Urban Pesticide Runoff from Neighborhoods in Northern California and their Contribution to Pesticide Contamination in Urban Creeks

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Since 2008 the California Department of Pesticide Regulation has conducted monitoring studies to determine the pesticide content in urban runoff. Water samples were collected from 13 storm drain outfalls and from seven urban creeks in the Sacramento and San Francisco Bay areas during rainstorm events and during California's dry season. Among both areas, 26 different herbicides and insecticides or their degradates were detected. Bifenthrin was the most commonly detected insecticide in all areas and site types. Fipronil (plus its degradates) was the second most frequently detected insecticide in the Sacramento area, but in the San Francisco Bay area, carbaryl and OP insecticides were detected about as frequently as fipronil. Imidacloprid was also detected, although this analysis was added later in the study and only in the Sacramento area. Synthetic auxin herbicides (2,4-D, dicamba, MCPA, triclopyr) and diuron were the most frequently detected herbicides in all areas and site types. However, diuron was detected less frequently in storm drain outfalls in the Sacramento area. Overall, there were no significant differences in the number of pesticides detected per sample from the two areas, although the Sacramento area had significantly more pesticides per sample during the dry season than did the San Francisco Bay area (median, 2 and 1, respectively; p=0.002). In both areas more pesticides were detected per sample during rainstorm events than during dry season monitoring (median, 6 and 1, respectively; p=0.00). Comparing site type (urban creek or storm drain outfall), the Sacramento area had significantly more pesticides in samples collected from storm drain outfalls whereas in the San Francisco area there were no significant differences between site type. Bifenthrin, fipronil, and malathion most frequently exceeded aquatic life benchmarks or water quality criteria.

Keywords: Pesticide urban monitoring, aquatic benchmark, bifenthrin, fipronil, malathion

Tuesday, October 16, 2012: Room 306, Organic Contaminants (I) – Order 1

Current Use Pesticides Detected in the San Francisco Bay-Delta during Spring 2011 and 2012

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Current-use pesticides pose a threat to aquatic organisms in the San Francisco Bay-Delta estuary. Pesticide use is constantly changing, presenting a challenge for resource managers and policy makers trying to understand the fate and effects of these contaminants. The U.S. Geological Survey Pesticide Fate Research Group routinely updates analytical methods to adapt to changing pesticide use. Our gas chromatography/mass spectrometry and liquid chromatography/mass spectrometry methods were designed and modified to analyze over 100 pesticides and pesticide degradates in water, including several newer use rice herbicides, six neonicotinoid insecticides, and 35 fungicides, many of which are rarely included in monitoring studies. As part of a collaborative study working to understand the occurrence of current-use pesticides and other contaminants in the San Francisco Bay-Delta estuary and their potential effects on phytoplankton, our updated methods were used to analyze water samples collected during the spring of 2011 and 2012. During each year, water samples were collected weekly for ten consecutive weeks (March-May) from three sites in the San Francisco Bay-Delta. In 2011, 18 pesticides of varying type and use, were detected including the herbicide diuron and its degradates 3,4-DCA and DCPMU, several fungicides, and clomazone, a rice herbicide. Maximum pesticide concentrations were generally less than 100 ng/L, with the exceptions of clomazone, and the fungicide tetraconazole, (535 and 511 ng/L, respectively). All concentrations were below U.S. Environmental Protection Agency aquatic life benchmarks, with the exception of one detection of the pyrethroid bifenthrin (4.1 ng/L) which exceeded the chronic invertebrate toxicity benchmark of 1.3 ng/L. Pesticide concentration results from the spring 2012 sampling will be compared with those from 2011 to gauge the types and concentrations of pesticides that occur in the San Francisco Bay-Delta, providing valuable data to scientists and resource managers working to understand the role of contaminants in the region.

