Update Concerning Toxicity in the Delta
October 2009

Water quality in the Bay-Delta has been a concern for the Water Boards for as long as the Boards have existed. Over the years the contaminants and discharge sources have changed, and there have been significant improvements in controlling most types of contaminants. Nevertheless, there still are a suite of contaminants and source categories that pose a concern for some Delta beneficial uses, and there is also concern for an emerging list of new contaminant categories (*e.g.*, pharmaceuticals and endocrine disrupters). Contaminants and other forms of water pollution in the Delta impair wildlife, aquatic life, recreation, hydropower, drinking water, and agriculture beneficial uses. As a result, the Bay-Delta is listed as impaired for unknown toxicity and a number of contaminants, such as pesticides and mercury. Sources of these contaminants include agricultural, municipal and industrial wastewater; urban storm water discharges; discharges from wetlands; channel dredging activities; and abandoned mines.

The Water Boards have regulatory programs that control discharges of wastes from wastewater treatment facilities, industrial facilities, urban areas, irrigated agricultural lands, dredging operations, and other sources of wastewater to the Bay-Delta and tributaries. If a single discharger is responsible for an impairment, the Water Boards can address the impairment by taking appropriate regulatory action (*e.g.*, revising the permit, taking enforcement action, etc). The Water Boards address water quality impairments that are caused by multiple dischargers by developing Total Maximum Daily Loads (TMDLs), which set water quality objectives or targets and allocate allowable loads to sources of contaminants. TMDLs are implemented through Waste Discharge Requirements (WDRs) and conditional waivers of WDRs. Implementation of TMDLs has reduced levels of some contaminants in the Delta. For example, the incidences of toxicity due to organophosphorus pesticides, such as chlorpyrifos, have significantly declined compared to observations in the early 1990's.

Irrigated agriculture is one source of pesticides and other pollutants in our waterways. The Central Valley Water Board has been working with agricultural water quality coalitions, through the Irrigated Lands Regulatory Program, to identify constituents of concern through monitoring, identifying sources of pollutants, and developing and implementing corrective actions when needed. Much work remains to be done, but monitoring data have not shown toxic concentrations of pesticides in Delta waterways that would indicate that runoff from agricultural lands is a definitive cause of the POD.

National Pollutant Discharge Elimination System (NPDES) permits for most wastewater treatment plants in the Delta adopted over the last decade have become more stringent over time after recognizing the critical conditions of the Delta, including limited dilution, receiving water toxicity, low dissolved oxygen, and the presence of threatened and endangered species. Many treatment plants have either completed major upgrades to include tertiary filtration and nitrification/denitrification to remove ammonia, or are nearing completion of the upgrades. Stockton, for instance, recently completed a major expansion of their facility that includes upgrading of its tertiary filtration system and installation of ammonia removal systems. The upgrades address toxicity and dissolved oxygen issues. One notable exception is the Sacramento Regional Wastewater Treatment Plant (SRWTP), which has less stringent permit requirements due to the large dilution effects of the Sacramento River to which they discharge. The Central Valley Water Board is working with the SRWTP to evaluate the potential impacts of their

discharge on delta smelt and algal primary production in the Delta. The need for more stringent permit requirements will be evaluated once the studies are complete.

State Water Board staff is currently working on revising the toxicity control provisions contained in the Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California. Elements of the proposed revisions include establishing numeric toxicity objectives, establishing the appropriate statistical methods to use in determining whether a sample is toxic, and establishing minimum test frequencies for inclusion in permits. Staff is also exploring possible revisions in determining when toxicity limits must be incorporated into permits (i.e., when a discharger has reasonable potential to cause or contribute to an exceedance of the objectives).

