Recommended Pesticide-Caused Aquatic Life Toxicity Monitoring[1]

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Presented below is a recommended approach for monitoring waterbodies for pesticide-caused aquatic life toxicity. It is based on the experience of the authors in conducting and reviewing the aquatic life toxicity studies of others over the past 10 years.

Dormant Pesticide Applications

One of the issues of concern regarding pesticide runoff monitoring is the application of dormant-spray pesticides to orchards just prior to major stormwater runoff events. In order to adequately monitor for potential discharges from dormant-spray applications, there is need to develop a technically valid approach for determining worst-case water quality objective violations due to the use of these pesticides. Agricultural interests will likely be able to control stormwater runoff of these pesticides during low to moderate runoff events. However, as Lee (2005a) indicated in his comments on the draft DPR-proposed regulations governing dormant application of the OP pesticides, there will be runoff events associated with large storms when violations of the pesticide TMDL goal will likely occur following application. It is under such conditions that there is the greatest potential for high concentrations of OP and other pesticides to be present in runoff from fields, even when the DPR-proposed required application restrictions are followed. A technically valid assessment of pesticide-caused aquatic life toxicity should specifically include monitoring immediately after major runoff events when there is the greatest likelihood of pesticide-caused aquatic life toxicity in ambient waters.

Non-Dormant Applications

The runoff/discharges following application of chlorpyrifos and/or other pesticides in the spring, summer and fall should be monitored to determine whether violations of the chlorpyrifos water quality objective occur. As part of developing the application protocol for non-dormant pesticides, an examination should be made of the conditions that have in the past led to aquatic life toxicity. The monitoring regimen should include periodic examination of how pesticides are being used in the watershed of the waterbody that is being monitored. This information should be used to guide the monitoring program.

Monitoring Methodology

The aquatic life toxicity/pesticide monitoring should include determination of the total amount of aquatic life toxicity measured in a sample and how much of that toxicity can be accounted for based on the concentrations of diazinon and chlorpyrifos found in the sample. This type of monitoring was used by Lee and his associates in stormwater runoff monitoring studies conducted in the mid-to-late-1990's in the Upper Newport Bay (Orange County, California) for the Santa Ana Regional Water Quality Control Board. Reports on those studies are available at http://www.gfredlee.com/punbay2.htm. These

[1] Reference as Lee, G. F., Jones-Lee, A., "Recommended Pesticide-Caused Aquatic Life Toxicity Monitoring," Submitted to the Central Valley Regional Water Quality Control Board, Rancho Cordova, CA November (2005).

interactive studies involved working closely with the laboratory that was doing the toxicity testing to determine the total toxicity in the sample; when a sample showed enough toxicity to kill several of the test organisms in one to two days, the study plan called for follow up testing on that sample.

Aquatic life toxicity/pesticide monitoring should incorporate a requirement that for each sample that shows potentially significant short-term toxicity, a fairly complete GC or other reliable method analysis of the sample be conducted to determine the amounts of the OP pesticide and carbamate pesticides present in the sample. With that information and by conducting additional toxicity testing on a refrigerated stored sample of the water of concern in a dilution series with and without piperonyl butoxide (PBO) at 100 µg/L, it is possible to determine how much of the toxicity may be caused by the OP pesticides (diazinon and chlorpyrifos). The inclusion of PBO in some of the test samples is part of a directed toxicity identification evaluation (TIE) procedure designed to determine whether the toxicity found is likely due to an OP pesticide. The recommended approach can save considerable funds in conducting TIEs in determining the potential role of OP and pyrethroid-based pesticides as a cause of aquatic life toxicity in the water column and sediments. It also identifies those situations where the water column and/or sediments are toxic due to substances that are not OP or pyrethroid-based pesticides.

If there are elevated concentrations of potentially toxic heavy metals relative to US EPA water quality criteria, their toxicity can be evaluated through the addition of EDTA to the water column sample. If some/all of the toxicity disappears upon the addition of EDTA, it is likely that one or more of the heavy metals is the cause of at least some of the toxicity found in the sample. This approach was used by Lee and Taylor (2001a) to find that the heavy metals in urban and rural stormwater runoff from the Upper Newport Bay watershed were not the cause of the aquatic life toxicity found in this runoff.

It is important to measure diazinon and chlorpyrifos concentrations with adequate sensitivity to detect their presence at potentially toxic levels considering the additive toxicity of diazinon and chlorpyrifos and other OP and carbamate pesticides. The US EPA 8141 Special Low-Level gas chromatographic procedures, with an increased evaporation step in order to achieve higher sensitivity, can be used for this purpose. The University of California, Davis, Aquatic Toxicology Laboratory has been using ELISA procedures which have a lower detection limit for diazinon of about 30 ng/L and for chlorpyrifos of about 50 ng/L.

