Stormwater Runoff Water Quality Newsletter
Devoted to Urban/Rural Stormwater Runoff
Water Quality Management Issues

* * * * *

Volume 8 Number 6
November 11, 2005

Editor: Anne Jones-Lee, PhD
Contributor to this Issue:
G. Fred Lee, PhD, PE, DEE

* * * * *

This issue of the Stormwater Runoff Water Quality Newsletter is devoted to providing updated information **on the regulation of pesticides which, in stormwater runoff from urban and agricultural areas, cause aquatic life toxicity**.

As mentioned in Newsletter 8-5, the September/October 2005 issue of *Stormwater* contains an article, **"Urban Stormwater Runoff Aquatic Life Toxicity: An Update – Regulating Pesticides,"** by Lee and Jones-Lee (2005a). This article is adapted from NL 8-1/2, February 2005 (Lee 2005a), and is a followup to Lee (2001a), which was published in *Stormwater* 2(1):68-71 January/February 2001. Since the publication of NL 8-1/2, new information has been developed on pesticide-caused aquatic life toxicity that is pertinent to regulating the use of pesticides that cause toxicity in stormwater runoff from urban and agricultural areas where they are applied. A summary of the new information on pesticide-caused aquatic life toxicity is presented in this Newsletter.

San Joaquin River CVRWQCB TMDL Basin Plan Amendment for OP Pesticides

In late October 2005 the California Central Valley Regional Water Quality Control Board (CVRWQCB) adopted a Basin Plan Amendment for the development of a TMDL to control diazinon- and chlorpyrifos-caused aquatic life toxicity in the San Joaquin River. This river drains part of the central Sierra-Nevada Mountains through the northern San Joaquin Valley. This valley is a highly productive agricultural area, where various pesticides are used extensively for crop production. The CVRWQCB regulates water quality through a Basin Plan, which contains water quality standards (objectives) adopted by the Board. The current Basin Plan is located at http://www.waterboards.ca.gov/centralvalley/available_documents/#anchor616381.

One of the CVRWQCB Basin Plan objectives is a narrative objective which requires that the State's waters under the jurisdiction of this Board (the Central Valley) be free of aquatic life toxicity. This Basin Plan also requires that pesticide-caused aquatic life toxicity not occur in the water column or sediments. It has been known since the early 1990s, through the work of the Board staff (principally, Dr. Chris Foe and Dr. Val Connor), that Central Valley rivers and streams contain aquatic life toxicity that is derived from agricultural stormwater runoff and irrigation tailwater discharges. Further, it has been known throughout this period that urban stormwater runoff was also toxic to some forms of aquatic life. This toxicity has been known to be caused by the organophosphorus (OP) pesticides diazinon and chlorpyrifos used for pest control in agricultural and urban areas. This toxicity caused the CVRWQCB to list the Sacramento and San Joaquin Rivers, and some other waterbodies in the Central Valley, as Clean Water Act (CWA) 303(d) "impaired" as a result of violating the Board's narrative "no aquatic life toxicity" objective.

The OP pesticide-caused toxicity in the Central Valley waterbodies was detected through the use of the US EPA standard three-species toxicity test (US EPA 2002), where toxicity was manifested to *Ceriodaphnia dubia*, a freshwater zooplankton. The OP pesticides, at the concentrations being found, are not toxic to fish, algae and some other forms of zooplankton. The concern about this toxicity to *Ceriodaphnia* is that zooplankters are an important component of larval fish food, and, therefore, a decline in their population could be adverse to fish populations. While it is possible that other zooplankters that are not impacted by OP pesticides are present in sufficient numbers to support the larval fish populations in a waterbody, the CVRWQCB Basin Plan objective of "no toxicity" requires that the *Ceriodaphnia* toxicity be controlled.

