Comments from Stephen Louie, California Department of Fish and Wildlife, Water Branch

Received via email Friday 12/5/2014 3:30 PM
Sent to: Tessa Fojut and Daniel McClure

Here are some comments for you to consider in your development of the Basin Plan Amendment.

Additive Toxicity

The Department of Fish and Wildlife supports the evaluation of pyrethroid pesticide impacts on water quality using methods that include the consideration of pesticide mixtures (e.g., additive toxicity equation). In addition, the use of the additive toxicity equation is consistent with the Basin Plan (CVRWQCB 2011). For example, in Chapter 3, Water Quality Objectives, it states, "All waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life. This objective applies regardless of whether the toxicity is caused by a single substance or the interactive effect of multiple substances." and "No individual pesticide or combination of pesticides shall be present in concentrations that adversely affect beneficial uses." As well, in Chapter 4, under "Policy for Application of Water Quality Objectives," it states, "Where multiple toxic pollutants exist together in water, the potential for toxicologic interactions exists. On a case by case basis, the Regional Water Board will evaluate available receiving water and effluent data to determine whether there is a reasonable potential for interactive toxicity. Pollutants which are carcinogens or which manifest their toxic effects on the same organ systems or through similar mechanisms will generally be considered to have potentially additive toxicity." Finally, under "Pesticide Discharges from Nonpoint Sources" it states, "In conducting a review of pesticide monitoring data, the Board will consider the cumulative impact if more than one pesticide is present in the water body. This will be done by initially assuming that the toxicities of pesticides are additive."

There is ample evidence in the literature that supports the concept that pyrethroids as well as other classes of pesticides have the potential to work in conjunction to adversely impact water quality and impair beneficial uses (as reviewed by Fojut *et al.* 2011). For example, in California Stormwater Quality Association's review of pyrethroid and toxicity monitoring data from California urban watersheds, a key conclusion was that "Because pyrethroid toxicity is generally considered to be additive, the level of toxicity estimated from chemistry results must account for the mixtures of pyrethroids and other pesticides found, including fipronil" (Ruby 2013). In addition, the author found that pesticide mixtures were likely a significant factor in contributing to the observed toxicity in urban creeks. Furthermore, mixtures of pesticides in surface waters are a true concern. For example, in the National Water-Quality Assessment (NAWQA) Program's monitoring of pesticides, they found that more than 90% of the streams located in developed areas contained two or more pesticides or degradates (Gilliom et al. 2006). In addition, more than 50% of the streams had five or more pesticides or degradates. More recently, USGS monitoring of Sacramento and San Joaquin River inputs to the Delta found that all filtered samples contained mixtures of 3 to 14 pesticides (Orlando 2014). These are the major migratory and rearing habitats for threatened and endangered Central Valley anadromous salmonid species, Delta Smelt, and Longfin smelt, and Green sturgeon, as well as other desired wildlife.

Not only do pesticide of similar classes or mechanisms of action (e.g., pyrethroids with pyrethroids or organophosphates with carbamates) work additively to adversely impact water quality, but pesticides with different mechanisms of action have been shown to work additively and synergistically to cause toxicity. For example, Denton and others (2003) observed synergistic toxicity and increased mortality to fathead minnows exposed to mixtures of esfenvalerate and diazinon. In addition, Westergaard and others (2012) observed "more-than-additive mixture toxicity" to the mobilization of *Daphnia magna* using copper and cypermethrin. Furthermore, even though they have different mechanisms of action at the cellular level (e.g., cholinesterase (ChE) inhibition or voltage-gated sodium channels), pyrethroids, organophosphates, carbamates, and metals have all been found to disrupt olfaction in salmonids (Scott and Sloman 2004; Scholz et al. 2000; Moore and Waring 2001; Hecht et al. 2007; NMFS 2008; NMFS 2009). Olfaction inhibition and other sub-lethal effects of pesticides often eliminates the performance of fish behaviors, such as predator avoidance, orientation, reproduction, kin recognition, etc. that are essential to fitness and survival in natural ecosystems (Potter and Dare 2003; Scott and Sloman 2004). It is reasonable to assume that pyrethroid pesticides can work additively with other classes of pollutants to cause sub-lethal toxicological effects.

