Using Whale Earplugs to Assess Chemical Profiles in Marine Ecosystems: Lifetime Contaminant Exposure and Hormone Profiles

Sascha Usenko, Baylor University, Sascha_usenko@baylor.edu
Stephen Trumble, Baylor University, Stephen_Trumble@baylor.edu
Eleanor Robinson, Baylor University, Eleanor_Robinson@baylor.edu
Charles Potter, National Museum of Natural History, Smithsonian Institution, POTTERC@si.edu
Michelle Berman-Kowalewskic, Santa Barbara Museum of Natural History, mberman@sbnature2.org

A technique combining aging with selective pressurized liquid extraction was used to reconstruct chemical profiles from an individual baleen whale earplug. Lifetime profiles for many lipophilic chemicals, including persistent organic pollutants, mercury, and hormones resulted in contaminant exposure and uptake as well as hormone response. Specifically, we quantified, DDTs, PCB's, trans-choradane and trans-nonachlor as a function of time as well as corresponding cortisol levels in a blue whale. We believe this demonstrates that long-lived whales are active marine monitoring systems with the ability record and archive data via earwax. The ecosystems these whales inhabit span the Arctic Ocean to the Southern Ocean and the development of earwax plugs as a new analytical tool for historical trend reconstruction could potentially improve our understanding of the fate and transport of contaminants on global scale as well as provide chronological profile on the health and/or stress of the whale.

Keywords: cetaceans, cerumen, persistent organic pollutants, hormones
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What do Contaminants Have to do with it? Lessons Learned from the Pelagic Organism Decline Investigations into Contaminant Effects on Fishes and Their Food Web

Randall Baxter, California Dept of Fish and Wildlife, randy.baxter@wildlife.ca.gov

Fishes in the Delta have been declining since monitoring began, but in the early 2000s the almost simultaneous sharp abundance declines of four pelagic fishes marked a dramatic tipping point now known as the Pelagic Organism Decline (POD). The diverse life histories of the four fishes suggested that more than one factor was involved and their dependence on the upper estuary for important aspects of life cycle suggested the region of effect. The conceptual model developed to investigate the POD included contaminants among the factors for investigation. Implementation of the POD investigation, started the most recent era of Interagency Ecological Program investment into contaminant effects on fishes. We learned several lessons from this work. First, effective investigations of contaminant effects on fishes takes "a village" of diverse knowledge to organize the approach to sampling and analyses. Second, development of a conceptual model incorporating individual fish species life histories and the when, where and under what conditions effects are likely to take place is invaluable. Model development should be interactive with initial stages of fieldwork and refinement ongoing thereafter. Third, a three-prong approach should be fostered: 1) field sampling near sensitive life stages to document likely contaminant actors, relevant concentrations and associated stressors; 2) laboratory studies using detected contaminants at observed concentrations and their mixtures in combination with associated stressors to determine lethal or more likely sublethal effects on the relevant life stage(s); and 3) development of quantitative models to examine the effects of multiple stressors on individuals and the population. I step through these lessons providing background and pointing out that learning occurred going through the process as well as by reviewing the results.

Keywords: Pelagic Organism Decline, collaboration, contaminants, life cycle model
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Session Time: Thursday 1:00PM – 2:40PM Room 308-310

Regulatory Challenges of Protecting Aquatic Life and Controlling Contaminants

Tessa Fojut, Central Valley Regional Water Quality Control Board,
Tessa.Fojut@waterboards.ca.gov

