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DATE: 7 October 2010

SUBJECT: **SUBJECT: 2010 AMMONIA UPDATE**

The purpose of this memorandum is to summarize the status of ammonia research since the August 2009 Ammonia Summit. Conclusions from the 2009 Summit were summarized in an earlier memorandum dated 24 September 2009[1]. It is important to recognize that many of the results discussed here have not yet been peer reviewed or published in final reports, so some of the conclusions may not yet be widely accepted. This review focuses on two questions:

1. *Does ammonia cause beneficial use impairments in the Delta?*
2. *What additional follow up studies are needed?*

Ammonia has been hypothesized to impact the aquatic ecosystem in three ways. The first is that ammonia concentrations may cause acute and/or chronic toxicity to resident fish and invertebrates. The second is that ammonia may inhibit diatom primary production in the Sacramento River below the Sacramento Regional Wastewater Treatment Plant (SRWTP) and further downstream in the Delta and in Suisun Bay. Finally, elevated ammonia levels may cause a shift in the algal community from nutritious species such as diatoms to less desirable forms for the aquatic foodchain such as *Microcystis* sp. A consensus at the Summit was that the SRWTP was the major source of ammonia to the Delta.

Toxicity Dr. Inge Werner from the U.C. Davis School of Veterinary Medicine reported at the Ammonia Summit on the results of seven day flow-through acute ammonia bioassays with delta smelt larvae[2]. The studies demonstrated that during the study period no acute ammonia toxicity was occurring in the Sacramento River or Delta to smelt. However, an additional test was performed in 2009 with SRWTP effluent mixed into upstream Sacramento River water from Garcia Bend. The results from this test demonstrated that the effluent was more toxic than predicted from the equivalent ammonia concentration alone. The no and low observed

[1] Foe memorandum of 24 September 2009 to Jerry Bruns and Sue McConnell

[2] Werner, I, L Deanovic, M. Stillway, D. Markiewicz 2008. The effects of wastewater treatment effluent associated contaminants on delta smelt. Final Report to the State Water Resources Control Board, p 60

Werner, I, L Deanovic, M. Stillway, D. Markiewicz 2009. Acute toxicity of ammonia/um and wastewater treatment effluent-associated contaminants on delta smelt—2009. Final Report to the State Water Resources Control Board, p 63

effect concentration for the effluent was nine and 18 percent effluent, respectively. The SRWTP discharge is typically about two percent of the Sacramento River but may on occasion be as high as seven percent. So, no acute ambient River toxicity was predicted from the effluent results but there was uncertainty about the actual range of the no and low observed effect concentrations because they were derived from only one set of test results. The effluent experiment was repeated on three occasions in 2010 using both delta smelt and rainbow trout larvae[3]. No toxicity was observed in 2010 to either species at 18 percent effluent. This suggests that the SRWTP effluent typically has an acute seven-day safety factor in the River of at least nine-fold to both fish species.

Currently, there is no method for assessing chronic toxicity to delta smelt. In such instances acute to chronic ratios (ACRs) derived from other freshwater fish species are often used to predict potential chronic toxicological endpoints. Dr. Werner used an ACR approach and concluded that chronic smelt toxicity could be occurring at ambient ammonia levels present in the River below the SRWTP[2]. In 2010 Regional Board staff completed a one-year nutrient monitoring study, including ammonia, in the Sacramento River and Delta[4]. Board staff also used an ACR approach and concluded that no chronic toxicity was likely to have occurred during the study period at either Hood or further downstream in the Sacramento River. Hood is eight miles below the SRWTP discharge point. The different conclusions obtained by U.C. Davis and the Regional Board result from the fact that U.C. Davis measured higher River pH levels than did the Board study. An analysis of California Data Exchange Center pH results for the Sacramento River suggest that pH concentrations as high as reported by U.C. Davis are rare, at least during the time period of the Regional Board study. The State Water Contractors (SWC) also performed an ACR analysis using ambient ammonia and pH levels from water samples collected about 1000 feet below the SRWTP outfall at Cliffs Marina. The SWC analysis indicated that repeated instances of chronic toxicity may have occurred in 2007 and 2008 to smelt[5].