While increased regulatory requirements on waste discharges to the Delta and upstream tributaries have reduced the frequency and severity of documented toxicity in the Delta, toxic events, at a reduced frequency and intensity, continue to occur. Despite the efforts of the Water Boards to control contaminants, recent declines in the abundance of pelagic fish species in the Delta have heightened concern about contaminants in the Delta and the role they might play in the declines. The Water Boards have initiated additional focused actions to address this heightened concern. Focused actions are targeted toward ensuring that adopted TMDLs are efficiently implemented and that new TMDLs are adopted in a timely manner, evaluating the potential impacts of pyrethroid pesticide and ammonia concentrations in Delta waters on organisms, increasing coordination of monitoring and assessment efforts, increasing oversight of regulated dischargers, decreasing response time to toxic incidences, and working with researchers to address water quality problems associated with blue-green algal blooms in the Delta.

In addition to its regulatory programs, the Central Valley Water Board has supported or is closely monitoring a number of efforts designed to identify, evaluate, and address existing and potential sources of toxicity in coordination with the State Water Board and San Francisco Bay Water Board through the Bay-Delta Team; the Interagency Ecological Program (IEP); CALFED Science Program; researchers; and other stakeholders.

<u>Development of a Delta Regional Monitoring Program for Contaminants</u>

A diverse array of agencies and other entities monitor water quality, flows, and ecological conditions in the Delta. However, under the current monitoring framework, our ability to develop an integrated assessment of water quality in the Delta is limited by a number of factors, including variability in the level of assessment, reporting, and access to the data among these programs. In addition, there is a general recognition that significant data gaps exist, notably with respect to contaminants.

The State Water Board and Central Valley Water Board have initiated an effort to develop a Delta Regional Monitoring Program (Delta RMP) for contaminants using a collaborative stakeholder process in coordination with similar efforts in the Bay-Delta and upstream tributaries. Development of the Delta RMP is expected to proceed in a phased approach. The first phase of program development will focus on mechanisms for regularly compiling, assessing and reporting data from existing, ongoing monitoring efforts. The goal is to complete Phase I with a visible, tangible product such as a “Pulse of the Delta” type of synthesis report that addresses an initial set of program questions.

The second phase is expected to define the long-term structure and goals of a Delta RMP that is fully integrated and coordinated among all programs.

Two key products are currently being prepared in support of this effort: (1) the Contaminants Synthesis Report (UC Davis researchers) and (2) a summary of existing water quality monitoring programs in the Delta (Aquatic Science Center). The Aquatic Science Center report was recently distributed to representatives of the monitoring programs discussed in that report for their review and comment prior to public distribution. The Delta RMP planning team (Water Boards, Aquatic Science Center, and Dr. Brock Bernstein) is currently revising the report in response to comments received and anticipates releasing the Draft Final report for public distribution in October 2009. Public distribution of the Contaminants Synthesis Report is anticipated in November 2009.

The planning team is also developing straw proposals for distribution to stakeholders that address a number of key issues including governance, monitoring questions, data integration, funding, and coordination with other programs. These proposals are made available on-line at the Central Valley Water Board's RMP website as they are completed. Following public distribution of the two reports discussed above, stakeholder meetings will be convened to further discuss governance options, and initiate discussions concerning monitoring questions, funding options, data integration, and other relevant topics.

Additional information concerning the Delta RMP planning effort can be found on-line at: http://www.waterboards.ca.gov/centralvalley/water_issues/delta_water_quality/comprehensive_monitoring_program/index.shtml.

Delta Smelt Sensitivity Studies

In 2008, the UC Davis Aquatic Toxicology Laboratory (UCD ATL) conducted a pilot study to assess the potential acute toxicity of ammonia and treated wastewater effluent from the SRWTP to larval delta smelt. The toxicity testing results suggest that ammonia concentrations present in the Sacramento River below the SRWTP were not acutely toxic to 55-day-old delta smelt (Werner *et al*. 2009). The results from this study were consistent with total ammonia and un-ionized ammonia effect concentrations established for 50-day-old delta smelt using filtered hatchery water (UCD ATL unpublished data, Werner *et al*. 2009). At 50 days old, delta smelt are about as sensitive to total ammonia and un-ionized ammonia as salmonid species, and about five times more sensitive than larval fathead minnows (UCD ATL unpublished data, Werner *et al*. 2009), a common toxicity test species.