Over the past few years the Board staff have been developing the information needed to formulate and begin to implement a total maximum daily load (TMDL) for the OP pesticides diazinon and chlorpyrifos. In 2003 the Board adopted a Diazinon TMDL for the Sacramento and Feather Rivers. In October 2005 the Board adopted a Diazinon and Chlorpyrifos TMDL for the San Joaquin River. In order to implement these TMDLs there is need to adopt a Basin Plan Amendment which becomes the legal basis for restricting loads of these pesticides to the 303(d)-listed waterbodies named in the TMDL. These TMDLs,

Sacramento and Feather Rivers Diazinon TMDL and Basin Plan Amendment

San Joaquin River Diazinon and Chlorpyrifos TMDL,

are available at

http://www.waterboards.ca.gov/centralvalley/programs/tmdl/index.htm#Projects

http://www.waterboards.ca.gov/centralvalley/programs/tmdl/sjrop/index.html

The CVRWQCB staff are also developing an OP pesticide TMDL for the Sacramento-San Joaquin Delta, which receives discharges from both the Sacramento and San Joaquin Rivers. As part of developing a Basin Plan Amendment for these TMDLs, the Board staff have developed comprehensive reports, which provide the technical background that supports the need for a TMDL to control aquatic life toxicity due to these pesticides in the listed waterbodies. The above URLs provide links to the staff reports on the OP pesticide TMDLs.

As discussed in previous newsletters (NL 8-1/2), other California Regional Water Quality Control Boards have also found OP pesticide-caused aquatic life toxicity in agricultural and urban area waterbodies. This has led to the other Regional Boards' also developing TMDLs to control this toxicity.

OP Pesticide Water Quality Objectives. In order to evaluate whether a potentially toxic chemical, such as diazinon or chlorpyrifos, is causing toxicity to aquatic life that occurs at concentrations below the concentration that causes toxicity in the standard toxicity test, it is necessary to develop a water quality standard (objective) that, if exceeded, will indicate that aquatic life toxicity is likely occurring below the sensitivity of the toxicity test. As part of developing the SJR OP pesticide TMDL Basin Plan Amendment, the CVRWQCB did not adopt a new water quality objective for diazinon. Instead, they adopted guideline values of 0.16 µg/L 1-hour average (acute) and 0.10 µg/L 4-day average (chronic), not to be exceeded more than once in a three-year period. These values are to be used to interpret the "no toxicity" narrative objective for diazinon. For chlorpyrifos, the CVRWQCB adopted new objectives derived using the US EPA method for water quality criteria development and applied to a dataset screened by the California Department of Fish and Game (CDFG). The new objectives for chlorpyrifos are 0.025 µg/L 1-hour average (acute) and 0.015 µg/L 4-day average (chronic), not to be exceeded more than once in a three-year period. The diazinon guidelines are based on the revised CDFG recommendations. These guidelines are about twice the original values recommended by CDFG, mentioned in previous Newsletters. This revision relates to the finding that one of the sources of information that was used to develop the original recommended diazinon objectives has been found to contain questionable data.

These guidelines/objectives serve as the primary basis for the implementation of the OP pesticide TMDL through serving as the TMDL target. Concentrations above these values represent violations of the Basin Plan, which require implementation of control programs to prevent further violations.

In developing the Basin Plan Amendment, in accordance with the existing Basin Plan the CVRWQCB adopted an implementation approach which assumes that the normalized toxicity of these pesticides (diazinon and chlorpyrifos) is additive. This additivity has been repeatedly demonstrated. The normalization factor is the water quality objective (guideline) for the pesticide. Further information on this approach is available in the Basin Plan at the URL cited above.

Inadequate TMDL Compliance Monitoring. As part of adopting a TMDL into the Basin Plan, California water quality management regulations require that an implementation plan be developed, which describes how the TMDL will be implemented. Lee (2005b) and Jennings (2005) have both found that the CVRWQCB's proposed approach for implementing the SJR OP pesticide TMDL is significantly deficient with respect to providing detailed definitive information on the TMDL compliance monitoring program that will be used by the Board to determine if compliance with the TMDL requirements is being achieved. Rather than providing definitive information on the monitoring program that will be implemented to evaluate compliance with the TMDL requirements, the CVRWQCB adopted an approach that ties the compliance monitoring to the yet-to-be-developed monitoring associated with the waivers of Waste Discharge Requirements for discharges from irrigated lands (Ag Waiver monitoring).

