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Recommended Aquatic Life Toxicity Testing Program for Urban Stormwater Runoff[1]

February 15, 1999

Eugene Bromley
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Dear Gene:

I am following up on reviewing the draft Riverside County stormwater NPDES permit issued by the US EPA Region IX, where I find a reference to Lee and Taylor (1997) presented as justification for measuring diazinon and chlorpyrifos in urban area stormwater runoff as part of NPDES permit monitoring requirements. Since the release of the Lee and Taylor (1997) report, we have done considerable additional work on this topic in Orange County and, to a limited extent, in the LA area. This work is being presented in a US EPA Region IX 205(j) report. I sent you a preprint draft of our 205(j) report discussion section last November summarizing these results.

In the future, this 205(j) report will be a more appropriate reference for diazinon and chlorpyrifos issues in that it covers not only the 1996 data which were presented in the 1997 report, but also all of the fall 1997 and spring and summer 1998 data. We have recently received initial review comments from Orange County, who is the primary grantee on the 205(j) project that is administered through the Santa Ana Regional Water Quality Control Board. This report is being released for general review as Lee *et al.* (1999a). After receiving the reviewers' comments we will be finalizing this 210-page report, hopefully within a month. I will send you a copy as soon as I have clearance from the County to do so.

While the Lee *et al.* (1999a) report presents a much larger database on *Ceriodaphnia* toxicity and the role of chlorpyrifos and diazinon as a cause of this toxicity to both freshwater and marine organisms, the conclusions are the same as were reported in the Lee and Taylor (1997) and Silverado (1997) initial reports on our Orange County/Upper Newport Bay work. They are also the same as are being found in the San Francisco Bay region (Hansen & Associates, 1995; Katznelson and Mumley, 1997), as well as in the Sacramento area (Larsen, 1998a,b; Larsen *et al.*, 1998; Deanovic *et al.*, 1998a; Larsen *et al.*, 1998). Based on the widespread use of diazinon and chlorpyrifos in urban

[1]Reference as 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).

areas throughout the country, it is likely that the urban stormwater runoff *Ceriodaphnia* toxicity problem that has been found throughout California is a national problem that has not yet been recognized. Waller *et al.* (1995) reported *Ceriodaphnia* toxicity in stormwater runoff in Fort Worth, Texas which was attributed to OP pesticides.

In general, the urban stormwater runoff toxicity testing, while showing high levels of *Ceriodaphnia* toxicity, has been found to be nontoxic to fathead minnow larvae and algae. Therefore, evaluation of the significance of this toxicity should focus on what pulses of toxic waters to certain zooplankton mean to higher trophic level forms of aquatic life of importance to the public.

We also found, as part of our Orange County studies, similar OP pesticide toxicity issues for the set of samples of stormwater runoff that were obtained last March in the LA area (Lee, 1998a). There is no longer any question about diazinon and chlorpyrifos causing urban stormwater runoff to be highly toxic to *Ceriodaphnia* and mysids. In many areas the toxicity is due to diazinon and chlorpyrifos. In some areas, such as the San Francisco Bay region, it appears to be primarily due to diazinon. In the Orange County stormwater runoff there are other unknown constituents causing this toxicity as well. This runoff, however, contains drainage from nurseries, agricultural areas and urban areas.

