Evaluation of the Impacts of California's Mandatory Minimum Penalty Enforcement Program on Effluent Quality and Surface Water Quality in the Sacramento-San Joaquin Delta

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Since 2000, California has issued mandatory minimum penalties (MMP) for violations of effluent limitations in National Pollution Discharge Elimination System (NPDES) permits for point-source facilities discharging to surface waters. California's water quality regulatory agencies issued MMPs through administrative civil liability (ACL) enforcement actions; however, whether MMPs improved effluent quality and ambient water quality has not been evaluated. A method is presented in this study to quantitatively estimate the impact of MMPs in improving effluent quality from wastewater treatment facilities (WWTFs) that discharge directly or indirectly to the Sacramento-San Joaquin Delta (Delta) and subsequently impact water quality within the Delta. Effluent monitoring results for total nitrogen (TN) and copper (Cu) and ACL enforcement action data for WWTFs inside and within 50 miles of the Delta between 2000 and 2012 were correlated using linear regression. The regression results suggest that effluent quality discharged from the WWTFs improved by as much 30 percent as a result of MMP ACLs, although there is a time lag between ACL issuance and effluent quality improvements. Quasi-physical models for effluent quality were determined from the regression analysis, and the amount of pollution prevented, apparently due to the issuance of MMPs, was calculated. Using a simple mixing model of the Delta and known flows of Delta rivers and tributaries, the reduction of TN and Cu concentrations at various points in the Delta, accounting for the pollution prevented due to MMPs, was calculated and compared with actual ambient monitoring results within the Delta. It is possible, however, that the pollution prevention impacts of MMPs may be obscured by other environmental processes. Difficulty in obtaining sufficiently complete data sets for analysis for this study highlights the need for comprehensive monitoring of effluent discharges and ambient waters across water quality regulatory programs, perhaps using a common water quality index.

Keywords: NPDES, wastewater treatment facilities, Sacramento-San Joaquin Delta, water quality
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Is there a Toxic Algae Problem in San Francisco Bay?

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San Francisco Bay (SFB) is an urbanized, nutrient-enriched estuary, and considered the most anthropogenically-altered estuary in the United States. SFB has historically resisted many classic symptoms of eutrophication; though recently, increased primary productivity and potential impairment is trending upwards. One indication of this impairment are the many toxin producing species of harmful algae that have been identified by microscopy and the recently documented trophic transfer of toxins to shellfish. A pilot program to identify toxin in SFB using particulate samples and Solid Phase Adsorption Tracking (SPATT) was conducted from 2011 - 2016 on bi-monthly USGS cruises. Results from each collection methods indicated persistent presence of both domoic acid and microcystin toxins throughout SFB., with periodic concentrations of high concern. This indicates the potential for persistent chronic toxin exposure in the marine food web from both toxins. In 2015-2016 this program was expanded to collect marine mussels from SFB, to identify any toxic impacts to the marine food web. In marine mussels, four toxins were consistently detected: domoic acid, microcystins, saxitoxins, and okadaic acid. Of particular concern was the detection of microcystins, a freshwater toxin, at concentrations 40-fold greater than the World Health Organization's Tolerable Daily Intake level for seafood. Currently, there is no regular monitoring of toxins in marine mussels in SFB. The findings of at least four toxins present in the marine food web indicates a need to not only monitor for these toxins in shellfish, which are consumed by humans and wildlife, but also to identify environmental factors that escalate the risk of exposure to the food web in order to provide a relevant management strategy for toxins in SFB.

Keywords: Domoic acid, Microcystin, Saxitoxin, Okadaic Acid, marine mussels, impairment, HAB
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Disrupting Aquatic Communities from Bottom-Up: A Long-Term Assessment of Herbicides

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Problem statement: Herbicides, used in both agricultural and urban areas, are found in the Sacramento-San Joaquin Delta watershed at concentrations that are potentially toxic to phytoplankton. Furthermore, herbicides are directly applied to control invasive aquatic vegetation. Consequently, there is increasing concern over direct effects on primary production, and indirect effects on zooplankton and other aquatic invertebrates.

Approach: Here we assessed long-term effects of five applications over 30 days of binary mixtures of the herbicides diuron and hexazinone at 'low' and 'high' concentrations as typically found in the Sacramento-San Joaquin Delta watershed. Phytoplankton, chlorophyll-α, zooplankton and macroinvertebrate communities were monitored over four months.

