CALFED Workshop Summary: The Development of a Research Framework to Assess the Role of Ammonia/Ammonium on the Sacramento-San Joaquin Delta and Suisun Bay Estuary, March 10 and 11, 2009, Sacramento

Executive Summary

On March 10 and 11, 2009, the CALFED Science Program hosted a workshop that led to the development of a framework for research to address the role of ammonia-ammonium (ammonia(um)) in the ecosystem of the Sacramento-San Joaquin Delta (Delta) and Suisun Bay (Research Framework).

Central to the workshop discussions were the low primary productivity in Suisun Bay and the role that ammonia(um) and other factors such as flow and grazing by *Corbula amurensis* (overbite clam) may have in the low productivity. A panel of national experts (Panel) provided recommendations for a path forward to identifying the role of ammonia(um) in the ecosystem. The principal recommendation of the Panel and the primary science gap identified is the need to develop an integrative model for the lower Sacramento River, Delta, and Suisun Bay. The components of this model are hydrology, biogeochemistry of nitrogen, and trophic structure and function. The model is to integrate these components and provide for feedback mechanisms between the components and resultant impacts on the food web.

Background

A paper was prepared for the workshop that provides background information on the Delta and Suisun Bay biological resources and summarizes recent studies on the occurrence and interactions of ammonia(um) with the Delta and Suisun Bay ecosystem. This document, along with relevant peer reviewed journal articles set the stage for the workshop discussions and can be found at CALFED Science web page for the ammonia(um) workshop.

Additional background information was provided in introductory presentations by CALFED Lead Scientist Dr. Cliff Dahm on ammonia(um) chemistry and by the Interagency Ecological Program Lead Scientist Dr. Anke Mueller-Solger who presented an overview of what is known about ammonia(um) in the Delta and Suisun Bay. These presentations can be found along with other workshop presentations and workshop materials at CALFED Science web page for the ammonia(um) workshop.

Introductory presentations

The Panel also provided introductory presentations on their professional experience as it related to the issues in the Delta and Suisun Bay. These presentations are also posted on the workshop website. Highlights of their presentations follows:

Dr. Hans Paerl, University of North Carolina

Dr. Paerl presented information on factors that regulate the quantity and quality of primary production. Of particular importance are the following points:

- Phytoplankton will use whatever form of nitrogen (ammonia, nitrate, or urea) is available. Uptake of the various forms of nitrogen reflects their availability and concentration (Paerl, Slides 6 and 7).
- Ammonia(um) is the preferred form of nitrogen by a wide range of phytoplankton and is more biostimulatory than nitrate (Paerl, Slide 9).
- Nitrogen source can affect cyanobacteria dominance. For example, in one study ammonia(um) enrichment favored the growth of cyanobacteria while nitrate favored a dinoflagellate (Paerl, Slide 10).
- Nitrogen and its speciation varies spatially and temporally within an estuary (Paerl, Slides 3, 5, and 6) and is an important consideration for the internal loading of ammonia(um).
- Phytoplankton groups with rapid growth rates such as diatoms are favored in estuaries with high flow rates (short residence times) while cyanobacteria are favored in slow moving waters (longer residence times) (Paerl, Slides 13 and 14).

Dr. Amelia Ward, University of Alabama
Dr. Ward has studied light intensity and its influence on the form of nitrogen utilized by cyanobacteria. In low light environments (high turbidity) ammonia(um) uptake is preferred over other forms of nitrogen for the growth of cyanobacteria, especially *Microcystis sp*.

Dr. Patrick Mulholland, Oak Ridge National Laboratory
Dr. Mulholland noted that while it may not be practical to add and trace isotopically distinct nitrogen in the Delta and Suisun Bay, specific sources such as wastewater may have a distinct isotopic signature (fractionation) that could be used to study ammonia(um) fate.

Dr. Joseph Meyer, University of Wyoming (retired)
Dr. Meyer presented information on recent developments in ammonia toxicity and important factors to consider in assessing ammonia(um) toxicity, including the following:

- The USEPA water quality criteria are based on total ammonia (un-ionized and ionized). Total ammonia 50% Lethal Concentration (LC_{50}) is a function of pH (Meyer, Slides 2 and 6).
- When considering the toxicity of un-ionized ammonia alone, the LC_{50} increases with pH up to about pH 8 (Meyer, Slides 3 and 4). The implication is that un-ionized ammonia is about five times as toxic at pH 6.5 as at pH 8.