An aspect of this situation is that diazinon is not toxic to *Mysidopsis* except at concentrations well above those being found in urban stormwater runoff. However, chlorpyrifos is highly toxic to this marine zooplankton. Further, the unknown caused toxicity to the stormwater runoff to Upper Newport Bay is also highly toxic to *Mysidopsis*. As discussed in our reports (Lee and Jones-Lee, 1998; Lee *et al.,* 1999a,b), the issue that needs to be resolved is what this toxicity means to the designated beneficial uses of the receiving waters for the urban stormwater runoff. It is unclear that this toxicity represents a significant adverse impact to the beneficial uses of these waters. Novartis, (1997) and Giesy *et al.* (1997) have presented risk assessments which purport to show that the OP pesticide toxicity to zooplankton is of limited impact on the aquatic life related beneficial uses of waterbodies. De Vlaming (1995), Grothe *et al.* (1996), and De Vlaming and Norberg-King (1999) have reported high correlations between aquatic life testing results similar to those that are showing OP pesticide toxicity in urban stormwater runoff and impacts on the aquatic life related beneficial uses of the waterbodies. However, the study conditions where there is a relationship between US EPA standard three species toxicity test results and water quality impacts in the receiving waters for wastewater discharges did not involve short-term pulse toxicity, of the type being found in urban stormwater runoff, to selected zooplankton. These issues are discussed in our 1999 205(j) report.

In addition to providing you with updated information on our Orange County/Upper Newport Bay studies, my primary purpose in contacting you is to indicate that the US EPA Region IX should be requiring that urban stormwater runoff water quality management agencies not only analyze for diazinon and chlorpyrifos, but also the US EPA Region IX and, for that matter, nationally should be requiring that NPDES-permitted urban area stormwater runoff be monitored for *Ceriodaphnia* toxicity for stormwater discharges to freshwater. For urban stormwater discharges to marine waters, either through a short freshwater channel or directly, measurements of *Ceriodaphnia* toxicity and *Mysidopsis* toxicity in which the test waters used for mysid testing have the salt content of the freshwater stormwater runoff raised to 20 ppt by the addition of a standard sea salt mixture should be conducted.

Please find attached a recommended stormwater runoff aquatic life toxicity monitoring program that I feel should be conducted by all NPDES permitted urban stormwater quality management agencies. While this program evolved out of the work that I have been doing in Orange County over the past three years, it is similar to what is being done by others studying urban area stormwater runoff aquatic life toxicity. A number of individuals involved in these types of studies have reviewed and commented on this recommended program.

In summary, it is recommended that the US EPA Region IX and each of the California Regional Water Quality Control Boards require, as part of the monitoring program in the NPDES stormwater runoff permits, that all permittees measure diazinon with the detection limit of 30 ng/L, and chlorpyrifos with the detection limit of 50 ng/L. Also, total *Ceriodaphnia* toxicity should be measured on all samples and for samples being discharged to marine waters. *Mysidopsis* toxicity using a standard sea salt mixture to bring the salinity to 20 ppt should be conducted.

In addition to determining whether the stormwater runoff is toxic, there is need to assess the magnitude of the toxicity. Further, a limited scope directed TIE should be conducted to determine if the toxicity is likely due to OP pesticides (Bailey *et al.*, 1996; Deanovic *et al.*, 1998b; Lee and Taylor, 1997; Lee *et al.*, 1999a). Aquatic life toxicity testing of stormwater runoff should be conducted as part of an Evaluation Monitoring program of the type described by Jones-Lee and Lee (1998) to determine the real significant water quality problems associated with urban area and highway stormwater runoff.

Adoption of this program will, within a couple of years, develop the database needed to determine the magnitude of the OP pesticide stormwater runoff toxicity problem and begin to meaningfully address its potential water quality significance.

If you wish additional information on any aspect of these recommendations, I suggest you contact Dr. Val Connor (Ph: 916-255-3111) or Dr. Chris Foe (Ph: 916-255-3113), both of the Central Valley Regional Water Quality Control Board; Dr. Victor deVlaming (Ph: 916-657-0795); Dr. Jeff Miller (Ph: 916-753-5456), *Aqua*Science; Dr. Scott Ogle (Ph: 925-313-8080), Pacific Eco-Risk; or Linda Deanovic (Ph: 530-752-0772), UCD Aquatic Toxicology Lab.

If you or others have questions about it, or would like further information, please contact me.

Sincerely yours,

G. Fred Lee

G. Fred Lee, PhD, DEE

Recommended Urban Stormwater Runoff OP Pesticide Toxicity Monitoring Program

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February 1999

Presented below is a recommended urban area stormwater runoff aquatic life toxicity monitoring program.