Results: In the mesocosm study, 16 of 95 phytoplankton taxa, 3 of 18 zooplankton taxa, and 6 of 14 macroinvertebrate taxa responded negatively to contaminant exposures. Herbicide applications significantly altered the phytoplankton community structure. Relative abundance of Cyanophyceae decreased following five applications from 52.1% in the control to 37.3% in the 'low' and to 25.9% in the 'high' treatment, while Chlorophyceae increased to 50.6% in the 'low' and 61.7% in the 'high' treatment compared to the control (39.7%). Chlorophyceae had the greatest number of affected species (8), while one species within the Cyanophyceae was negatively affected on more than one sampling day. Further, chlorophyll *a* was reduced on 4 and 5 days out of the 8 total sampling days in the 'low' and 'high' treatment, respectively, compared to the control.

Relevance: These results highlight that herbicides can cause long-term effects that can affect multiple levels of organisms disrupting population structure from bottom-up. Integrating multiple taxa and contaminants with long-term exposures in ecological risk assessments of herbicides can facilitate the ability to make predictive and mechanistic generalizations about the role of herbicides in shaping patterns of species abundance in natural systems.

Keywords: mesocosm, macroinvertebrate, herbicides, zooplankton, ecotoxicology, diuron, hexazinone
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Mixtures of Current-Use Pesticides Detected in Surface Waters of the Sacramento/San Joaquin Delta Watershed

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Current-use pesticides pose a potential threat to aquatic organisms, highlighting the need for up-to-date and robust data characterizing inputs of these contaminants to the Sacramento/San Joaquin Delta. Over the past three years, the USGS Pesticide Fate Research Group has conducted multiple research projects focused on understanding the occurrence of current-use pesticides in surface waters within the Delta watershed. Each of these studies employed consistent analytical methods and provide data for a suite of over 150 current-use pesticides and pesticide degradates. Locations sampled during these studies included small watercourses receiving runoff from adjacent agricultural lands or suburban neighborhoods, larger streams and rivers with direct input to the Delta, as well as sites located within sensitive habitats within the Delta. Although specific objectives varied from project to project, the use of common analytical methods and sampling procedures allows the data to provide a more complete perspective of pesticide inputs to the Delta.

Analysis of data acquired during these projects shows that waters entering the Delta contain mixtures consisting of a wide variety of both agricultural and urban use pesticides, with a total of over 70 different fungicides, herbicides, insecticides, and their degradates detected. The exact makeup of these pesticide mixtures varies seasonally due to changes in pesticide application patterns, as well as in response to rainfall and irrigation runoff events. Overall pesticide concentrations tend to be higher in the smaller, near-source tributary sites and lower in the tidally-mixed Delta sites. Through the use of common analytical methods, these data can provide valuable information to scientists and resource managers working to understand the role of contaminants in the Sacramento/San Joaquin Delta.

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An Investigation of Pesticide Input to the Bay-Delta Area

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This study evaluated recent pesticide input to the Bay-Delta area through physical modeling and comparison to environmental monitoring data. The model estimated pesticide mass loading to the area by assuming that all pesticides applied in the contributing hydrological areas would immediately travel toward the nearby waterways and degrade following first-order kinetics through the stream network. Pesticides were ranked after normalizing the estimated mass loading by its toxicity benchmark value. The pesticides that ranked the highest based on their use in 2012-2014 include 15 insecticides (6 pyrethroids, 4 organophosphates, diflubenzuron, etoxazole, fenpyroximate, fipronil, and pyriproxyfen), 4 herbicides (atrazine, oxyfluorfen, paraquat dichloride, and pendimethalin) and a fungicide (mancozeb). Monitoring data exist for all the pesticides listed above, except etoxazole, fenpyroximate, pyriproxyfen, and mancozeb, in the Department of Pesticide Regulation's SURF database. The limit of quantification values for several pyrethroids, organophosphates, fipronil and atrazine were sometimes above their benchmarks, which hindered the evaluation of exceedance. If only the samples with reportable concentrations are counted, bifenthrin, cyfluthrin, permethrin, chlorpyrifos, and diazinon exceeded acute and chronic benchmarks for aquatic animals; deltamethrin, lambda-cyhalothrin, dimethoate, and fipronil exceeded the chronic benchmark for aquatic animals; atrazine exceeded the acute benchmark for aquatic plants. The database also contains monitoring data for an additional 143 pesticides; only diuron had one exceedance. These findings indicate the necessity to prioritize the monitoring target and reduce the analytical methods' reporting limit.