Facilitated Discussions
Following the introductory presentations, facilitated discussions were lead by Drs. Dahm and Mueller-Solger. The discussions were organized into the three topic areas of 1) sources, fate and transport, 2) food web interactions, and 3) ecotoxicology.

1) Sources, Fate and Transport
The discussion on fate and transport focused on a system modeling approach that integrates the biogeochemistry (transformation processes such as nitrification and

denitrification), biological processes (nutrient uptake and primary production) and hydrodynamics in the Delta and Suisun Bay. This approach will provide a better understanding of how the system functions and the how various components interact to make predictions of how changes in nutrient loading and transport will impact the ecosystem; for example reductions in ammonia loading or conversion of ammonia discharges to nitrate are scenarios that could be tested with a systems modeling approach.

The Delta Simulation Model II (DSM2) model developed by the California Department of Water Resources (DWR) was discussed as a possible starting point. This one-dimensional hydrodynamic model has been used in the lower San Joaquin River and has a salinity component and the capability to include nitrogen and dissolved oxygen (DSM2-Qual). This model could potentially be adapted for the integrative modeling effort. The need for more sophisticated modeling approaches was also discussed.

Another discussion involved the need to construct nitrogen budgets and in particular consider other sources of nitrogen beyond ammonia(um) from the Sacramento Regional Wastewater Treatment Plant (SRWTP). These include:

- Organic nitrogen from the SRWTP and other sources,
- Internal sources of ammonia(um) from the cycling of nitrogen (see Dahm, Slide 8),
  - Excretion by bivalves
  - Biotic processes such as nitrogen fixation, nitrification, and denitrification.
  - The role of macrophytes in the nutrient budget.
- Atmospheric deposition including wet and dry nitrogen inputs, and
- Agricultural sources of nitrogen and forms (e.g. nitrate, ammonia(um), and organic-N).

Workshop participants discussed their experience with the DSM-2 model in the San Joaquin River and potential limitations and additional factors to consider:

- Internal ammonia(um) loading from sediments was found to be very small.
- The Delta and Suisun Bay environment is different from the San Joaquin River, including differences in water movement, oxygen stratification and redox potentials that would impact the fate of ammonia(um).
- Stable isotopes are an important tool to discern sources, identify fate pathways, and rate constants.
- Tidal influences must be considered and included in the modeling.
- Internal regeneration of ammonia(um) from nitrogen cycling is likely to be an important process in the Delta and should be considered in the modeling.

2) <u>Food Web Interactions</u>

The discussion of the interactions of ammonia(um) with the food web centered on three topic areas most frequently raised by workshop participants; 1) the role of nutrients, 2) the form of nitrogen in the aquatic ecosystem, and 3) gradual changes in the Delta environment in relation to rapid shifts such as the POD.

Two inter-related questions were raised relating to nutrients; are nutrients important and what if all of the nitrogen was in the form of nitrate rather than ammonia(um)? The discussions over these topic areas were interrelated and centered on the observed low primary productivity in Suisun Bay and the potential role of ammonia(um) versus grazing of phytoplankton by the voracious filter feeding non-native clam species. Points raised during the discussion concerning the potential linkage of ammonia(um) to reduced primary production in Suisun Bay included the following:

- Low primary production in Suisun Bay may correspond with increasing ammonia(um) discharges from consolidation of wastewater discharges at the SRWTP, which occurred in 1983.
- Two recently published studies show that ammonia(um)-nitrogen concentrations greater than 4 µM (56 µg/L) inhibits the uptake of nitrate in Suisun Bay.
- Phytoplankton nitrogen uptake rate on ammonia(um) is about half that with nitrate. Likewise, carbon productivity is half in an ammonia(um) system as compared to nitrate (i.e. cabon uptake is linked directly with N uptake rate).
- Based on reduced N uptake on ammonium (bullet 3) and the link between C uptake and N uptake, a maximum reduction in primary productivity in the Delta and Suisun Bay of 75% can be calculated. This may have resulted in the near complete suppression of spring diatom blooms in Suisun Bay.
- According to some accounts, overbite clams may be largely absent from Suisun Bay in the spring due to grazing by scaups (diving ducks) and other migratory birds. As such, low primary productivity in Suisun Bay can then not be attributed to overbite clam grazing of phytoplankton.
- Diatom blooms occur in Suisun Bay in wet years when ammonia(um) is diluted to concentrations low enough not be inhibitory to nitrate uptake and freshwater conditions are not conducive to overbite clam proliferation.

Others argued that reduced productivity in Suisun Bay could not be explained by ammonia(um) alone and alternative potential explanations were proposed, including:

- The proliferation of the overbite clam is in “lock step” with the decrease in primary productivity.
- The salinity of Suisun Bay is increasing and becoming hospitable to the overbite clam.
- Scaups are not active in Suisun Bay and thus do not limit overbite clam populations.
- Ammonia(um) levels are twice as high in the Sacramento River downstream of the SRWTP discharge and into the northern and central Delta as compared to Suisun Bay. Yet there is a trend to increasing primary production in the Delta (Engle, Slides 3 - 8).
- Diatom spring blooms in Suisun Bay occur in wet years due to high flow rates (short residence times) that favor rapidly growing phytoplankton (diatoms) over the slow growing cyanobacteria.
- Diatom blooms occur in Jamaica Bay, New York, where ammonia(um) concentrations are an order of magnitude higher than the Delta and Suisun Bay.

3) Ecotoxicology

Information was provided by local researchers as to the current approach to toxicity monitoring. This involves integrative acute toxicity monitoring at a frequency of every 2-weeks in the large water bodies. The following are major discussion points regarding this approach:

- Need to improve our understanding of the life stages of the four pelagic fish species of concern and include this information in the monitoring of sensitive life stages;
- Need to monitor toxicity and ammonia(um) near sources;
- Need to monitor diurnal variation in pH, temperature and ammonia(um);
- Need to go beyond acute toxicity; look at chronic (long-term sub-lethal) effects;
- Need to study mixtures of contaminants to assess potential for synergistic effects and interactions.

It was noted that resource and technological limitations have not allowed expansion of the monitoring effort. Only acute toxicity has been found and this has been associated with pesticides. In general, total and un-ionized ammonia concentrations in the Delta are too low to cause acute mortality in the most sensitive species. Based on the estimated chronic levels of 1/10 of the LC_{50}, (approximately 15 µg/l) chronic exposures are potentially occurring in the Delta. The 1999 USEPA Ambient Water Quality Criteria document notes histopathological effects on fish at levels of ammonia(um) that can be encountered in the Delta. It is unknown if these potential impacts translate to impacts on survival, growth, and/or reproduction.

Second Day Presentations and Facilitated Discussions

On the morning of the second day, the Panel developed the outline for the Research Framework in private. At the same time, the other workshop participants continued the facilitated discussion, lead by Dr. Dahm. Some of the workshop participants presented information in PowerPoint slides. The following are some of the highlights of these presentations and the discussion that ensued.

Cliff Dahm, PhD, CALFED Lead Scientist

Dr. Dahm presented information on the use of nitrogen-15 (^{15}N) stable isotopes to study the fate of sewage effluent in Moreton Bay, Australia. Sewage effluent has a particular ^{15}N fractionation signature (enriched with ^{15}N) and can be distinguished from other sources of nitrogen. One question posed for which no one had an answer was- does nitrogen from refinery waste have a distinctive ^{15}N signature? This is important because refineries in the San Francisco Estuary are discharging ammonia(um).

Carol Kendall, PhD, USGS

Dr. Kendall discussed her work using stable isotopes to study nitrogen and organic matter processes in the San Joaquin River and San Francisco Bay Estuary. Through contour plots of the various isotopes from the lower San Joaquin River into the San Francisco Bay, she demonstrated where algal blooms, nitrification and uptake of nitrogen were likely occurring. This approach could be used in the lower Sacramento River, the

northern Delta and into Suisun Bay to study the fate of ammonia(um) derived from the SRWTP and the movement of the ammonia(um) through the food web.