The state of California water quality management regulations (the Porter-Cologne Water Quality Control Act, http://www.swrcb.ca.gov/water_laws/docs/portercologne.pdf) require that all waste discharges that cause an impairment of the beneficial uses of the State's waters be controlled. Exceedance of a water quality objective is defined to be an impairment of the beneficial uses of the State's waters. The requirement that no discharge cause violations of water quality objectives applies to nonpoint source discharges, such as stormwater runoff and tailwater discharges from irrigated agriculture. Discharges from these areas can be regulated under Porter-Cologne waste discharge requirements (WDRs). For many years, agricultural stormwater runoff/tailwater discharges' compliance with WDRs was waived (Ag Waiver). In July 2003 the CVRWQCB adopted Resolution R5-2003-0105, "Conditional Waivers of Waste Discharge Requirements for Discharges From Irrigated Lands Within the Central Valley Region" and associated Monitoring and Reporting Programs (MRPs). Information on the original, current and

proposed revision of the regulatory requirements covering discharges from irrigated lands is available at
http://www.waterboards.ca.gov/centralvalley/programs/irrigated_lands/index.html#Downloads

A key component of the current Ag Waiver water quality monitoring program is the requirement that agricultural interests monitor waters receiving stormwater runoff and tailwater discharges from their lands for aquatic life toxicity. Of particular concern is toxicity caused by pesticides, such as diazinon and chlorpyrifos, used on agricultural lands. At this time the aquatic life toxicity monitoring program that is being implemented under the Ag Waiver program is a greatly abbreviated program compared to that needed to adequately and reliably monitor the State's waters for aquatic life toxicity due to pesticides used on agricultural lands. Agricultural interests are resisting conducting such monitoring programs.

Therefore, as Lee and Jones-Lee (2005b) have discussed, there are many questions about the adequacy and reliability of the OP pesticide and other pesticide aquatic life toxicity water quality monitoring programs that are now and will likely in the future be conducted under the Ag Waiver program. It will likely be many years before a credible aquatic life toxicity monitoring program is fully implemented under the CVRWQCB Ag Waiver program. Lee and Jones-Lee (2005b) recommend that the State Water Resources Control Board (SWRCB) require that the CVRWQCB develop details of the SJR OP pesticide TMDL compliance monitoring that can be implemented in the near term. If and when the Ag Waiver monitoring program becomes credible for detecting and managing pesticide-caused aquatic life toxicity in the SJR watershed, then the SJR OP pesticide TMDL compliance monitoring can be coordinated with the Ag Waiver monitoring.

As part of developing their comments on the deficiencies in the currently proposed Ag Waiver water quality monitoring program, Lee and Jones-Lee (2005c) have developed recommended guidance on the type of monitoring that should be used to detect aquatic life toxicity in a waterbody and to readily discern whether the OP pesticides are likely responsible for this toxicity. This recommended monitoring approach is appended to this Newsletter.

Pyrethroid Pesticides as a Cause of Aquatic Life Toxicity
One of the issues of particular concern in developing TMDLs for OP pesticide-caused aquatic life toxicity is the potential for replacement pesticides to cause aquatic life toxicity. As discussed in NL 8-1/2, pyrethroid-based pesticides are replacing OP-based pesticides for pest control in both urban and agricultural areas. It should be noted, however, that the pyrethroid-based pesticides are not new pesticides; they have been used for many years. The studies of Lee and Taylor (2001) in the Upper Newport Bay (Orange County, CA) watershed that were conducted in the late 1990s found strong evidence for pyrethroid-based pesticides' causing aquatic life toxicity in urban and agricultural area streams in this watershed.

Weston et al. (2004) have found that some Central Valley waterbody sediments receiving agricultural stormwater runoff and tailwater discharges are toxic to *Hyalella azteca*. *Hyalella azteca* is one of the US EPA (2000) standard test organisms for assessing sediment toxicity. Lee (2005a) predicted, based on the current type of pesticide use in urban areas, that urban stream sediments could be toxic to *Hyalella* due to the accumulation of pyrethroid-based pesticides in these sediments. Weston et al. (2005) will soon publish a paper that reports on finding urban stream sediments to be toxic to *Hyalella*, apparently due to the pyrethroid-based pesticides. Weston et al. (2005) took samples of urban creek sediments from creeks that drain residential areas in Roseville, California. They found that nearly all of the sediments were toxic to *Hyalella*, with about half of the samples causing complete mortality under the test conditions. The toxicity found by Weston et al. (2005) was apparently due to pyrethroid-based pesticides that had accumulated in the sediments, with bifenthrin as the primary cause. They also reported that cyfluthrin and cypermethrin likely contributed to the sediment toxicity.