Keywords: pesticide input, modeling, environmental monitoring
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Comprehensive Organic Contaminant Assessment and Link to Effects on Invertebrates in the Cache Slough Ecosystem

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The Cache Slough complex in the Sacramento–San Joaquin River Delta is an important habitat for endangered fish species. In order to assess toxicity towards important fish prey, the present study involved deployment of a sensitive amphipod, *Hyalella azteca*, combined with a comprehensive pesticide/organic contaminant screening of water samples during storm events. The use of high-resolution mass spectrometry allowed detection of target chemicals, but also facilitated a broad screening for suspect chemicals without reference standards. Grab samples were taken during two rain events in January and March 2016. Extracted water samples and suspended solids were analyzed by both gas chromatography high-resolution mass spectrometry (GC-TOF-MS) and liquid chromatography high-resolution mass spectrometry(LC-TOF-MS). Nearly 50 target pesticides were evaluated and the samples were screened for additional pesticides using two large spectral libraries containing over 2000 compounds. Data of the first (small) rain event showed low acute toxicity towards *H. azteca*, but more than 30 target pesticides were detected. The second (large) rain event showed high toxicity which suggests a much higher pesticide load. Obtained data are providing crucial information about chemicals that were the cause of observed toxicity, which will represent a valuable resource for future watershed management.

Keywords: toxicity, pesticides, pyrethroid insecticides, Hyalella azteca, Cache Slough, nontarget analysis
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A New Approach to Identifying the Substance Causing Mortality in Bay-Delta Toxicity Monitoring

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Problem: Monitoring programs often rely upon toxicity testing, and when toxicity is found, efforts to mitigate it require identifying the chemical(s) responsible. The approach generally used is a Toxicity Identification Evaluation (TIE) in which the sample is subjected to physical or chemical manipulations. This approach often only identifies the toxicant to major class (e.g., metal), and identification is often suggestive, rather than definitive.

Approach: We have found that the amphipod, *Hyalella azteca*, when collected from waterways routinely exposed to pyrethroid pesticides, is often resistant to them due to a mutation that prevents binding of the pyrethroid to its target site. This finding suggests a novel "biological TIE" approach in which both resistant and wild-type *H. azteca* are simultaneously exposed. Greater survival of those pyrethroid resistant would provide strong evidence that these pesticides are the agents responsible for toxicity to the wild type strain lacking the mutation.

Results: The approach was tested in Cache Slough following two rain events. Four samples were found to be toxic to the wild type strain when they were held in situ in Cache Slough throughout the rain. However, two other strains bearing the pyrethroid resistance mutation were simultaneously exposed yet unaffected. Similar results were obtained in six other waterbodies in the Bay-Delta. In all cases, the biological TIE indicates that pyrethroids were responsible for the toxicity.

Relevance: Our approach provides evidence, consistent with chemical and conventional TIE data, that pyrethroids are often the substances responsible for toxicity to the common testing species, *H. azteca*, and that toxicity is widespread throughout the Bay-Delta. As monitoring and regulatory efforts are increasingly focused on this group of pesticides, the biological TIE approach may be the best approach yet developed to establish causality. We are exploring its application to other pesticides, for which the technique also holds promise.

Keywords: Pesticides, Pyrethroids, Hyalella, Toxicity Identification Evaluation, Stormwater runoff
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Pyrethroid Insecticide Resistance is Widespread in the Non-Target Crustacean *Hyalella azteca*

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Pyrethroid insecticides are prevalent in sediments throughout the Bay-Delta Region. These pesticides are extremely toxic to aquatic invertebrates, the base of the food web for many important and declining fish species within the delta. However, our research shows that highly exposed populations of the crustacean *Hyalella azteca* have evolved resistance, with up to 550-fold increased tolerance to pyrethroids compared to base-line sensitivity of all other natural populations including those commonly used for laboratory toxicity testing. Resistance results from mutations in the target site for pyrethroids, the voltage-gated sodium channel (*VGSC*). The *VGSC* resistance mutations in wild *H. azteca* populations represent the first identified in a non-target aquatic organism, suggesting previously undescribed environmental impacts associated with pyrethroid use. Determining the extent of resistance and its correlation with pesticide levels is necessary to quantify this impact.

Approach: We sampled sixteen populations of *H. azteca* throughout California including many areas of the Bay-Delta system. Nine populations were from residential or agricultural areas with suspected insecticide use and seven populations were collected from pristine areas. Pyrethroid use was determined by measured sediment concentrations of insecticides, and 96-h toxicity bioassays were used to determine each population's sensitivity to pyrethroids. The *VGSC* was sequenced in twenty individuals from each population to determine the extent of genetic resistance.