In 1999 the U.S. EPA synthesized the toxicological information for ammonia and published recommended acute and chronic criteria for the protection of freshwater organisms[6]. These criteria are important because the Central Valley Water Board relies upon them for setting National Pollutant Discharge Elimination System permit limits unless other scientifically defensible information exists demonstrating the presence of more sensitive local aquatic organisms. In 2009 the U.S. EPA released an updated draft ammonia criteria document with lower acute and chronic values[7]. The revised criterion is to protect freshwater unionid mussels. Unionid mussels are more sensitive than larval fish to ammonia and have been reported in the Sacramento watershed[8]. The proposed chronic ammonia criterion for freshwater mussels is five to ten times lower than the 1999 chronic criterion for juvenile fish. No exceedance of either U.S. EPA recommended acute or chronic fish or mussel criteria was

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[3] Werner, I., L. Deanovic, M. Stillway, D. Markiewicz. 2010. Acute toxicity of SRWTP Effluent to delta smelt and surrogate species. Draft final report to SWRCB, p. 54.

[4] Foe, C., A Ballard, and S. Fong, 2010. Nutrient Concentrations and Biological Effects in the Sacramento-San Joaquin Delta, Regional Board report, 87 p

[5] Comments on Aquatic Life and Wildlife Preservation Issues Concerning the Sacramento Regional Wastewater Treatment Plant NPDES Permit Renewal June 2010

[6] U.S. EPA 1999. Update of Ambient Water Quality Criteria for Ammonia. EPA-822-R-99-014, U.S. EPA , Office of Water, Washington, D.C

[7] U.S. EPA 2009. Draft 2009 Update Aquatic Life Ambient Water Quality Criteria for Ammonia—freshwater. EPA-822-D-09-001. U.S. EPA , Office of Water, Washington, D.C.

[8] J. Howard. 2010. Sensitive freshwater mussel surveys in the Pacific Southwest Region: Assessment of conservation status. Prepared for the USDA Forest Service. 56p.

observed in the three-hundred and thirty-four ammonia measurements made by Regional Board staff in 2009 and 2010[3]. Dr. Diane Engle of Larry Walker and Associates also compared ambient ammonia concentrations collected in the Sacramento River and Delta by the Interagency Ecological Program between 1974 and 2000 and found only one exceedance of the chronic 1999 criterion in 10,543 measurements[9]. Finally, the SWC compared ambient ammonia levels immediately downstream of the SRWTP mixing zone with the draft 2009 U.S. EPA ammonia criteria. The SWC report that the 2009 criterion was exceeded 21 percent of the time between 2007 and 2008 and 41 percent of the time in 2009 [5].

Dr. Swee Teh from the U.C. Davis School of Veterinary Medicine reported at the August 2009 Ammonia Summit on the results of acute toxicity testing with *Eurytemora affinis* and *Pseudodiaptomus forbesi.* Both invertebrate species are important forage organisms for larval fish in the Delta. Ten percent mortality occurred to both species at ambient ammonia concentrations present in the Sacramento River below the SRWTP. Dr. Teh also used an ACR analysis and concluded that ambient ammonia concentrations below the SRWTP might be causing chronic toxicity to both invertebrate species. Follow-up chronic toxicity studies were recommended by the IEP Contaminant Work Team. Thirty-day full-life cycle tests were conducted with *P. forbesi* to evaluate the possibility of chronic instream ammonia toxicity. The preliminary testing has now been completed. Dr. Teh reported at a recent IEP Contaminant Work Team meeting that *P. forbesi* reproduction and nauplii survival was negatively affected by ammonia concentrations as low as 0.36 mg-N/L. Ammonia concentrations of this magnitude were measured by Regional Board staff in 2009 and 2010 for about 30 miles below the SRWTP[10]. Additional experiments are now being performed to confirm the *P. forbesi* findings and to attempt to determine a chronic no and low observed effect concentration. Reduction in ambient ammonia concentrations that would be needed in the River to protect *P. forbesi* cannot be estimated until a no observed effect concentration has been determined.