The *Hyalella* toxicity that has been found in Central Valley waterbody sediments impacted by pesticide use in urban and agricultural areas is a violation of the CVRWQCB Basin Plan requirements for control of pesticide-caused aquatic life toxicity. This situation should lead to the CVRWQCB's listing those waterbodies where this toxicity has been found as Clean Water Act 303(d) "impaired," which will require the development of a TMDL to control the use of pyrethroid-based pesticides that cause sediment toxicity in waters of the State. Therefore, it is now clear that the restriction/reductions of the use of OP pesticides in urban and agricultural areas had led to pyrethroid-based pesticides' causing aquatic life toxicity in stormwater runoff from areas that have received these pesticides in the receiving waters' water column at the time of runoff, and in the sediments following runoff events.

An example of inadequate OP pesticide TMDL compliance monitoring is the situation where the CVRWQCB is not requiring that the city of Sacramento monitor for sediment toxicity as part of the city's stormwater NPDES permit even though pyrethroid pesticides have been used in the Sacramento area for several years as replacements for the formerly used OP pesticides. This issue was reviewed in NL 8-1/2.

Pelagic Organism Decline (POD) in the Delta

Recently, it has been found that the Sacramento-San Joaquin River Delta has experienced a significant decline in the numbers of pelagic organisms. Of concern are small fish, some of which are on the endangered species list. It has also been found that there have been significant decreases in the numbers of zooplankton that are considered important sources of larval fish food in the Delta. This situation has been reviewed by Weiser (2005). Because of the importance of the Delta ecosystem as a large freshwater estuary, various state and federal agencies responsible for managing fisheries have organized a study program to investigate the potential cause of the POD.

One of the issues of concern is the potential for pyrethroid-based pesticides that are used in agricultural and urban areas within the Delta to cause aquatic life toxicity to fish and zooplankton. A limited-scope aquatic life toxicity monitoring program was conducted at selected locations in the Delta during the summer of 2005. The data from this program have not yet been made available. Those responsible for conducting this program are planning a large-scale monitoring program, which would begin in 2006. The public will soon have an opportunity to review the results of the summer 2005 studies and the proposed 2006 studies. The reports and proposed workplan will likely be posted on the California Bay-Delta Authority's website, http://science.calwater.ca.gov/. Information on a meeting to review the current POD issues is available at http://calwater.ca.gov/.

One of the reasons for singling out the pyrethroid-based pesticides as a possible cause of the decline of pelagic organisms in the Delta is that pyrethroid-based pesticides are highly toxic to zooplankton and fish. The OP pesticides were not highly toxic to fish. With increased use of the pyrethroid-based pesticides, there is the potential that they could be causing toxicity not only to some forms of zooplankton, but also to fish.

Proactive Approach to Pesticide Registration

The situation has developed where the OP-based pesticides are being replaced by pyrethroid-based pesticides, which are even more toxic to some forms of aquatic life. This demonstrates the gross inadequacies of the US EPA Office of Pesticide Programs' (OPP's) approach for registration of pesticides. As reviewed in NL 8-1/2, the US EPA OPP will register pesticides that are highly toxic to zooplankton and/or fish, for use under conditions where stormwater runoff and wastewater/fugitive water discharges (such as from agricultural and urban areas) would transport some of these pesticides to waterways.

Since the problem of inadequate registration of pesticides by the US EPA OPP to prevent aquatic life toxicity from labeled (permitted) use has been well known for several years, and the US EPA OPP has inadequately addressed this issue, it will be necessary to implement additional studies on fate and transport of pesticides after labeled use to screen new or expanded-use pesticides for potential aquatic life toxicity problems. Jones-Lee and Lee (2000) and Lee (2001b) have discussed a Proactive Approach for evaluating new and expanded-use pesticides for the potential to cause aquatic life toxicity in waterbodies receiving stormwater runoff and wastewater discharges from areas where the pesticides are first being used. This approach is designed to make up for the deficiencies in the approach used by the US EPA OPP in registering pesticides. It would be implemented by state and local regulatory agencies to detect, before widespread use occurs, aquatic life toxicity in the water column and sediments caused by a new or expanded-use pesticide.