Results: All populations collected from areas with elevated insecticide concentrations in sediments showed reduced sensitivity. Preliminary results from our genetic analysis suggests that these populations have developed resistance through genetic mutations.

Relevance: Insecticide resistance is widespread in *H. azteca* populations throughout California and is highly correlated with insecticide use. As resistant *H. azteca* could be vectors for the trophic transfer of insecticides to fish, or may be more susceptible to other climate related stressors, the widespread occurrence of insecticide resistance is concerning for the health of the delta ecosystem.

Keywords: insecticides, *Hyalella azteca*, toxicity testing, resistance
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Toxicity, Bioaccumulation and Tropic Transfer of Permethrin in Pyrethroid-Resistant *Hyalella azteca*

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Problem Statement: Some field populations of the freshwater amphipod, *Hyalella azteca*, from pesticide-exposed waterbodies demonstrate resistance to pyrethroid insecticides. However, there is a debate whether these populations will retain their resistance if held in the lab without continued pyrethroid exposure. In addition, if resistant *H. azteca* experience pyrethroid exposure, one of the possible consequences is bioaccumulation, which increases the potential for transfer of pyrethroids from the resistant individuals to higher trophic level organisms.

Approach: These issues were addressed in the current study by conducting toxicity tests with the standard laboratory-cultured *H. azteca* and resistant populations. Resistant and non-resistant *H. azteca* also were exposed to ^{14}C-labeled permethrin, and bioaccumulation and proportion biotransformed were quantified. Finally, the trophic transfer potential of permethrin via resistant *H. azteca* was demonstrated by daily feeding of permethrin-exposed *H. azteca* to fathead minnows.

Results: Toxicity tests in water with permethrin showed the 96-h LC50 of resistant *H. azteca* was 53 times higher than that of non-resistant *H. azteca*, even after the resistant animals had been held in the lab without pyrethroid exposure for 16 months. Resistant *H. azteca* were shown to bioaccumulate increasing amounts of permethrin as exposure concentrations increased. Since resistant organisms can survive in habitats that have higher pyrethroid concentrations, our results indicate they are able to accumulate more of these compounds in their tissues than their non-resistant counterparts. In the current study, fathead minnows were shown to bioaccumulate permethrin after consumption of contaminated resistant *H. azteca*.

Relevance: These results suggest that that the mutation responsible for conferring resistance in these organisms is retained within the population for many generations after exposure to pyrethroids has ceased. In addition, we found consumption of pyrethroid-resistant individuals may increase fish exposure to permethrin and its biotransformation products, which may impact wild fish populations.

Keywords: Pyrethroid-resistant Hyalella, Bioaccumulation, Permethrin, Mutation
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Multiple Stressors over Multiple Generations: Assessing the Combined Risk of Endocrine Disruptors and Climate Change

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Understanding anthropogenic impacts such as climate change and pollution on aquatic ecosystems is critical for preserving biodiversity and maintaining water quality. The pyrethroid pesticide bifenthrin is a known endocrine disrupting compound (EDC) found in biologically active concentrations in the San Francisco Bay-Delta estuary. Little is known about how elevated temperatures associated with climate change may affect the estrogenic activity of bifenthrin, particularly in species that exhibit temperature-dependent sex determination (TSD), such as the introduced species Menidia beryllina. This study investigated the effects of temperature and bifenthrin exposure on reproductive output in M. beryllina across multiple generations. Fish in the parental generation were exposed to bifenthrin, ethinylestradiol (EE2 - positive control) and methanol (solvent control) at 22°C and 28°C for 14 days prior to spawning. Embryos in the F1 generation were exposed to EDCs as larvae (until 21 dph) and then reared to adulthood (8 months) in clean water at experimental temperatures. In all F1 treatments, elevated temperature resulted in fewer viable offspring. At the time of maturity, the F1 generation underwent spawning trials to assess reproductive output and offspring viability following larval exposure. Sex ratios of the F1 generation were influenced by elevated temperature and EDCs, resulting in alteration of adaptive TSD. Fish exposed to bifenthrin during development exhibited developmental deformities. Tissues were collected from each generation to assess the effects of these stressors on the expression of genes involved in reproduction and growth. Findings from this study will be useful in determining how EDCs will impact organisms and community structure in the face of global climate change.

Keywords: Endocrine disruptors, multigenerational, ecotoxicology, multiple stressors, menidia, bifenthrin, pesticides, temperature
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