Through a sample dilution series (e.g., 100%, 50%, 33%, 25%, 20%, 16.6%, 12.5% and, for highly toxic samples, 6.25%), it should be possible to detect whether pyrethroid pesticides present in the sample are contributing to the aquatic life toxicity in the sample. Use of this approach in the Orange County Upper Newport Bay studies revealed that there was a substantial amount of toxicity caused by unmeasured/unidentified chemicals or conditions that needed to be addressed through further TIE studies (Lee and Taylor, 2001b).

The US EPA methods (US EPA, 2002a,b,c) should be used for the toxicity testing done using *Ceriodaphnia* and for some samples, fathead minnow larva. For samples that could involve discharges to marine/estuarine waters, the toxicity testing should be conducted with mysids after adjusting the salinity of the freshwater to 20 parts per thousand using sodium chloride.

Sediment Toxicity

Some pesticides, such as the pyrethroid-based pesticides, tend to sorb strongly to sediments. This results in water column toxicity and sediment toxicity. The pesticide aquatic life toxicity monitoring should include sediment toxicity testing using the US EPA (2002d) procedure with *Hyalella azteca* as the test organism. Only the acute testing procedure should be conducted since the chronic testing procedure has been found by Weston (2005) to be unreliable.

The studies by Weston et al. (2004, 2005) have demonstrated that pyrethroid-based pesticides can cause aquatic life toxicity in sediments of waterbodies receiving runoff/discharges from areas receiving pyrethroid-based pesticides. They have established LC50 values for several pyrethroid-based pesticides in aquatic sediments. These values can be used to determine if the toxicity in a sediment is likely caused by pyrethroid-based pesticides. Weston et al. (2004) have found that the toxicity of pyrethroid-based pesticides is dependent on the total organic carbon (TOC), with sediments with higher TOC being less toxic.

Lee (2005b) has reviewed the development of TIEs for pyrethroid-based pesticides in sediments. Then and now, definitive TIEs are not available for identification of pyrethroid-based pesticide aquatic life toxicity in sediments. The complexity of the aquatic chemistry of pyrethroid-based pesticides in sediments makes it very difficult to develop reliable TIEs to determine the cause of aquatic life toxicity in sediments.

Gan et al. (2005) have recently presented a summary of studies on the bioavailability of pyrethroid-based pesticides associated with aquatic sediments. They have shown, as expected, that those pesticides that are attached to sediment particles are not toxic – non-bioavailable. They also reported – again, as expected – that the amount of TOC in sediments influences the toxicity of pyrethroid-based pesticides, with higher TOC leading to less bioavailable pesticides – less toxicity. They also found that the amount of dissolved organic carbon (DOC) in a water sample impacts the water column toxicity of pyrethroid-based pesticides. There is an interaction between DOC and pyrethroid-based pesticides that causes the pesticides to be less toxic.

The results of Gan et al. (2005) for the pyrethroid-based pesticides are similar to the results of Ankley et al. (1994) for the OP pesticides, diazinon and chlorpyrifos. As with many organics, particulate TOC in sediments sorbs the organics, resulting in their being non-bioavailable-non toxic. Since the determination of the bioavailable forms of a pesticide is not readily accomplished, this situation means that the toxicity tests will need to be the primary basis for regulating those pesticides and, for that matter, other organics that can cause toxicity to aquatic life in aquatic sediments. Because of the complexity of the aquatic chemistry of pyrethroid-based pesticides in aquatic sediments, it will not likely be possible to use chemical analysis to reliably regulate the pesticides that cause aquatic life toxicity in sediments.

Pyrethroid Toxicity in the Water Column

While the current focus of pyrethroid-based pesticides is sediment toxicity, these pesticides can also cause toxicity in the water column. Lee and Taylor (2001b) found evidence for pyrethroid-based pesticide toxicity in the Upper Newport Bay (Orange County, CA) watershed stormwater runoff studies. The Gan et al (2005) studies support that pyrethroid-based pesticides can be the cause of water column aquatic life toxicity.

Identifying the Cause of Sediment Toxicity

There may be situations, such as those encountered in the Upper Newport Bay watershed stormwater runoff studies of Lee and Taylor (2001b), where it is not possible to identify the cause of aquatic life toxicity through chemical analysis and LC 50 data and/or TIEs. Under these conditions it may be possible to use a forensic approach of conducting toxicity testing upstream of the monitoring station where toxicity was found to determine the source of the toxicity. The forensic approach can lead to determining the source of the toxicity, which, through knowledge of the pesticides used in the source area, can identify the cause of the toxicity.

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