The Central Valley Regional Water Quality Control Board has the responsibility and authority to control discharges of contaminants to the Delta and upper watersheds. The goal is to develop effective regulation to protect beneficial uses (e.g., aquatic life) using available toxicity and environmental monitoring data. This presentation will use pesticides as an example to illustrate the regulatory process from an LC_{50} to regulation to environmental results. The Central Valley Water Board is working on a variety of regulatory approaches to control pesticide contamination, including the use of existing regulatory authority and tools (adoption of numeric water quality objectives and total maximum daily loads), as well as outreach to other agencies to request that they take action to prevent water quality degradation (e.g., Department of Pesticide Regulation and U.S. Environmental Protection Agency). Collaborative approaches, such as the Delta Regional Monitoring Program, are also being pursued to improve the quality and quantity of information available to inform decision-making and to fulfill regulatory requirements. There are challenges in all approaches and success can be difficult to measure because the effects of reducing a few contaminants may be masked by the presence of other stressors (e.g., other contaminants, degraded habitats or environmental conditions). Challenges to controlling pesticide discharges include limited toxicity and monitoring data, coordination with agencies that have authority over pesticide registration and application, and the sheer number of pesticides that are applied in the environment. Good science and creative thinking are needed to build and refine regulatory approaches and metrics of successful regulation that accomplish our goals of ecosystem protection and restoration.

Keywords: pesticides, contaminants, aquatic life, water quality, regulation, Central Valley Water Board
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Stormwater Transport of Urban and Agricultural Pesticides into Suisun Marsh

Donald Weston, University of California Berkeley, dweston@berkeley.edu
Michael Lydy, Southern Illinois University, mlydy@siu.edu

Suisun Marsh is generally regarded as important foraging and/or nursery habitat for a wide variety of fish species, including delta smelt. The main freshwater inputs to the marsh are five creeks along the northern margin, some of which drain primarily agricultural land, and some receive runoff from urban areas of Fairfield. Pesticide concentrations and aquatic toxicity were assessed in these creeks and in the marsh during a major rain event in February 2014. The creeks with primarily urban lands within their watershed contained several insecticides, any one of which would represent a threat of toxicity to aquatic species. *Hyalella azteca* toxicity was commonly seen, and there were sufficient concentrations of the pyrethroid bifenthrin to explain it. *Chironomus dilutus* toxicity was common, and fipronil concentrations were high enough to expect toxic effects to that species. Imidacloprid was present in most creeks, and present in acutely toxic concentrations in one of them. In contrast to the urban creeks, creeks draining mostly agricultural lands contained the same pesticides, though at considerably lower concentrations. In the sloughs of Suisun Marsh, dilution with waters of the Bay reduced fipronil concentrations to about 10% of those in the creeks, pyrethroids were no longer detectable, and no acute toxicity was seen. These results indicate that several pesticides in runoff are a clear threat to invertebrates of the urban creeks, and fish dependent upon these invertebrates as prey. Upon dilution in the marsh, the threat of acute toxicity to fish or their prey diminishes. Pesticide impacts, if any, to fish populations in the marsh would likely be through any trophic dependency on export of prey from the creeks, or through subtle sublethal routes such as endocrine disruption.

Keywords: Suisun, pyrethroids, fipronil, *Hyalella*, *Chironomus*, pesticides, urban runoff
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Contaminant-Related Thyroid Endocrine Disruption in California Fish

Jesus A. Reyes, Pacific Coast Environmental Conservancy, reyes@pceconservancy.org
Evan Lee, Environmental Endocrinology Laboratory, Department of Biological Sciences, California State University, Long Beach, bob71488@gmail.com
Kristy Forsgren, Department of Biology, California State University, Fullerton, kforsgren@fullerton.edu
Stephen Laczko, Environmental Endocrinology Laboratory, Department of Biological Sciences, California State University, Long Beach, Stephen.Lacsko@student.csulb.edu
Jeffrey Armstrong, Orange County Sanitation District, jarmstrong@ocsd.com
Kevin M. Kelley, Environmental Endocrinology Laboratory, Department of Biological Sciences, California State University, Long Beach, Kevin.Kelley@csulb.edu

