* in certain ambient waters, compared to the toxicity found in standard laboratory waters. It is important to understand that the LC₅₀ values for the OP pesticides, like many other LC₅₀ values, are not unvarying, fixed numbers, but depend on a variety of factors which, at this time, are poorly understood.

Impact of Alternatively Used Pesticides

While there are some who advocate that there is no need to use pesticides in urban areas to control pests, it is unlikely that restrictions on the use of the OP pesticides diazinon and chlorpyrifos will result in the adoption of non-pesticide-based methods of pest control. While such approaches should be supported, it should be realized that restrictions on the use of diazinon and chlorpyrifos will result in substantial use of other pesticides. An important topic in the implementation of a TMDL for OP pesticide-caused aquatic life toxicity is the potential public health and environmental impact of the alternative pesticides that are used as replacements for diazinon and chlorpyrifos. Of particular concern are the pyrethroids and OP pesticides other than diazinon and chlorpyrifos that are being used in substantial amounts in urban and agricultural areas. Some of the pyrethroids and other OP pesticides that are being used in place of diazinon and chlorpyrifos are as toxic to some cladocerans and shrimp as diazinon and chlorpyrifos.

It is important in any aquatic life toxicity studies to measure the total toxicity present in a sample through a dilution series and then estimate from the results of the chemical analyses and the LC_{50} s for diazinon and chlorpyrifos the amount of the toxicity that is likely due to the OP pesticides diazinon and chlorpyrifos. Lee (1999) has provided guidance on the type of monitoring program that should be conducted on urban stormwater runoff to assess the magnitude, cause and significance of OP pesticide-caused aquatic life toxicity. While, in the San Francisco Bay region and in the Central Valley, the urban stormwater runoff toxicity has been found to be due primarily to diazinon and chlorpyrifos, in an urban area in Yorba Linda, Orange County, California in March 1999, the authors (Lee *et al.*, unpublished) found that

the total toxicity to *Ceriodaphnia* was 16 TUa, of which only half could be accounted for by diazinon and chlorpyrifos. It appears that there is an appreciable amount of pesticide(s) used in this urban area other than diazinon or chlorpyrifos.

An issue of concern is that some of the pyrethroids and other OP pesticides are not normally measured in pesticide toxicity studies. In any location where there is a substantial difference between the total toxicity measured through a toxicity test dilution series and the predicted toxicity based on summing the concentrations of diazinon and chlorpyrifos, normalized based on their LC_{50} values, studies need to be done to determine if this unknown toxicity is due to other pesticides such as pyrethroids and unmeasured OP pesticides.

As part of forcing a switch from one type of pesticide to another through restricting the allowed uses by commercial applicators and the public, it will be important to properly evaluate, before the TMDL is implemented and then during implementation, the potential aquatic life, terrestrial life and other impacts of the alternative pesticides that are being used. This evaluation should be an integral part of any properly developed credible TMDL.

Appropriate TMDL Monitoring

The conventional approach of grabbing a sample of stormwater runoff and measuring aquatic life toxicity and the concentrations of diazinon and chlorpyrifos present in the sample is appropriate for establishing that there is a <u>potential</u> aquatic life toxicity problem in the waterbody due to OP pesticide-caused aquatic life toxicity that impairs water quality - beneficial uses of the waterbody. However, in order to determine whether there is a real, significant water quality use impairment associated with the presence of laboratory-measured OP pesticide-caused aquatic life toxicity that should restrict the use of the OP pesticides, it is necessary to conduct a much more sophisticated monitoring program. Of particular concern is a reliable assessment of the magnitude, duration, and areal extent of aquatic life toxicity associated with the stormwater runoff event or fugitive irrigation water.

This will mean that comprehensive, site-specific studies will need to be done in which total toxicity, OP pesticide-caused toxicity, diazinon and chlorpyrifos, as well as other pesticides that have been found in the waters that are potentially toxic will need to be measured before, during, and after a runoff event at a variety of locations in the runoff waters and especially the receiving waters for the runoff. It should never be assumed that a laboratory-based toxicity test result can be directly translated to a field toxicity situation, where measurement of laboratory toxicity is assumed to represent field conditions that are of significance to water quality use impairment. It is important to assess the magnitude of the toxicity and the potential decrease in this magnitude associated with controlling the use of diazinon and chlorpyrifos, as part of TMDL development.