Monitoring for Aquatic Life Toxicity

Urban stormwater runoff should be monitored using standard US EPA aquatic life toxicity testing procedures (Lewis *et al.*, 1994; US EPA, 1994, 1995). These procedures have been used at the University of California, Davis, the Central Valley Regional Water Quality Control Board for *Ceriodaphnia* testing, and at Pacific Eco-Risk Laboratories, Martinez, California, for mysid toxicity testing for urban stormwater runoff. The application of these procedures to urban stormwater runoff have been described by Neiter and Lee, (1998) in the Upper Newport Bay 205(j) Quality Assurance Project Plan. Additional information on these procedures is provided by Bailey *et al.* (1996), Deanovic *et al.* (1998b), and Foe *et al.* (1998). The Lee *et al.* (1999a) Upper Newport Bay study QAP Plan consists primarily of the University of California, Davis procedures for *Ceriodaphnia* testing and the Pacific Eco-Risk Laboratories procedures for mysid testing. These plans have been reviewed and approved by the US EPA Region IX.

Use Adequate Sensitivity for OP Pesticide Measurement

It is important to measure diazinon and chlorpyrifos with adequate sensitivity to detect their presence at potentially toxic levels. The University of California, Davis Aquatic Toxicology Laboratory has been using ELISA procedures which have a detection limit for diazinon of about 30 ng/L and for chlorpyrifos of about 50 ng/L. Occasionally, split samples between laboratories have been analyzed where reasonably good agreement between two different labs, sometimes using different ELISA testing reagents and reagent sources, has been obtained. Also, good agreement has been achieved with an independent dual column GC analysis conducted by Appl Lab, Fresno, CA. Appl is using standard US EPA 8141 Special Low-Level gas chromatographic procedures with an increased evaporation step in order to achieve higher sensitivity.

Assessment of Total Toxic Units and OP Pesticide Toxicity

In addition to measuring total toxicity to *Ceriodaphnia* and mysids, where toxicity is found, a dilution series with or without piperonyl butoxide (PBO) should be conducted (Bailey *et al*, 1996; Deanovic *et al.*, 1998b; Lee and Taylor, 1997; Lee *et al.*, 1999a; Foe *et al.*, 1998). This additional toxicity testing determines the magnitude of the toxicity, i.e. how many toxic units are present and whether the toxicity is likely due to an organophosphate pesticide (diazinon or chlorpyrifos). A dilution series consisting of 100%, 50%, 33%, 25%, 20%, 16.6%, 12.5% and, for highly toxic samples, 6.25% of the stormwater runoff should be tested. These tests should be run with and without PBO at 100 µg/L. The inclusion of PBO in some of the test samples is part of a directed TIE procedure designed to determine whether the toxicity found is likely due to an OP pesticide.

There are a number of commercial laboratories that can reliably conduct aquatic life toxicity testing. In addition to using the University of California, Davis Aquatic Toxicology Lab in the Upper Newport Bay studies, Lee *et al.* (1999a) has been using Pacific Eco-Risk of Martinez, California (Scott Ogle) and *Aqua*Science of Davis, California (Jeff Miller).

Seasonal Sampling

The stormwater sampling should be done for the first significant (>0.3 inch) rainfall event of the fall at the point where the stormwater runoff enters the receiving waters of concern. In addition, it is desirable to have a mid-winter sample and especially a late spring sample. If there is a base flow of water into the receiving waters during non-runoff events, then dry weather flow samples should be taken during the summer and fall/winter.

It is also recommended that at least for the fall stormwater runoff sample, toxicity testing be done using fathead minnow larvae and algae following the US EPA procedures of Lewis *et al.* (1994).