In selected locations in San Francisco Bay and in other urban coastal aquatic environments in California, indigenous fish species have been observed to exhibit significant disruption of their thyroid endocrine system, which may be associated with impacts that threaten their health. Circulating plasma concentrations of the two thyroid hormones [thyroxine (T4) and and triidothyronine (T3)] can be substantially disrupted, commonly observed in fish residing in environments contaminated by elevated polychlorinated biphenyls (PCBs; mostly non-coplanar, lower-chlorinated congeners), chlordane pesticide compounds, and polybrominated diphenyl ethers (PBDEs). Our studies have traced these impacts to two principal underlying mechanisms. The first is an impact on the enzyme, 5'-monodeiodinase, responsible for conversion of T4 into the more active T3. The second is a direct thyroid gland effect, observed morphologically as evaluated by histological methods, and also observed by a failure of the thyroid gland to normally produce thyroid hormones. These mechanisms of effect are related to distinct classes of contaminants present in the environment. This presentation will discuss results from continuing studies on the relationships between contaminants of emerging concern (CECs) and thyroid endocrine disruption, and the associated impacts on physiological function and potential impacts on health. [Supported by NOAA-USC Sea Grant Program and Pacific Coast Environmental Conservancy]

Keywords: Contamination Thyroid Disruption, Aquatic CEC's, Compounds, Histology
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Predicted Population Decline in Fish Due to Bifenthrin Exposure: Implications for Aquatic Ecosystems in the Bay-Delta

Susanne Brander, University of North Carolina, Wilmington, branders@uncw.edu
Bryan Cole, University of California, Davis, bjcole@ucdavis.edu
Ken Jeffries, University of California, Davis, kmjeffries@ucdavis.edu
Bethany DeCourten, University of North Carolina, Wilmington, bmd5520@uncw.edu
Will White, University of North Carolina, Wilmington, whitejw@uncw.edu
Nann Fangue, University of California, Davis, nafangue@ucdavis.edu
Richard Connon, University of California, Davis, reconnon@ucdavis.edu

Bifenthrin, now one of the most commonly used pyrethroid pesticides, is known to interfere with hormonal signaling in fishes at concentrations commonly present in the San Francisco Bay and the Sacramento-San Joaquin Delta. As such, our work with *Menidia beryllina*, an established estuarine model species that frequently encounters pyrethroids in stormwater run-off and effluent, seeks to clarify how low concentrations of bifenthrin interfere with hormonal signaling and reproduction in fish, and how this can be extrapolated to the population level. We conducted 14d exposures with juveniles (60 day old) to three part per trillion concentrations of bifenthrin (0.5, 5, 50 ng/L) and evaluated global gene expression. We also exposed reproductive adult *fish* to 0.5 ng/L bifenthrin for both 7 and 21 days, collecting eggs following the 7d exposure and collecting eggs daily during the 21 day exposure. Exposure to bifenthrin caused significant differential expression of genes related to reproduction and immune function, with indications that bifenthrin could be a carcinogen. Both the 7 and 21 day spawning assays resulted in a 30% reduction (ANOVA, $p < 0.05$) in fertilized egg output from bifenthrin-treated animals. Our population dynamic model predicts that this reduction in fertilized egg abundance would cause a significant decline in a putative population over time, dependent on the degree of masculinization or feminization potentially caused by bifenthrin exposure. Currently work is underway to determine whether *M. beryllina* exposed during the larval period of sex determination have an altered sex ratio upon adulthood. Taken together these experiments quantify the impact of this now ubiquitous pyrethroid on multiple fish life stages, forges links between molecular and reproductive effects, and allows for better assessment of risk to aquatic ecosystems and to human health.