Keywords: Pesticides, contaminants, phytoplankton

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Pyrethroid Concentrations in the American River: Historical Assessment and Impact of Proposed Regulatory Controls

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A watershed pyrethroid insecticide exposure model was developed for the lower American River watershed located in California, USA. The model incorporated empirically derived washoff functions based on previously run small scale rainfall simulations, along with actual pyrethroid insecticide use and watershed properties for Sacramento County, California. The model was calibrated to in-stream monitoring data and utilized to predict daily river pyrethroid concentration for a period spanning 1995 through 2010. Based on model predictions, a marked increase in pyrethroid toxic units is observed starting in the calendar year 2000, coincident with a watershed-wide increase in pyrethroid use. Approximately 80% of the predicted toxic unit exposure in the watershed was associated with the pyrethroids bifenthrin, cyfluthrin, and cypermethrin. Pyrethroid applications for above-ground structural pest control purposes utilizing suspension concentrate categorized product formulations accounted for greater than 93% of the total toxic unit exposure for all modeled years except 1995. Application of mitigation strategies, such as curtailment of structural perimeter band and barrier treatments as proposed by the California Department of Pesticide Regulation, yielded an approximate 80% reduction in predicted total toxic unit exposure in all modeled years. The model also predicted that similar mitigation gains could be achieved through a switch from suspension concentrate categorized products to emulsifiable concentrate categorized products. Even with these mitigation gains, the predicted concentration of some pyrethroids would continue to exceed chronic aquatic life criteria for pyrethroids on a frequent basis, illustrating the recalcitrant nature of the pyrethroid problem.

Keywords: Insecticide, stormwater, toxicity, modeling, water quality, bifenthrin, pyrethroid, pesticide regulation

Tuesday, October 16, 2012: Room 306, Organic Contaminants (I) – Order 3

Distribution of the Pyrethroid Insecticide Concentration between Freely Dissolved and Particle-Bound Forms in Sacramento Wastewater Effluent

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Pyrethroid insecticides are a major current use insecticide class in the US. Whole water concentrations of pyrethroids have been reported in the dechlorinated final effluent (DFE) of Sacramento Wastewater Treatment Plant (SWTP). Tests with 100% effluent reported toxicity to aquatic arthropods, however, upon 50-50 dilution with river water no toxicity was observed. Research has shown that the form of the pyrethroid, freely dissolved, complexed with organic matter, or adsorbed to sub-micron particles, can affect its toxicity to aquatic organisms and have implications for fate and transport. Effluent from the SWTP was sampled six times in the course of a yearlong study. The DFE was fractionated by laboratory centrifugation to different particle size cuts. The pyrethroid concentration associated with each fraction was quantified to determine if there was a particular size fraction that treatment operations could focus on to maximize pyrethroid removal. Solid phase microextraction (SPME) was used with pyrethroid serial additions to measure an organic carbon normalized distribution coefficient (K_{oc}) between pyrethroids and the suspended wastewater particulate matter. Values for log K_{oc} ranged between 6.5-7.4 depending on sampling date and chemical. Calculation with the measured K_{oc} and whole water pyrethroid concentration predicts that < 5% of the pyrethroid is in the freely dissolved phase. The SWTP effluent discharge represents 1-2% of the Sacramento River volume. The form of pyrethroids in effluent has implications for their transport down the river and their effect on organisms that reside downstream in the Sacramento - San Joaquin River Delta.

Keywords: pyrethroids, sorption, partition coefficient, wastewater, effluent

Tuesday, October 16, 2012: Room 306, Organic Contaminants (I) – Order 4

Asking the Fish: Using Tissue Concentrations to Understand Pesticide Exposure

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Current-use pesticides are of concern in the Sacramento-San Joaquin Delta (Delta) and are considered a possible contributor to the Pelagic Organism Decline (POD). Hundreds of pesticides are applied annually within the Delta watershed in agricultural and urban areas and are transported into surface waters throughout most of the year. Interactions between life histories of the fishes and the temporal and spatial variability of pesticides in the environment make understanding routes of potential exposure difficult. A different approach is to "ask the fish". Most current-use pesticides are only moderately lipophilic and will not biomagnify but have the potential to accumulate in organisms. Other advantages of measuring fish tissue concentrations rather than environmental concentrations are implicit bioavailability and inclusion of all exposure pathways.

A new robust and sensitive method was developed to extract pesticides from specific organs or whole bodies using solvent extraction at high temperature and pressure followed by cleanup using size exclusion chromatography and Florisil. As fish are typically exposed to complex mixtures of pesticides, the tissue extracts are analyzed for over 100 pesticides using gas chromatography/mass spectrometry. Three fish species from three central California coastal estuaries with intense-agricultural watersheds were analyzed for pesticides. Five insecticides (3 organophosphate and 2 pyrethroid insecticides) and five fungicides were detected in the tissue. Pesticide residues in fish tissues demonstrate exposure and tissue concentrations may serve as a metric that can be linked to biological endpoints. The next steps are to characterize tissue concentrations in species of concern and link back to potential effects. This information is critical for resource managers and biologists to assess the potential risks of multiple stressors as well as long-term contaminant exposure to aquatic organisms.