In summary, no evidence for acute fish toxicity or exceedance of U.S.EPA recommended ammonia criteria have been obtained for the Sacramento River downstream of the Hood sampling site. Hood is the closest downstream sampling site regularly monitored in the Sacramento River. The site is eight miles below the outfall for the SRWTP. Evidence for potential chronic delta smelt toxicity (as measured by an ACR analysis) and exceedance of the 2009 draft chronic mussel criteria have been reported in the River about 1000 feet below the SRWTP outfall. Finally, ammonia from the SRWTP may be reducing *P. forbesi* reproduction and nauplii survival for about 30 miles downstream of the SRWTP. The *P. forbesi* findings need to be confirmed with additional research.

Inhibition of Diatom Primary Production Several presentations were made at the 2009 Ammonia Summit on the effect of ammonia on phytoplankton primary production. Low primary production rates and standing chlorophyll levels are hypothesized to be one factor contributing to the pelagic organism decline (POD) in the Delta[11]. Dr. Richard Dugdale from the San

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[9] Engle, D and G. Lau. 2009. Total and unionized ammonia concentrations in the upper San Francisco Estuary: A comparison of ambient data and toxicity thresholds. 9th Biennial State of the San Francisco Estuary Conference, Oakland CA 29 Sept-1Oct 2009.

Engle, D. and G. Lau. 2010. Does ammonia exceed toxicity thresholds in the upper San Francisco Estuary? A comparison of ambient data and toxicity thresholds for 1974-2010. Interagency Ecological Program (IEP) Annual Workshop, Sacramento, CA 25-26 May 2010.

[10] Average annual ammonia concentration at Isleton, about 30 miles downstream of the SRWTP, was 0.31 mg-N/l with a range of 0.04 to 0.54 mg-N/l, n=16

[11] Sommer, T., C. Armor, R. Baxter, L. Brown, M. Chotkowski, S. Culberson, F. Feyrer, M. Gingras, B. Herbold, W. Kimmerer, A. Mueller-Solger, M. Nobriga, and K. Souza. 2007. The collapse of pelagic fishes in the upper San Franisco Estuary. Fisheries 32(6):270-277.

Francisco State University Romberg Tiburon Center presented evidence that an ammonia concentration greater than 0.056 mg-N/l inhibited nitrate uptake by diatoms in Suisun Bay[12]. Ammonia induced suppression of nitrate uptake prevents spring algal blooms from developing when conditions are otherwise favorable[13]. High filtration rates by the introduced clam *Corbula* and high turbidity levels are additional factors that may be responsible for reducing diatom production and standing algal biomass in Suisun Bay. A combination of the above three factors could explain the low diatom abundance now present in the Bay.

The San Francisco Regional Water Quality Control Board is responsible for regulating water quality in Suisun Bay. The Executive Officer from the San Francisco Water Board has informed staff from the Central Valley Water Board that ammonia levels in Suisun Bay may be impairing aquatic life beneficial uses in the Bay by having a detrimental effect on primary production and algal species composition[14]. Staff from the San Francisco Regional Board followed up on their letter and monitored ammonia and chlorophyll concentrations and algal species composition in Suisun Bay in the spring of 2010[15]. Al Machi presented some results from this monitoring at the 6th Biennial Bay-Delta Science Conference[16]. He reported that two diatom blooms (>30 µg/l chlorophyll) were observed in the Bay. Both occurred when ammonia concentrations were below 0.056 mg-N/L. At all other times ammonia levels were above concentrations reported to inhibit algal production and no blooms were observed. These results are consistent with the earlier observations of Drs. Dugdale and Wilkerson that high ammonia levels inhibit diatom production and reduce standing chlorophyll levels in both laboratory and field experiments. A written report is expected on all the Suisun Bay monitoring results in the spring of 2011.