At the last meeting I mentioned that impairments caused by multiple pesticides should consider the impact on the ecosystem as whole and not just to individual organisms (e.g., reduced food web production). Understandably, it is very difficult to quantify actual impacts that pesticide stressors have on fish populations because the effects can be direct or indirect, lethal or sublethal, long-term or short-term, etc. However, to determine the possible combined effects that pesticides might have on salmon populations, researchers at the Northwest Fisheries Science Center used models to predict the effects of ChE inhibitors on anadromous Chinook salmon populations in the western United States (Baldwin et al. 2009; Macneale et al. 2014). The model evaluated salmonid population growth impacts from direct (e.g., to fish physiology) and indirect (e.g., to invertebrate prey) effects of pesticides. The model results indicated that short-term exposures that were representative of real-world seasonal use patterns were enough to reduce the growth and size of juvenile chinook at the time of ocean entry. Consequently, the reduced size at ocean entry was enough to reduce the survival of individuals, which would, over successive years, reduce the intrinsic productivity of the population. Overall, the magnitude of the responses indicates that common pesticides may significantly limit the conservation and recovery of threatened and endangered species in California (Baldwin et al. 2009). It is possible that similar impacts to salmonid populations could occur, if pyrethroid pesticides also have the ability to reduce salmonid prey and fish growth rates.

In summary, there is overwhelming evidence that pesticides in mixtures can interact to collectively cause toxic effects to aquatic life, even if the toxicants' biochemical or cellular mechanisms appear to be different. Furthermore, evidence from the modeling efforts suggests that population level impacts to salmonid species are likely occurring as the result of pesticides targeting fish both directly and indirectly (e.g., ecosystem impacts). In addition, to be consistent with the narrative Water Quality Objectives for Toxicity and Pesticides, it is recommended that Water Board staff evaluate the use of an additive toxicity equation that includes pyrethroid pesticides as well as other pertinent pesticides and pollutants because there is explicit evidence that many diverse classes of pollutants "manifest their toxic effects on the same organ systems or through similar mechanisms" and in combination can be "toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life."

Methods for Compliance Determinations

Significant environmental harm could result, if the control program disregards samples where individual pyrethroids have been detected but at levels below the "reporting limit" (e.g., J-Flag data). The pyrethroids that have been reported as above the method detection limit are defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero (40 CFR Part 136). So, the substitution of zero for pesticide concentrations in samples, where there are most certainly pesticides present, essentially assumes that the pesticides present in the sample have no environmental impact. These data are "J-flagged" because they are estimates (e.g., MDL < J < QL), and not because they are invalid. As well, substitution for censored data is not recommended for the evaluation of environmental data, and many more scientifically defensible methods are readily available (Helsel 2005).

This is particularly important for pyrethroid pesticides because they have been shown to impact aquatic life at concentration levels at or below technical detection limits. For example, many of the proposed water quality objectives are below current best analytical laboratory method detection limits or reporting limits (Caltest 2014; Hladik *et al.* 2009; Mekebri 2011). The proposed chronic water quality objective for cyfluthrin is 30-fold lower than the lowest advertised reporting limit for cyfluthrin (RL = 1.5 ng/L, Caltest 2014). In addition, this reporting limit for cyfluthrin is higher than the lower range of 96-hour LC50 values for *Hyalella azteca* used in the development of water quality criteria (Fojut *et al.* 2010). Clearly, concentrations of cyfluthrin in the aquatic environment between 0.05 and 1.5 ng/L would pose major risks to aquatic life beneficial uses, even if the concentrations were not "quantifiable".

Furthermore, it is expected that sub-lethal effects to aquatic life would occur more often and at lower concentrations than the observed mortality. For example, Brander and others (2014) observed that exposures to bifenthrin caused significant differential expression of genes related to reproduction and immune function at sub-lethal concentrations. As well, Brander and others (2014) reported a statistically significant 30% reduction in fertilized eggs from adult *Menidia beryllina* (inland silversides) exposed to 0.5 ng/L bifenthrin (RL = 1.5 ng/L, Caltest 2014), and their population dynamic modeling predicted that these reductions in reproductive success would cause a significant decline in fish population over time. Furthermore, the pyrethroid insecticide cypermethrin (at <4 ng/L, the MDL at the time) inhibited male Atlantic salmon from detecting and responding to the reproduction priming pheromone prostaglandin, which is released by ovulating females (Moore and Waring 2001). The males exposed to cypermethrin did not respond to prostaglandin with the expected increased levels of plasma sex steroids and expressible milt. The disruption of spawning synchronization could result in an increase in the number of unfertilized eggs (NMFS 2009).