Keywords: pyrethroid, endocrine disruptor, population decline, reproduction, silversides
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Integration of both Exposure and Effect in a Complex Watershed

Debra Denton, U.S. Environmental Protection Agency, Region IX, denton.debra@epa.gov
Adam Biales, U.S. Environmental Protection Agency, biales.adam@epa.gov
Dan Riordan, California Department of Water Resources, dan.riordan@water.ca.gov
Richard Breuer, State Water Resources Control Board, Rich.Breuer@waterboards.ca.gov
Angela Batt, U.S. Environmental Protection Agency, batt.angela@epa.gov
David Crane, California Department of Fish and Wildlife, david.crane@wildlife.ca.gov
Heiko Schoenfuss, Aquatic Toxicology Laboratory, St. Cloud State University, schoenfuss@stcloudstate.edu

Due to the diversity of sources of contaminants and stressors, linking exposure and effects in complex watersheds is difficult. This linkage typically relies upon relatively limited chemical occurrence data loosely coupled with population or community level assessments. Increased discriminatory power may be gained by approaching watershed level assessment in a more holistic manner drawing from a number of disciplines that target endpoints spanning levels of the biological hierarchy. Using the Sacramento River, from the Colusa Basin Drain to Hood station as a case study, the present study aimed to 1) characterize the effects of geographic and temporal variability through the integration of suborganismal, tissue and individual level endpoints, as well as extensive chemical analyses; 2) evaluate the added benefit of non-traditional assays, such as C-start performance, in linking cause and effect in a complex watershed; and 3) provide an experimental design workflow for these types of assessments. Sites were selected to target inputs into the Sacramento River as it transitions from an agricultural to an urban landscape. Chemical analyses were conducted on surface water samples at each site in both the spring and fall for pesticides, hormones, pharmaceutical and personal care products (PPCPs). PPCPs were more often detected across sampling events in the fall; however, at the farthest downstream site more analytes were detected and their concentrations were greater in the spring. The results of gene and protein expression assays targeting endocrine and reproductive effects were inconsistent across seasons. Larval mortality as a response to effluent was seen in both seasons; however, behavioral changes were only observed in the spring. Together results indicate significant influence of seasonality on chemical and biological endpoints, which contributes to a complicated view of the watershed.

Keywords: Contaminants, Sacramento River, Pharmaceutical and Personal Care Products, Endpoints
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Connecting Fish Tissue Selenium Concentrations to Sources and Exposure in a Dynamic Estuary: The Case of Sacramento Splittail

Robin Stewart, US Geological Survey, arstewar@usgs.gov
Amy Kleckner, US Geological Survey, kleckner@usgs.gov
Frederick Feyrer, US Geological Survey, ffeyrer@usgs.gov
Rachel Johnson, Cramer Fish Sciences and UC Davis, rachel.johnson@fishsciences.net

We identify several key factors controlling the transfer of selenium (Se) from water through an invasive clam *Potamocorbula amurensis* to a migratory native fish Sacramento splittail in the San Francisco Bay and Delta ecosystem. First, Sacramento splittail showed a significant difference in tissue Se concentrations depending on size and time spent foraging in the estuary. Sulfur isotope ratios indicated that these differences were linked to an ontogenetic shift in splittail diets to include the clam *P. amurensis* found in the estuarine portions of the Bay. Second, clam Se concentrations were spatially variable, with the highest concentrations focused in the northern reach of San Francisco Bay, nearest Carquinez Strait and Suisun Bay, resulting in variable dietary exposures depending on where the splittail were feeding. A third factor was the influence of freshwater inflow on seasonal and inter-annual variation in Se bioaccumulation by clams whereby the highest concentrations in clams were observed in the late fall and early winter, just prior to spawning of several native fish species, as well as in years of low freshwater inflow. Collectively, these factors highlight the importance of considering both ecology (foraging location and diet) and hydrology/hydrodynamics (e.g. freshwater inflow) in determining the timing and potential range of aqueous Se concentrations and how that translates into risk to native species.