Keywords: Current-use Pesticides, Tissue, Accumulation, Fish

Tuesday, October 16, 2012: Room 306, Organic Contaminants (I) – Order 5

Effect of Diuron and Imazapyr Herbicides on Phytoplankton in the San Francisco Estuary in an Experimental Study

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Herbicides may be used widely within estuarine watersheds and have the potential to negatively affect estuarine organisms living downstream of the site of their application. Diuron is one herbicide of concern in the northern San Francisco Estuary (SFE) because it is used extensively and persists for long periods in the environment. Despite measured concentrations in the SFE, little is known about the potential impact of diuron on phytoplankton communities. A second herbicide in use in the SFE is imazapyr, which is applied to marsh habitat adjacent to the SFE to control invasive plants. This study investigated the impact of additions of diuron and imazapyr on carbon assimilation, nitrogen uptake and community composition of natural phytoplankton assemblages collected in the SFE. Results show that diuron reduced carbon assimilation number at concentrations as low as 1 µg L^{-1} during both acute (t=0 hr) and chronic (t=48 hr) exposure treatments. This concentration is within the range of diuron concentrations previously reported for the northern SFE. Imazapyr exposure did not negatively affect carbon assimilation number during acute exposure, but carbon assimilation number decreased with the addition ofimazapyr (mg L^{-1}) in chronic exposure experiments. Phytoplankton biomass and abundance was lower in treatments with diuron and imazapyr, and the phytoplankton community composition shifted with the addition of diuron and imazapyr. These data have important implications for management, especially if they are used for invasive plant removal.

Keywords: herbicide, phytoplankton, carbon assimilation, nitrogen uptake, community composition, contaminants

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Effects of Pesticides to Critical Zooplankton Species of the San Francisco Estuary

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The calanoid copepods, *Eurytemora affinis* and *Pseudodiaptomus forbesi*, are a critical link between primary producers and fish in the San Francisco Estuary (SFE). Since these meso-zooplankton play an important role as food sources to larval fish and pelagic organisms, factors affecting their changes in abundance in recent years warrants an investigation. Insecticide exposure from nearby agricultural and urban run-off may be one of several factors acting to lower pelagic productivity in the estuary. The goal of this study is to estimate mean lethal concentrations (96-hr-LC50s) of five pesticides (Bifenthrin, Permethrin, Lambda-cyhalothrin, Chlorpyrifos and Fipronil) and to assess if ambient field water samples from critical spawning and nursery habitat are affecting the survival of *E. affinis* and *P. forbesi*. The 96-hr-LC 50 values of five pesticides investigated are near environmentally relevant concentrations. Of the five pesticides studied the most toxic to least toxic are Bifenthrin, Lambda-cyhalothrin, Permethrin, Fipronil with96-hour LC 50 values ranging from 10 to 1000 ng/L. Chemical analyses of these pesticides are currently under investigation. Ambient water testing is a work in progress, where pilot studies indicate acute toxicity of ambient water of critical habitats to copepods. Findings from this study may lead to changes in types of pesticides used and timing of pesticide applications in the SFE. Changes in pesticide regulation may lead to a more sustainable ecosystem by decreasing the population level effects of pesticides on zooplankton, resulting in an increase of food supply to higher trophic level organisms.

Keywords: acute toxicity, *Eurytemora affinis*, pesticides, *Pseudodiaptomus forbesi*,

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Assessment of the Effects of Tertiary Pesticide Mixtures upon Aquatic Invertebrates

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Aquatic communities in California are often adjacent to areas of intense pesticide use that discharge complex mixtures of contaminants into surface waters. The objective of this study was to address the effects of mixtures of pesticides commonly used in agriculture and urban pest control on aquatic invertebrates.

We focused on the effects of type-I (permethrin) and type-II (lambda-cyhalothrin) pyrethroid pesticides, along with chlorpyrifos (organophosphate) on two aquatic invertebrates, the midge *Chironomus tentans,* and the amphipod *Hyalella azteca*. Both organisms represent important and potentially vulnerable components of the food web in the Sacramento-San Joaquin Delta.