Identification of the Source of Toxicity

If toxicity is found, then a forensic (Toxicity Reduction Evaluation, TRE) study should be conducted through the use of a combination of toxicity measurements and chemical analyses to determine the source of the toxicity within the watershed. Lee *et al.* (1999a) provide an example of this approach. While the urban stormwater runoff *Ceriodaphnia* toxicity appears in many areas to be due to the residential use of diazinon and chlorpyrifos, there can also be other significant sources of OP pesticides and *Ceriodaphnia* toxicity. For example, in the Lee *et al.* (1999a) work in Orange County, it was found that commercial nurseries located in the Upper Newport Bay/San Diego Creek watershed are major sources of diazinon and unknown-caused toxicity.

Based on the work of Scanlin (1997) and Lee (1998b), it has been found that the use of OP pesticides in accord with the registration label causes stormwater and fugitive water runoff from residential properties to be toxic to *Ceriodaphnia*. There can be little doubt that the use of these OP pesticides on lawns and residential shrubbery can lead to stormwater runoff *Ceriodaphnia* toxicity. An issue that needs to be addressed is whether the use of these and other pesticides for termite and ant control, where the pesticides are injected below the surface, leads to stormwater and fugitive water runoff *Ceriodaphnia* toxicity. This is an area that needs attention as part of developing a regulatory program for the OP pesticide *Ceriodaphnia* toxicity.

Thus far, the work on OP pesticide caused toxicity has focused on diazinon and chlorpyrifos. There are other OP pesticides used in residential areas for structural pest control that could be responsible for part of the *Ceriodaphnia* toxicity. For example, approximately 8,000 pounds of propetamphos was used in Orange County in 1990 for residential structural pest control. Propetamphos is an OP pesticide that can only be used by commercial applicators. The ELISA testing procedures, as well as the gas chromatographic procedures normally used, do not detect the presence of this pesticide.

If four or more units of unknown (cannot be accounted for based on the use of PBO and ELISA testing) caused toxicity are found in the samples, then US EPA Toxicity Identification Evaluation (TIE) procedures should be followed to determine the cause of this toxicity (US EPA, 1989a,b, 1991, 1992; Deanovic *et al.*, 1998b; Foe *et al.*, 1998). It may be necessary to use some of the new TIE techniques, such as Miller *et al.* (1997), and Kuivila and Crepau (1999) to identify the cause of the *Ceriodaphnia* toxicity. It is possible, as found in our Orange County studies, that standard TIEs may not be able to determine the specific chemicals responsible for the toxicity. Under these conditions it is appropriate to use forensic studies to determine the source of the unknown caused toxicity in the watershed. This could lead to control programs without having to spend large amounts of money in Phase IV TIEs determining the cause of the toxicity.

Agriculture as a Source of Urban Pesticides

While urban use of diazinon and chlorpyrifos for residential structural and lawn and garden pest control appears to be the primary source of diazinon and chlorpyrifos toxicity in urban stormwater runoff (Scanlin, 1997), there can be situations such as those reported by Connor (1995) where agriculturally applied diazinon can cause rainfall and fogfall to be toxic to *Ceriodaphnia* at considerable distances from the point of application. This is the result of airborne transport of this pesticide associated with its use in the winter as a dormant spray in orchards. Also, upstream agricultural uses of diazinon and chlorpyrifos can cause *Ceriodaphnia* toxicity (Foe, 1995; Kuivila, 1993; Kuivila and Foe, 1995; USGS, 1993; Deanovic *et al.*, 1998a; Foe *et al.*, 1998; Panshin *et al.*, 1998).

Assessing the Water Quality Significance of the OP Pesticide Toxicity

In addition to determining if the stormwater runoff is toxic as it enters the receiving water, there is need to determine the fate of this toxicity in the receiving waters for the stormwater runoff. Site-specific receiving water studies should be conducted to determine the magnitude, areal extent, and persistence of chlorpyrifos, diazinon and total toxicity in these waters (Lee and Taylor, 1997; Lee *et al.*, 1999a). This information is essential to assessing whether the OP pesticide toxicity found in urban stormwater runoff is significantly adverse to the designated beneficial uses of the receiving waters for the stormwater runoff.

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