Keywords: Selenium, bioaccumulation, ecology, food webs, invasive clams
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Physiological Responses to High Water Temperature in Longfin Smelt and Delta Smelt

Ken Jeffries, University of California Davis, kenmjeffries@gmail.com
Richard Connon, University of California Davis, reconnon@ucdavis.edu
Brittany Bjelde, University of California Davis, bebjelde@ucdavis.edu
Lisa Komoroske, University of California Davis, lmkomoroske@ucdavis.edu
Monica Britton, University of California Davis, mtbritton@ucdavis.edu
Galen Tigan, University of California Davis, gttigan@ucdavis.edu
Joan Lindberg, University of California Davis, jclindberg@ucdavis.edu
Ted Sommer, California Department of Water Resources, ted.sommer@water.ca.gov
Nann Fangue, University of California Davis, nafangue@ucdavis.edu

Climate change is one of the most serious issues faced by Bay-Delta managers now and into the future. Most fishes, as ectotherms, are unable to regulate their body temperature and therefore must perform all physiological processes at the temperature of the surrounding environment. Because of the importance of water temperature on physiological function and determining habitat suitability, temperature has been termed the "ecological master factor" in fishes. Predicted future increases in water temperature may greatly influence the ability of some fish species to survive or respond to other environmental stressors in the Bay-Delta system. Two species of concern are the critically endangered delta smelt (*Hypomesus transpacificus*) and the threatened longfin smelt (*Spirinchus thaleichthys*). However, little is known about the mechanistic processes involved in thermal tolerance, and whether these species can cope with increases in water temperature in the Bay-Delta. We determined the critical thermal maximum, a repeatable and standardized method to estimate tolerance to acute temperature changes, for 50 day old fish which was 27.5°C and 25°C for delta smelt and longfin smelt, respectively. We then acutely exposed fish to an environmentally-relevant temperature of 20°C and compared metabolic rate and gene expression responses to a 14°C handling control group. We used a direct RNA-sequencing approach, and compared gene expression with metabolic rates changes, to identify physiological responses associated with temperature in these important Bay-Delta species. Because of the direct and indirect role of temperature on fish, characterizing the physiological responses to changes in water temperature will enable a better understanding of how temperature might interact with other stressors in the Bay-Delta system and impact fish populations. This project uses state-of-the-art approaches to generate molecular tools for understanding the effects of environmentally-relevant high water temperatures on longfin smelt and delta smelt to aid in conservation efforts and management of these species.

Keywords: Longfin Smelt, Delta Smelt, Climate Change, Physiology
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Characteristics of Suspended Solids Affect Bifenthrin Toxicity to Calanoid Copepods of the San Francisco Estuary

Sarah A Lesmesiter, University of California Davis, Sarah.Lesmeister@water.ca.gov
Emily Parry, University of California Davis, Emily.Parry@dtsc.ca.gov
Swee J. Teh, University of California Davis, sjteh@ucdavis.edu
Thomas M. Young, University of California Davis, tyoung@ucdavis.edu

Bifenthrin is a pyrethroid pesticide that is highly toxic to aquatic invertebrates. The dissolved concentration is generally thought to be the best predictor of acute toxicity. However, for the filter feeding calanoid copepods, *Eurytemora affinis* and *Pseudodiaptomus forbesi*, ingestion of pesticide-bound particles could prove to be another route of exposure. This study investigated bifenthrin toxicity to *E. affinis* and *P. forbesi* in the presence of suspended solids from municipal wastewater effluent and surface water of the San Francisco Estuary. Suspended solids mitigated the toxicity of total bifenthrin to *E. affinis* and *P. forbesi* but mortality was higher than what would be predicted from dissolved concentrations alone. Our results indicate toxicity and bioavailability of particle associated bifenthrin was significantly correlated with high counts of particle sizes at 0.5-2µm. Potential explanations could include direct ingestion of bifenthrin bound particles, changes in food consumption and feeding behavior, and physical contact with small particles. The complex interactions between pesticides and particle types and sizes demonstrate a need for future ecotoxicological studies to investigate the role of particle sizes on aquatic organisms in San Francisco Estuary.

Keywords: Copepods, Bifentrhin, Pyrethroid pesticide
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