By using the toxic unit approach based on the median lethal concentrations (LC50) for each compound, we compared the effects of pesticide mixtures and their respective individual concentrations on survival, growth, and swimming performance following 10d-exposures.

Exposure to pesticide mixtures resulted in additive responses on survival and synergistic responses on growth in *C. tentans.* Swimming velocity was diminished at concentrations close to the LC25 of permethrin and chlorpyrifos when compared to lambda-cyhalothrin. There was no significant difference in swimming velocity at LC25 of the respective mixtures indicating an antagonistic response, whereas at LC50 the response was additive.

The concentrations of lambda-cyhalothrin to which *H. azteca* were exposed did not result in significant mortality, however there was a significant decrease in growth following exposure. Conversely, organisms exposed singly to permethrin and chlorpyrifos resulted in an increase in growth. Using pesticide mixtures, the response on growth was antagonistic, whereas the response on swimming velocity was additive.

This study highlights the importance of using a number of different endpoints to adequately assess the effects of contaminants, both single and in mixture. We conclude that mortality alone is not an informative endpoint, especially since environmentally relevant concentrations do not generally occur at levels that result in direct mortality.

Keywords: pesticide mixtures, pyrethroids, sublethal effects, effect assessment, invertebrates

Tuesday, October 16, 2012: Room 306, Organic Contaminants (II) – Order 8

Variation in Pyrethroid Sensitivity among *Hyalella azteca* from Different Sources

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There have been reports of water or sediment samples causing toxicity when tested in the laboratory with *Hyalella azteca*, yet the same waterbodies contain thriving populations of the same species. To further explore these reports, the sensitivity of ten populations of *H. azteca* to pyrethroid insecticides was determined. Three populations were from established laboratory cultures, and seven were from wild collections. The three lab cultures, and some of the wild populations, shared comparable sensitivity to pyrethroids, with LC50s within a factor of three of another. Yet some field populations had LC50s two orders-of-magnitude greater. The relative sensitivity to pyrethroids did not appear to be a function of the extent of prior pyrethroid exposure within the habitat from which they were collected. However, pyrethroid sensitivity was related to the degree of genetic similarity among the populations. DNA sequencing supported previous findings that *H. azteca* represents not a single species, but a species complex. Based on the genetic data, four members of this complex appeared to be represented within the ten populations we examined, and one member in particular was extraordinarily tolerant of pyrethroids. These findings have substantial ramifications to use of *H. azteca* for environmental monitoring in the Bay-Delta related to the source of the animals used, and how cultures are maintained.

Keywords: Pyrethroids, *Hyalella azteca*, Toxicity testing

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Effects of Endocrine Disrupting Chemicals on *Menidia beryllina*, a Resident Fish in the Sacramento-San Joaquin Delta

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A diverse and growing number of endocrine disrupting chemicals (EDCs) are known to be present in the waters of the Sacramento-San Joaquin (SSJ) Delta. These EDCs can come from natural sources or from a range of anthropogenic sources including agricultural and urban runoff, as well as in treated wastewater effluent. We have developed *Menidia beryllina*, the Inland Silverside, as a model resident species for studying effects of EDCs on fish, and ultimately on fish populations, in the SSJ Delta and other impacted waterways in the United States. Currently there is only a limited understanding of the impacts of exposure to combinations of EDCs, particularly when estrogenic and androgenic EDCs are mixed. As such this study focused on the biological response of *Menidia* to natural SSJ Delta waters throughout the seasons. We have quantified the expression of a suite of endocrine-related response genes and of choriogenin protein levels, using a *Menidia*-specific antibody to choriogenin, in wild populations around the Delta. Similar assays have also been performed on naïve juvenile fish exposed to SSJ Delta water in one-week long flow-through exposures at two sites spread throughout the seasons. These latter experiments will enable direct comparison of the endocrine response in exposed fish to that in controls which have only experienced EDC-free water. This study will provide time-integrated mechanistic data on the effects of EDCs on fish throughout the SSJ Delta, and should ultimately be able to inform the extent to which EDCs are responsible for the pelagic organism decline in the SSJ Delta.

Keywords: Endocrine disrupting chemicals, fish, SSJ Delta

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