Two follow-up studies were completed recently: (1) a confirmation test designed to assess whether Delta smelt survival is negatively impacted by one or more contaminant(s) that are positively correlated with ammonia from SRWTP and (2) a test to establish ammonia effect concentrations (*e.g.*, LC_{50}) for two delta smelt life stages (larval and juvenile). The preliminary results from the first of these tests were presented at the Ammonia Summit. Consistent with previous results, the test demonstrated that ammonia levels in the Sacramento River below SRWTP are not acutely toxic to delta smelt. However, the test results also suggest that additional toxic contaminant(s) were present in the effluent. The additional contaminant(s) have not been identified yet. The acute no observed effect concentration (NOEC) and lowest observed effect

concentration (LOEC) of the unknown contaminant(s) (effluent mixed into upstream river water) were nine and 18 percent effluent, respectively. The SRWTP discharge flow volume is typically two to three percent of river flow volume, but on occasion may be as high as seven percent. The present NOEC and LOEC values are based on only one set of toxicity testing results. Additional studies are needed to better characterize the range of NOEC and LOECs of the unknown contaminant(s). This information is needed to assess the likelihood of chronic toxicity to delta smelt in the river and determine whether toxicity identification evaluations are needed. Draft final reports are currently in preparation and are anticipated to be completed in November 2009.

Additional information concerning ammonia-related research can be found in the ammonia update and on-line at:
http://www.waterboards.ca.gov/centralvalley/water_issues/delta_water_quality/ambient_ammonia_concentrations/index.shtml

Interagency Ecological Program Toxicity Testing

Since 2005, the UCD ATL has conducted toxicity testing of waters collected from the Bay-Delta as part of the IEP's investigation of the role of contaminants in the POD. Studies in 2005 and 2006 focused on the summer months when juvenile delta smelt are present in the Delta. To characterize toxicity during the smelt spawning period better, bi-weekly toxicity screening was initiated in January 2007 and continued through 2009.

In 2005 and 2006, a low (<5 percent) frequency of occurrence of toxicity was observed in laboratory toxicity tests using the amphipod *Hyalella azteca* (Armor *et al*. 2006). The frequency of toxic events was higher in 2007, and observed in locations where delta smelt larvae were present and where delta smelt were presumed to be spawning (i.e., lower Sacramento River and the Cache Slough complex). The screening tests suggested organophosphorus (OP) pesticides or pyrethroid pesticides were potential causes of the toxicity to *H. azteca*; however, follow-up studies were inconclusive and chemical analyses either detected no pesticides, or the concentrations detected were not high enough to cause toxicity to the test species.

Larval delta smelt toxicity tests were conducted simultaneously with a subset of the *H. azteca* toxicity tests. Results from 2006 indicate that delta smelt may be more sensitive to toxicants, or perform poorly (*e.g.*, higher mortality due to physical stress) in laboratory toxicity tests, when waters tested were of low turbidity and salinity. There is preliminary indication that disease organisms may play a role in reducing survival under low salinity conditions (Werner *et al*. 2008a). No significant mortality of larval delta smelt was found in the 2006 toxicity tests, but there were two instances of significant mortality in June and July of 2007 (Werner *et al*. 2008a). In both cases, the water samples were collected from sites along the Sacramento River and had relatively low turbidity and salinity. Neither of these instances coincided with toxicity to *H. azteca*. The delta smelt toxicity test procedures are under development and continue to be refined. As yet, no toxicity identification evaluation methods are available to determine the cause of the observed toxicity.

In 2008, few incidents of toxicity to *H. azteca* or delta smelt were observed (Werner *et al*. 2009, Werner *et al*. unpublished data). Based on preliminary results of tests conducted through May, few incidents of toxicity to delta smelt and no incidents of toxicity to *H. azteca* have been observed in 2009 (Werner *et al*. unpublished data).