For situations where the stormwater runoff enters a larger waterbody and a toxicity plume is generated, the fate and persistence of the total and OP pesticide-caused toxicity in the plume, as well as

the diazinon, chlorpyrifos, and other pesticides, should be assessed. This will require an assessment of the mixing patterns of the stormwater runoff with the receiving waters, in which the duration of exposure which a planktonic organism would receive to toxic conditions is measured. Lee *et al.* (1999b) have recently conducted studies of this type as part of assessing the impact of OP pesticide-caused aquatic life toxicity present in tributaries to Upper Newport Bay on the beneficial uses of the Bay. These studies showed that there was a limited area near where the primary tributary, San Diego Creek, enters the Bay that showed toxicity to *Mysidopsis* of sufficient magnitude and duration to be potentially adverse to marine zooplankters like Mysidopsis that would migrate into a mixed fresh water/marine water lens that occurs associated with the stormwater runoff event.

With increasing attention being given to managing toxicity in aquatic sediments, consideration should be given not only to the toxicity to water column organisms, but also to benthic organisms, associated with the passage of an OP pesticide-caused toxic plume/pulse. This is an area that has not been addressed thus far.

It is extremely important not to make the mistake of assuming, based on a limited number of measurements, that what is found at one time with respect to the toxicity being accounted for by diazinon and chlorpyrifos is applicable to other times. It is essential that the primary toxicity assessment tools be toxicity tests, and not diazinon and chlorpyrifos concentrations. Season-to-season and year-to-year variability, and especially now with changes in types of pesticides being used in urban areas, could readily cause such assumptions to be in significant error.

The bottom line assessment that should be addressed in an aquatic life toxicity control TMDL monitoring program is whether the numbers, types, and characteristics of desirable forms of aquatic life in a waterbody are being significantly adversely impacted by OP pesticide-caused aquatic life toxicity in urban stormwater runoff. The characteristics of the OP pesticide-caused aquatic life toxicity, where it is restricted to very few types of organisms for short periods of time, mandates that a critical evaluation be made of what laboratory-based toxicity test results mean to beneficial use impairment of the receiving waters for the stormwater runoff. This assessment will likely involve detailed studies of aquatic organism assemblages in areas where toxic pulses of urban stormwater runoff occur due to the OP pesticides diazinon and chlorpyrifos.

Conclusion

Diazinon and chlorpyrifos are useful products to urban dwellers. They are highly toxic to a limited number of types of aquatic life. The water quality-use impairment significance of this toxicity is largely unknown at this time. It is extremely important that TMDLs developed for aquatic life toxicity and diazinon and chlorpyrifos concentration control properly evaluate the real water quality significance of OP pesticide-caused toxicity and the projected and actual improvements in the beneficial uses of urban streams and their receiving waters due to the replacement of diazinon and chlorpyrifos with other pesticides or other non-pesticide-based pest control programs. An Evaluation Monitoring approach of the type developed by

Jones-Lee and Lee (1998) can be used to determine the real, significant water quality impairments associated with OP pesticide-cause aquatic life toxicity.

Additional information on the regulation of OP pesticides is found in Lee *et al.* (1999a,b) and Lee and Jones-Lee (1998). Many of the Lee and Jones-Lee references are available from their web site, www.gfredlee.com.

REFERENCES

Anderson, B.S., Hunt, J.W., Tudor, S., Newman, J., Tjeerdema, R., Fairey, R., Oakden, J., Bretz, C., Wilson, C.J., LaCaro, F., Stephenson, M., Puckett, M., Long, E.R., Fleming, T. and Summers, K. "Chemistry, Toxicity, and Benthic Community Conditions in Sediments of the Southern California Bays and Estuaries," Report to the California State Water Resources Control Board, Environmental Protection Agency, National Oceanic and Atmospheric Administration, California Department of Fish and Game, University of California, Santa Cruz, and the Moss Landing Marine Laboratories, 140 pp. + appendices (1997).