The use of censored data for regulatory environmental evaluations is consistent with other Water Board control programs. For example, the Sacramento-San Joaquin Delta Estuary TMDL for Methylmercury and the developing Statewide Mercury Control Program for Reservoirs rely heavily on the use of censored data (both data <MDL and <QL) to develop the linkage analyses, loading estimates, allocations, etc. for water bodies that have been identified as being impaired (Louie *et al.* 2011; Wood *et al.* 2010). These programs have determined that censored data (from analytical laboratories) are environmentally valid. Similarly, pyrethroids have been found to be environmentally relevant at concentrations less than detection limits. This is characterized by the proposed water quality objectives for pyrethroids, which concentrations are estimated to be necessary to protect beneficial uses.

The proposed control program does not require the proper monitoring methods to assess chronic impacts from pyrethroid pesticides for all types of discharges. For example, the control program proposes to rely on current regulatory programs for evaluating discharges for irrigated agriculture. The adopted Waste Discharge Requirements for irrigated agriculture (Order NO. R5-2014-0032, R5-2012-0116, etc.) do not require chronic water column toxicity testing for invertebrate or fish species. Since pyrethroid pesticide concentrations below the limits of quantification are not being assessed, then assessments for chronic impacts to water quality will not be evaluated for irrigated agriculture discharges or other programs with similar monitoring requirements when low concentrations are present. Due to the limitations of the proposed data evaluations of analytical results, chronic water column toxicity testing, bioassessment investigations, etc. are likely the best available methods to evaluate chronic impacts to the water column and aquatic environment. Concurrent chronic water column toxicity testing, sediment toxicity testing, bioassessment investigations, or other appropriate chronic toxicity evaluation should likely be a requirement for monitoring until analytical methods allow for the reliable measurement of pyrethroid pesticides at levels lower than expected to affect aquatic life.

In summary, the proposed method of evaluation of analytical data (i.e., J-flag = concentration of 0) will likely underestimate adverse environmental impacts from pyrethroid pesticides. These “J-flag” results are valid data, and they should be used for the evaluation of impacts to water quality, attainment of water quality objectives, meeting of water quality criteria, etc. At a minimum, exceedances of water quality objectives or criteria determined solely by use of “J-flag” values should trigger additional evaluations or assessments of water quality (e.g., accelerated monitoring, water column or sediment toxicity testing, or bioassessment monitoring). As well, methods that provide the sensitivity to evaluate chronic impacts to water quality are necessary to supplement water chemistry data until analytical methods for pyrethroids are found to be acceptable for Water Board regulations.

Thank you for your consideration.

Stephen Louie
Senior Environmental Scientist
California Department of Fish and Wildlife, Water Branch
830 S Street, Sacramento, CA 95811
(916) 327-8758
Stephen.Louie@wildlife.ca.gov

References Cited

Baldwin, D., J. Spromberg, T. Collier, and N. Scholz. 2009. A fish of many scales: extrapolating sublethal pesticide exposures to the productivity of wild salmon populations. Ecological Applications, 19(8): 2004-2015.

Brander, S., B. Cole, K. Jeffries, B. DeCourten, W. White, N. Fangue, and R. Connon. 2014. Predicted Population Decline in Fish Due to Bifenthrin Exposure: Implicatons for Aquatic Ecosystems in teh Bay-Delta. Oral Abstract from the 8th Biennial Bay-Delta Science Conference. October.

Caltest. 2014. Advertised Pyrethroid Pesticide Analyses. Website: http://www.caltestlabs.com/Services/Pyrethroids/PyrethroidsCompoundsandRLs.aspx. Accessed November 6, 2014.

CVRWQCB. 2011. The Water Quality Control Plan for the California Regional Water Quality Control Board Central Valley Region, Fourth Edition, Revised October 2011.

Denton, D., C. Wheelock, S. Murray, L. Deanovic, B. Hammock, and D. Hinton. 2003. Joint Acute Toxicity of Esfenvalerate and Diazinon to Larval Fathead Minnows (Pimephales promelas). Environmental Toxicology and Chemistry, 22(2): 336-341.

Fojut T., R. Mulligan, and R. Tjeerdema. 2011. Water Quality Criteria Report for Cypermethrin. Phase III: Application of Pesticide Water Quality Criteria Methodology. Report Prepared for the Central Valley Regional Water Quality Control Board. September.

Fojut T., S. Chang, and R. Tjeerdema. 2010. Water Quality Criteria Report for Cyfluthrin. Phase III: Application of Pesticide Water Quality Criteria Methodology. Report Prepared for the Central Valley Regional Water Quality Control Board. September.