Pyrethroid Pesticides Studies

The Surface Water Ambient Monitoring Program (SWAMP) recently funded a study conducted by Dr. Weston (UC Berkeley) to assess the sources (*e.g.*, municipal wastewater treatment plants, urban runoff, agricultural discharges, and rivers), seasonality, and toxicity of pyrethroid pesticides in the Sacramento-San Joaquin River Delta. Dr. Weston found that virtually all urban runoff from the three urban areas studied (Sacramento, Stockton, and Vacaville) contained pyrethroids, typically at four times the concentration that would be toxic to the toxicity test species (i.e., paralyze *H. azteca)*. Approximately two-thirds of the undiluted effluent samples from the wastewater treatment plants contained detectable pyrethroids, typically at about 0.5-1.5 times the concentrations that would be expected to cause toxicity. Approximately ten percent of agricultural runoff samples tested were toxic, and in every case, could be linked to the pyrethroid lambda-cyhalothrin or the organophosphorus insecticide, chlorpyrifos. Dr. Weston also found repeated toxicity, linked to pyrethroids, in the American River after several storm events. Pyrethroid pesticides were detected in the Sacramento River and San Joaquin River, but the two rivers rarely tested toxic. The results from this study will be summarized in manuscripts that will be submitted for publication in peer-reviewed scientific journals.

Copepod Toxicity Studies

In April and May 2008, Dr. Teh (UC Davis) conducted a pilot study with the copepod *Eurytemora affinis*, an important food species for delta smelt and other larval fish. Significant toxicity was observed in samples from the lower Sacramento River and Cache Slough area (Teh *et al*. 2009). The same samples were not toxic to *H. azteca*, indicating that *E. affinis* may be more sensitive than the standard test species. Dr. Teh recently conducted a follow-up study to determine the LC_{10} and LC_{50} values of copper, un-ionized ammonia, and three pyrethroid pesticides (bifenthrin, cyfluthrin, and permethrin) for *E. affinis*. The preliminary results of which were presented at the Ammonia Summit, an IEP Workshop held on 18-19 August 2009, and are included below in Table 1. Follow-up monitoring and data evaluation are needed to determine whether concentrations of these contaminants occur in the Delta at levels that approach or exceed those that would be expected to cause acute toxicity and to assess the potential for chronic toxicity.

Table 1. 96-hour LC_{10} and LC_{50} values for *Eurytemora affinis* using the EPA Probit Analysis Program[1]

Chemicals	**LC_{10}**	**LC_{50}**
Total Ammonia (mg/L; pH 8.1)	7.01 (5.50, 8.71)[2]	10.97 (9.76, 11.96)
Un-ionized Ammonia (mg/L; pH 8.1)	0.46 (0.35, 0.55)	0.78 (0.68, 0.86)
Copper (ug/L)	1.42 (0.61, 1.45)	3.48 (2.85, 4.15)
Bifenthrin (ng/L)	3.93 (1.49, 5.99)	13.27 (8.88, 17.60)
Permethrin (ng/L)	83.37 (38.71, 110.83)	158.08 (125.55, 175.99)
Cyfluthrin (ng/L)	1.40 (0.05, 2.89)	12.72 (8.05, 55.55)

[1] Source – Preliminary unpublished data as presented at the Ammonia Summit, the presentation can be viewed on-line at: http://www.waterboards.ca.gov/centralvalley/water_issues/delta_water_quality/ambient_ammonia_concentrations/index.shtml

[2] 95% confidence intervals are indicated in parentheses

[3] Need additional test at lower concentration

IEP Pelagic Organism Decline Contaminants Work Team

Central Valley Water Board staff serves as active members of the IEP Pelagic Organism Decline (POD) Contaminants Work Team (CWT). This work team, composed of agency staff and stakeholders, is tasked with helping to determine whether contaminants can be implicated in the POD by: identifying studies investigating contaminant impacts on Delta species; reviewing contaminant data and population dynamics of key species, producing conclusions about which stressor or stressors are causing the impairment, identifying data gaps and providing managers recommendations on areas where research should be undertaken to better evaluate contaminant impacts; and recommending follow-up work to confirm or refute important study results. The CWT tracks IEP- and non-IEP-funded studies investigating the POD. Whenever possible, the CWT acts as a liaison to encourage cooperation and coordination among such studies to allocate resources most efficiently and promote greater understanding of study results.