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

Fox, J.C., personal communication to G. Fred Lee, Assistant Administrator, US Environmental Protection Agency, Office of Water, Washington, D.C., May 3 (1999).

Giesy, J.P., Solomon, K.R., Coats, J.R., Dixon, K., Giddings, J., Kenaga, E., "Chlorpyrifos: Ecological Risk Assessment in North American Aquatic Environments," Reviews of Environmental Contamination and Toxicology, <u>160</u>: 1-129, Springer, New York, NY (1999).

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

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

Lee, G.F., "Recommended Aquatic Life Toxicity Testing Program for Urban Stormwater Runoff," Comments submitted to E. Bromley, US EPA Region IX, San Francisco, CA, February (1999). Lee, G.F. and Jones-Lee, A., "Water Quality Issues in Pollutant Trading," Report of G. Fred Lee & Associates, El Macero, CA, February (1996a).

Lee, G.F. and Jones-Lee, A., "Aquatic Chemistry/Toxicology in Watershed-Based Water Quality Management Programs," In: Proc. Watershed '96 National Conference on Watershed Management, Water Environment Federation, Alexandria, VA, pp. 1003-1006 (1996b).

Lee, G.F. and Jones-Lee, A., "Development of TMDLs from Evaluation Monitoring Program Results," Report of G. Fred Lee & Associates, El Macero, CA, May (1997).

Lee, G.F. and Jones-Lee, A., "Development of a Regulatory Approach for OP Pesticide Toxicity to Aquatic Life in Receiving Waters for Urban Stormwater Runoff," Presented at NorCal SETAC meeting, Reno, NV, June (1998).

Lee, G.F., Jones-Lee, A., Taylor, S., and Neiter, D., "Evaluation of the Water Quality Significance of OP Pesticide Toxicity in Tributaries of Upper Newport Bay, Orange County, CA," *Ninth Symposium on Environmental Toxicology and Risk Assessment: Recent Achievements in Environmental Fate and Transport, ASTM STP 1381* (1999a).

Lee, G.F., Taylor, S., and Neiter, D., "Review of Existing Water Quality Characteristics of Upper Newport Bay, Orange County CA and its Watershed and Results of Aquatic Life Toxicity Studies Conducted During 1997-98 in the Upper Newport Bay Watershed," Final Report G. Fred Lee & Associates, Submitted to State Water Resources Control Board, Santa Ana Regional Water Quality Control Board, and Orange County Public Facilities and Resources Department, To Meet the Requirements of the US EPA 205(j) Project, June (1999b).

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

Menconi, M. and Cox, C., "Hazard Assessment of the Insecticide Diazinon to Aquatic Organisms in the Sacramento-San Joaquin River System," California Fish and Game, Pesticide Investigations Unit, Environmental Services Division, Administrative Report 94-2, Rancho Cordova, CA (1994).

Menconi, M. and Paul, A., "Hazard Assessment of the Insecticide Chlorpyrifos to Aquatic Organisms in the Sacramento-San Joaquin River System," Department of Fish and Game, Environmental Services Division, Pesticide Investigations Unit, Administrative Report 94-1, Rancho Cordova, CA (1994).

Miller, J., (personal communication) Aqua Science, Davis, CA (1998).

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

SARWQCB, "Water Quality Control Plan, Santa Ana River Basin," Regional Water Quality Control Board, Santa Ana Region, Riverside, CA (1995).

US EPA, "Quality Criteria for Water 1986," EPA 440/5086-001, US Environmental Protection Agency, Office of Water Regulations and Standards, Washington, D.C. (1987).

US EPA, "Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms. Second Edition," EPA-600-4-91-003, US Environmental Protection Agency, Cincinnati, OH (1991).

University of Wisconsin-Superior and Great Lakes Environmental Center, "Draft Ambient Aquatic Life Water Quality Criteria: Diazinon," prepared for US EPA Office of Water, Washington, DC (1998).

Woodward-Clyde Consultants, "Sediment Diazinon Special Study," Prepared for Alameda Countywide Clean Water Program, Oakland, CA (1996).