Diana Engle, PhD, Larry Walker Associates

Dr. Engle compiled time-series plots of chlorophyll-a concentrations from a variety of sources since 1975 on a monthly basis and for various reaches of the Sacramento River. The main discussion points included:

- Chlorophyll-a shows an increasing trend in the lower Sacramento River.
- Productivity in the Sacramento River as measured by chlorophyll-a concentrations (2-3 µg/L) is much lower than in the San Joaquin River (20 to 30 µg/L);
- Low production in the Sacramento River will result in low production in Suisun Bay (seed effect);
- Changing water management is resulting in less of the San Joaquin River flowing beyond Turner Cut and into the main portions of the Delta.
- It was suggested that box cores off of the Farallons could be collected and the organic matter content be evaluated for stable isotopes to assess historic levels of productivity.

Alex Parker, PhD, California State University San Francisco

- Low production was inferred for Suisun Bay as compared for other segments of the San Francisco Bay, from changes in dissolved inorganic carbon (DIC) in grow-out studies. Suisun Bay results deviated significantly from Redfield ratios, with a low C:N ratios (Parker, Slide 1).
- Photosynthetic performance in Suisun Bay is half of other portions of San Francisco Bay (e.g. South Bay).
  - This conclusion was reached by plotting depth integrated production (PN) against the composite parameter of the product of biomass and light intensity divided by the attenuation coefficient. This relationship showed a slope of half of the slope originally reported by Coel and Cloern (1984) (Parker, Slides 3-5).

Richard Dugdale, PhD, California State University San Francisco

The main discussion point from Dr. Dugdale's presentation was that based on f ratios (proportion of nitrate uptake to nitrate plus ammonia(um) fixation) (Dugdale, Slide 1), Suisun Bay, and the Sacramento River and San Joaquin River have lower nitrate uptake rates and chlorophyll production than the central San Francisco Bay (Dugdale, Slide 3).

David Fullerton Metropolitan Water District of Southern California

- Suisun Bay and the Sacramento River at Hood ammonia(um) concentrations are correlated when temperature is included in the correlation (Fullerton, Slide 4).
- Ammonia(um) is on an increasing trend such that yearly low ammonia(um)-nitrogen concentrations are frequently exceeding 56 µg/l. From the research of Dugdale and others, above this level, ammonia(um) may be inhibitory to diatom production (Fullerton, Slide 9).

Outline for Research Framework

In the afternoon of the second day, the Panel rejoined the workshop and presented their findings on their understanding of concerns, crucial data gaps and recommendations. Their presentation is posted on the CALFED Science web page for the ammonia(um) workshop. Central to their recommendations is a conceptual framework of drivers and responses in the Delta ecosystem (Slide 4). The conceptual framework ties together the variable factors of hydrology and climate to the factors and processes that drive primary production. They identified an integrative model as the primary data gap and an important initial focus fore future research efforts.

The remainder of the discussion focused on crucial data gaps and the process necessary to develop the model. Among the gaps are the need to identify sources and sinks of nitrogen and to quantitatively provide for nitrogen transformations and fate in the continuum from the lower Sacramento River to the Delta and into Suisun Bay. To accomplish this, the Panel suggested the use of stable isotopes transects and high frequency rate measurements at key locations.

There was also discussion and recommendations that first cut approximations be made to see if the approach is even possible – a so-called "bread board model." For example, the initial effort could focus on major processes thought to be governing nitrogen fate, with initial approximation of rate constants or use of lump parameters to estimate processes. Subsequently, this effort could be build upon by refining the rate constants and including the full suite of processes. The use of the DSM2 model was suggested as a starting point for this effort. It was cautioned, however, that there is a need to conduct periodic peer review of the model. As one workshop participant noted this is needed "to ensure that we were not going down a false path."

Following the workshop, with input received at the workshop and from public comments on the draft Research Framework, the Panel prepared the final Research Framework. The Research Framework is posted at CALFED Science web page for the ammonia(um) workshop.