Gilliom R., J. Barbash, C. Crawford, P. Hamilton, J. Martin, N. Nakagaki, L. Nowell, J. Scott, P. Stackelberg, G. Thelin, and D. Wolock. 2006. The Quality of Our Nation's Waters—Pesticides in the Nation's Streams and Ground Water, 1992–2001: U.S. Geological Survey Circular 1291, 172 p.

Hecht, S., D Baldwin, C. Mebane, T. Hawkes, S. Gross, and N. Scholz. 2007. An overview of sensory effects on juvenile salmonids exposed to dissolved copper:
Applying a benchmark concentration approach to evaluate sublethal neurobehavioral toxicity. U.S. Dept. Commer., NOAA Tech. Memo. NMFS-NWFSC-83, 39 p.

Helsel, D. 2005. More than Obvious: Better Methods for Interpreting Nondetect Data. Environmental Science and Technology. 419-423. October.

Hladik, M., K. Smalling, and K. Kuivila. 2009. Methods of analysis—Determination of pyrethroid insecticides in water and sediment using gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods 5–C2, 18 p.

Louie, S., C. Austin, M. Wood. 2013. Important Factors Influencing Predatory Fish Mercury Concentrations in California Reservoirs: A Statistical Approach. Presentation from the North American Lake Management Society, 33rd International Symposium, November 1, 2013. Available: http://www.waterboards.ca.gov/water_issues/programs/mercury/reservoirs/docs/131101_nalms_louie.pdf

Macneale K, J. Spromberg, D. Baldwin, N. Scholz. 2014. A Modeled Comparison of Direct and Food Web-Mediated Impacts of Common Pesticides
on Pacific Salmon. PLoS ONE 9(3): e92436. doi:10.1371/journal.pone.0092436

Mekebri, A. 2011. Recent advances in the analysis of pyrethroid insecticides in surface water and sediment. Presentation. California Department of Fish and Game, Office of Spill Prevention and Response, Fish and Wildlife Water Pollution Control Laboratory. Surface Water Ambient Monitoring Program. California State Water Resources Control Board. Sacramento, CA. Available: http://www.waterboards.ca.gov/water_issues/programs/swamp/tools.shtml#qa

Moore, A. and C. Waring. 2001. The effects of a synthetic pyrethroid pesticide on some aspects of reproduction in Altalntic salmon (Salmo salar L.). Aquatic Toxicology, 52: 1-12.

NMFS. 2008. National Marine Fisheries Service endangered species act section 7 consultation: Environmental Protection Agency registration of pesticides containing chlorpyrifos, diazinon, and malathion. Biological Opinion. Silver Spring, MD, U.S. Department of Commerce: 482 p.

NMFS. 2009. National Marine Fisheries Service endangered species act section 7 consultation: Environmental Protection Agency registration of pesticides containing carbaryl, carbofuran, and methomyl. Biological Opinion. Silver Spring, MD, U.S. Department of Commerce: 609 p.

Orlando, J. and M. Hladik. 2014. Concentrations and Loads of Current-Use Pesticides Entering the Sacramento/San Joaquin Delta May 2012-April 2013. Oral Abstract from the 8th Biennial Bay-Delta Science Conference. October.

Potter, E. and P. Dare. 2003. Research on migratory salmonids, eels, and freshwater fish stocks and fisheries. Science Series Technical Report, CEFAS Lowestoft, 119: 64 p.

Ruby, A. 2013. Review of Pyrethroid, Fipronel and Toxicity Monitoring Data from California Urban Watersheds. Prepared for the California Stormwater Quality Association (CASQA). July.

Scholz, N., N. Truelove, B. French, B. Berejikian, T. Quinn, E. Casillas, and T. Collier. 2000. Diazinon disrupts antipredator and moning behavios in chinook salmon (Onchorhynchus tshawytscha). Canadian Journal of Fisheries and Aquatic Sciences, 57: 1911-1918.

Scott, G. and K. Sloman. 2004. The effects of environmental pollutants on complex fish behavior: integrating behavior and physioogical indicators of toxicity. Aquatic Toxicology, 68: 369-392.

Westergaard, C., L. Vahlgren, P. Poulsen, R. Herlau, N. Dam, C. Osuji, A. Jensen, and K. Norregard. 2012. The Effect of Cypermethrin and Copper on Daphnia magna. An experimental project on the single and combined toxicity of copper and cypermethrin. Roskilde University, Denmark.

Wood, M., C. Foe, J. Cooke, and S. Louie. 2010. Sacramento – San Joaquin Delta Estuary TMDL for Methylmercury. Central Valley Regional Water Quality Control Board Staff Report. Sacramento. April.