Dr. K. Moran of TDC Environmental, in a report to the Urban Pesticide Committee, has indicated that the US Environmental Protection Agency is making available on the Web a database that provides information about what happens to pesticides after they are used in the environment. It currently includes data for about 200 of the approximately 900 registered pesticide active ingredients. The database contains summary information on the physical and chemical properties and the environmental fate and transport of pesticides found in products registered in the United States. This database could provide insight into the potential for pesticides to cause aquatic life toxicity through stormwater runoff and/or wastewater discharges. The Pesticide Fate Database and instructions for using this database can be found at the following address: http://cfpub.epa.gov/pfate/index.cfm

Chlorpyrifos Use in Urban Areas

As discussed in NL 8-1/2, the US EPA has greatly restricted the use of diazinon and chlorpyrifos in urban areas. These restrictions were based on the potential cumulative toxicity to children, and did not consider aquatic life toxicity issues. In August 2005 the US EPA has issued a notice (US EPA 2005), "Notice to Distributors, Retailers, and PCOs Regarding Chlorpyrifos Products

Labeled for Pre-Construction Termite Use." Some of the uses that will still be allowed after December 31, 2005, include:

- Underground utility cable and conduit (Non-residential)
- Utility poles and Fence Posts (Non-residential)
- Treatment of Wood Products (Applications must be made in manufacturing, industrial, or right-of-way settings only)
- Pest Control on Outside Surfaces and Around Buildings (Industrial plant sites only)
- Chlorpyrifos containing products may be used in industrial plant sites such as outdoor perimeter treatments of commercial facilities, office buildings, and other non-residential buildings
- Chlorpyrifos-containing products may not be used in or around schools, motels, hotels, grocery stores, hospitals, restaurants, dining areas, athletic fields, parks, and any other settings not discussed above.

Questions related to this notice should be directed to Tom Myers, Team Leader, Special Review and Reregistration Division, (703) 308-8589, e-mail: myers.tom@epa.gov.

These continued allowed uses, while generally protective of children from exposure to chlorpyrifos at the place of application, can potentially continue to contribute chlorpyrifos in stormwater runoff from these areas.

Bioavailability of Sorbed Pesticides

Gan et al. (2005) have recently presented a summary of studies on the bioavailability of pyrethroid-based pesticides associated with aquatic sediments. Their 85-slide PowerPoint presentation is available at http://www.cdpr.ca.gov/docs/sw/presentations.htm. They have shown, as expected, that those pesticides that are attached (sorbed) to sediment particles are not toxic – non-bioavailable. They also reported – again, as expected – that the amount of total organic carbon (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 chlorpyrifos. As with many organics, particulate TOC in sediments sorbs the chlorpyrifos, resulting in its being non-bioavailable (nontoxic). Since the determination of the bioavailable forms of a pesticide is not readily accomplished, this situation means that 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.

Restricting Dormant-Spray Pesticide Use

In an effort to reduce the amount of OP pesticides present in stormwater runoff from orchards that receive these pesticides as a dormant (winter) spray, the California Department of Pesticide Regulation (DPR) has developed some proposed restrictions on how the dormant-spray pesticides can be applied to orchards. These restrictions include restrictions on application just prior to anticipated runoff events, near the edge of the orchard where drift could carry the applied pesticides out of the orchard area, when there is elevated wind speed or saturated soil moisture conditions, etc. They also potentially require that the user of the pesticides monitor the runoff for aquatic life toxicity. Lee (2005c) has commented that, while DPR's proposed restrictions on the application of dormant-spray pesticides will reduce the potential for stormwater runoff to carry these pesticides into surface waters, this approach will likely not eliminate aquatic life toxicity in receiving waters associated with major runoff events. It is those types of events that can cause the greatest aquatic life toxicity associated with dormant-spray application of OP and other pesticides.

In regulating pesticide-caused aquatic life toxicity, some are focusing on average conditions, such as the average concentrations that are found over a season. This approach is technically invalid, in that it ignores the fact that a single major toxic runoff event can be highly detrimental to aquatic life populations in a waterbody. It is, therefore, important that all pesticide runoff impact monitoring be based on event-based monitoring, with particular attention to major runoff events.

References

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*, 13(4):621-626 (1994).