Total Maximum Daily Loads

TMDLs have previously been adopted for diazinon and chlorpyrifos in the Delta, Sacramento River, and San Joaquin River. These TMDLs are being implemented in NPDES permits (wastewater and municipal storm water) and our Irrigated Lands Regulatory Program. In addition, urban uses have been reduced as a result of use restrictions. A valley-wide pesticide TMDL is under development that will address chlorpyrifos and diazinon in valley floor water bodies that are tributary to the water bodies mentioned above and address pyrethroid pesticides. The pyrethroid pesticide TMDL is scheduled for Regional Board consideration by June 2011.

The Delta is impaired due to elevated concentrations of mercury in fish. A primary impact on the Delta is that some types of wetlands enhance production of methylmercury. The Delta mercury TMDL is scheduled for completion in early 2010.

Additional Research Needs

All our work will be closely coordinated with the State Water Board and San Francisco Bay Water Board through the Bay-Delta Team. In addition, staff will discuss these recommendations at the IEP POD Contaminants Work Team meetings, along with recommendations of other parties.

American River Pyrethroid Follow-up Study - The repeated appearance of pyrethroid-related toxicity to *H. azteca* in the lower American River, following winter storm events is of particular concern. Toxicity to *H. azteca* extended over at least 20 miles of the river on one occasion and intermittently over 30 miles on another. There was a significant correlation between bifenthrin concentration and *H. azteca* toxicity. These findings indicate a compelling need to further investigate the sources and effects of pyrethroid pesticide inputs to the lower American River. Findings from such a study would support general SWAMP objectives, and would be of particular relevance to the NPDES storm water program and the Department of Pesticide Regulation's on-going pyrethroid re-evaluation.

Sediment Toxicity Identification Evaluation - Pollutants can concentrate at toxic levels in benthic environments (*e.g.*, bedded sediments in depositional areas of streams), and sediment toxicity is commonly observed in numerous California waterways. A critical

need has been identified for the development of better techniques to extract and recover organic chemicals in sediment interstitial water, as part of the TIE Phase II toxicant identification process.

Toxicity of Contaminant Mixtures and Multiple Stressors - Contaminants in the Delta and the majority of other surface water bodies often occur as complex mixtures and usually come from a variety of sources. The toxicity of contaminant mixtures may be significantly different than that of individual chemicals (Buhl 2002). The effects of contaminant mixtures in the presence/absence of multiple stressors, and their influence on the susceptibility of resident aquatic species are little understood and warrant further investigation.

Delta Smelt, Unidentified Toxicant Follow-up – Recent UC Davis Aquatic Toxicology Laboratory test results suggest that additional toxic contaminant(s) were present in the SRWTP effluent. The additional contaminant(s) have not yet been identified. The NOEC and LOEC of the unknown contaminant(s) (effluent mixed into upstream river water) are nine and 18 percent effluent, respectively. The present NOEC and LOEC values are based on only one set of bioassay measurements. Additional studies are needed to better characterize the NOEC and LOEC ranges of the unidentified toxicant.

Additional research is also needed to determine the effects of emerging contaminants, such as endocrine disrupting chemicals, on the Delta ecosystem. Further studies designed to validate the ecological relevance of biomarkers are also warranted. The identification of causal mechanisms and ecological relevance associated with the results of biomarker studies are necessary to evaluate the need for additional regulation. As these issues are not unique to the Delta, they are better addressed on a statewide basis.