Gan, J., Yang W., Hunter, W. Bondarenko S., and Spurlock, F., "Bioavailability of Pyrethroids in Surface Aquatic Systems," Presented at Department of Pesticide Regulation, Sacramento. October 11 (2005). http://www.cdpr.ca.gov/docs/sw/presentations.htm

Jennings, W., Presentation at the CVRWQCB SJR OP Pesticide Basin Plan Amendment hearing, Rancho Cordova, CA, October 21 (2005).

Jones-Lee, A. and Lee, G. F. , "Proactive Approach for Managing Pesticide-Caused Aquatic Life Toxicity," Report of G. Fred Lee & Associates, El Macero, CA, October (2000). http://www.gfredlee.com/proactivepest_1000.pdf

Lee, G. F., "The Urban Pesticide Problem: How Do We Know the Substitutes Aren't Worse Than the Ones They're Replacing?" Feature Article, Journal *Stormwater* 2(1):68-71, Forester Press, January/February (2001a). http://www.members.aol.com/annejlee/UrbanPestStormwater1.pdf

Lee, G. F., "Proactive Approach for Managing Pesticide-Caused Aquatic Life Toxicity," PowerPoint Presentation to the Sacramento River Watershed Program Toxics Subcommittee, Sacramento, CA, September 26 (2001b). http://www.gfredlee.com/ProActivePest.pdf

Lee, G. F., "Pesticide-caused aquatic life toxicity in urban stormwater runoff after residential use ban on diazinon and chlorpyrifos," *Stormwater Runoff Water Quality Science/Engineering Newsletter* 8(1/2):1-24, February 18 (2005a). http://www.gfredlee.com/newsindex.htm

Lee, G. F., "Inadequate Approach for Implementation of the SJR OP Pesticide TMDL Compliance Monitoring," Comments submitted to William Jennings, California Sportfishing Protection Alliance, by G. Fred Lee & Associates, El Macero, CA, November 8 (2005b). http://www.members.aol.com/annejlee/OPPestSJRBasinPlanAmend.pdf

Lee, G. F., "Comments on DPR Proposed Revision of Dormant Pesticide Application Requirements," Report of G. Fred Lee & Associates, El Macero, CA, Aug 1 (2005c). http://www.members.aol.com/annejlee/DPR-DormantSprayReg.pdf

Lee, G. F., and Jones-Lee, A., "Urban Stormwater Runoff Aquatic Life Toxicity: An Update - Regulating Pesticides," Journal *Stormwater* 6(6):62-67, Forester Press, Sept/Oct (2005a). http://www.members.aol.com/annejlee/RegulatingPesticides.pdf

Lee, G. F. and Jones-Lee, A., "Comments on 'Draft Conditional Waivers of Waste Discharge Requirements for Discharges from Irrigated Lands - Tentative Table 1 List of Receiving Water Limitations to Implement Water Quality Objective Guidance for Implementing the MRP,'" Submitted to Central Valley Regional Water Quality Control Board, Rancho Cordova, CA, by G. Fred Lee & Associates, El Macero, CA, November (2005b). http://www.members.aol.com/annejlee/Agwavtable_1_com.pdf

Lee, G. F. and Jones-Lee, A., "Recommended Pesticide-Caused Aquatic Life Toxicity Monitoring," Report of G. Fred Lee & Associates, El Macero, CA, November 4 (2005c). http://www.members.aol.com/annejlee/PestToxMonitor.pdf

Lee, G. F. and Taylor, S., "Results of Aquatic Toxicity Testing Conducted During 1997-2000 within the Upper Newport Bay Orange County, CA Watershed," Report of G. Fred Lee & Associates, El Macero, CA (2001). http://www.members.aol.com/apple27298/295-319-tox-paper.pdf

US EPA, "Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates," Second Edition, US Environmental Protection Agency, EPA/600/R-99/064, Washington, D.C. (2000).

US EPA, "Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms," Fifth Edition, US Environmental Protection Agency, Office of Water, Washington, D.C. (2002). http://www.epa.gov/OST/WET/disk2/

US EPA, "Notice to Distributors, Retailers, and PCOs Regarding Chlorpyrifos Products Labeled for Pre-Construction Termite Use," Office of Prevention, Pesticides and Toxic Substances, US Environmental Protection Agency, Washington, D.C., August (2005). http://www.epa.gov/oppsrrd1/op/chlorpyrifos.htm

Weiser, Matt, “Delta danger - A decline in fish species and their food source is a reminder of a recurring worry in the West: A broad ecosystem collapse,” *Sacramento Bee*, July 3 (2005). http://www.pcl.org/pcl/pcl_files/pcl_deltadanger_070305.pdf

Weston, D. P.; You, J. and Lydy, M. J., “Distribution and Toxicity of Sediment-Associated Pesticides in Agriculture-Dominated Water Bodies of California’s Central Valley,” *Environmental Science & Technology* 38(10):2752-2759 (2004).

Weston, D. P., Holmes, R. W., You, J., and Lydy, M. J., “Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides,” *Environmental Science Technology*; (2005); ASAP Web Release Date: 19-Oct-2005; (Article) DOI: 10.1021/es0506354
http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/es0506354

Recommended Pesticide-Caused Aquatic Life Toxicity Monitoring[1]

G. Fred Lee, PhD, DEE and Anne Jones-Lee, PhD
gfredlee@aol.com www.gfredlee.com
November 4, 2005

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 interactive studies involved working closely with the laboratory that was doing the toxicity testing to determine the total toxicity in the sample;

[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).

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 the fact 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.

References

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*, 13(4):621-626 (1994).

Gan, J., Yang W., Hunter, W. Bondarenko S., and Spurlock, F., "Bioavailability of Pyrethroids in Surface Aquatic Systems," Presented at Department of Pesticide Regulation, Sacramento. October 11, 2005. (PDF, 308 mb)
http://www.cdpr.ca.gov/docs/sw/presentations.htm

Lee, G. F., "Comments on DPR Proposed Revision of Dormant Pesticide Application Requirements," Report of G. Fred Lee & Associates, El Macero, CA, Aug 1 (2005a).
http://www.members.aol.com/annejlee/DPR-DormantSprayReg.pdf

Lee, G. F., "Pesticide-caused aquatic life toxicity in urban stormwater runoff after residential use ban on diazinon and chlorpyrifos," Stormwater Runoff Water Quality Newsletter, Volume 8 Number 1/2 G. Fred Lee & Associates El Macero, CA February 18, 2005 (2005b). http://www.gfredlee.com/newsindex.htm

Lee, G. F. and Taylor, S., "Results of Heavy Metal Analysis Conducted During 2000 in the Upper Newport Bay Orange County, CA Watershed," Report of G. Fred Lee & Associates, El Macero, CA (2001a). http://www.members.aol.com/apple27298/Heavy-metals-319h.pdf

Lee, G. F. and Taylor, S., "Results of Aquatic Toxicity Testing Conducted During 1997-2000 within the Upper Newport Bay Orange County, CA Watershed," Report of G. Fred Lee & Associates, El Macero, CA (2001b).
http://www.members.aol.com/apple27298/295-319-tox-paper.pdf

US EPA, "Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Marine and Estuarine Organisms," US Environmental Protection Agency, Washington, D.C. (2002a). http://www.epa.gov/OST/WET/disk1/

US EPA, "Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms," Fifth Edition, US Environmental Protection Agency, Office of Water, Washington, D.C. (2002b).
http://www.epa.gov/OST/WET/disk2/

US EPA, “Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Freshwater Organisms,” EPA-821-R-02-013, US Environmental Protection Agency, Office of Water, Washington, D.C. (2002c).
http://www.epa.gov/OST/WET/disk3/

US EPA. “Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates.” Second Edition, U.S. Environmental Protection Agency, EPA/600/R-99/064, Washington, D.C. (2000d).
http://www.epa.gov/ost/cs/freshfact.html

Weston, D., Presentation to the CVRWQCB TIC, Rancho Cordova, CA (2005).

Weston, D. P.; You, J. and Lydy, M. J., Distribution and Toxicity of Sediment-Associated Pesticides in Agricultural-Dominated Water Bodies of California’s Central Valley,” Environmental Science & Technology 38(10):2752-2759 (2004).

Weston, D. P., Holmes, R. W., You, J., and Lydy, M. J., “Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides,” Environmental Science Technology; (2005); ASAP Web Release Date: 19-Oct-2005; (Article) DOI: 10.1021/es0506354
http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/es0506354