Nutrient monitoring by Central Valley Water Board staff has confirmed that the Central Valley watershed is an ammonia source to the Sacramento River channel off Chipps Island[4]. Chipps Island was the most seaward site monitored in the Regional Board study and is about 2-miles upstream of the entrance to Suisun Bay. Average annual ammonia concentrations increased 11.5-fold in the River below the SRWTP. Total dissolved nitrogen (TDN) concentrations (NH_3+NO_2+NO_3) were statistically similar between the SRWTP and Chipps Island. A stable TDN concentration implies that there are no large nitrogen sources or sinks between the two locations. More than three quarters of the SRWTP ammonia, on average, was converted to nitrate (NO_3) by the time the River water mass reached Chipps Island. Annual average ammonia concentrations at Chipps Island were 0.10 mg N/l in 2009 and 2010[17]. As noted previously, ammonia begins to suppress nitrate assimilation at 0.014 mg-N/l with complete shutdown by 0.056 mg-N/l. Preliminary calculations suggest that ammonia loads from the Central Valley may need to be reduced by a factor of 2 to 7 to eliminate ammonia-induced suppression of diatom production in Central Valley water entering Suisun Bay[18].

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[12] Dugdale, R. f. Wilkerson, V. Hogue, and A. Marchi. 2007. The role of ammonium and nitrate in spring bloom development in San Francisco Bay. Estuarine, Coastal and Shelf Science, 73:17-29

[13] Wilkerson, F. R. Dugdale, V. Hogue, and A. Marchi, 2006. Phytoplankton blooms and nitrogen productivity in San Francisco Bay. Estuaries and Coasts 29(3):401-416.

[14] June 4, 2010 letter from Mr. Bruce Wolfe to Ms. Kathy Harder.

[15] SWAMP Suisun Bay study design 020810 entitled “Study Design for Suisun Bay Ammonia Study (R2)”.

[16] Machi, A. 2010. Spring 2010 Phytoplankton Blooms in Northern San Francisco Estuary: Influences of Climate and Nutrients. Presented at the 6th Biennial Bay-Delta Science Conference held in Sacramento California on 27-29 September 2010.

[17] Ammonia concentrations at Chipps Island ranged between 0.01 and 0.16 mgN/L, n=16 samples.

[18] 0.1/0.014 = 7 and 0.1/0.056 = 2.

Ammonia concentrations are higher in the Sacramento River below the SRWTP than in Suisun Bay. This observation led to the development of the hypothesis that ammonia might also be inhibiting algal production downstream of the SRWTP in the Sacramento River and Delta. Two studies have been undertaken to determine the effect of ammonia on phytoplankton primary production in the River and Delta. The first study evaluated the impact of elevated ammonia levels on nitrogen uptake and primary production rates immediately above and below the SRWTP in the Sacramento River. A final report has been received from Dr. Alexander Parker of the Romberg Tiburon Center describing the results of this work[19]. The second study by the same authors measured nitrogen uptake and primary production rates along a much longer transect (about 100 miles) from above the SRWTP to San Pablo Bay. Some results from the second study were presented at the 6th Biennial Bay-Delta Science Conference[20]. A manuscript has also been submitted to a peer reviewed journal. Preprints of the manuscript may be available this winter. Board staff has not examined the draft manuscript. Both transect studies concluded that the SRWTP discharge changed the Sacramento River from a nitrate to an ammonia dominated nitrogen system and that ambient ammonia concentrations reduced total nitrogen uptake (NH_3 + NO_3) by the algal community. In contrast, inverse correlations between primary production and ambient ammonia levels were only measured in the longer transect study. A U-shaped pattern of primary production and chlorophyll was observed on both cruises with a maximum in the river above the SRWTP and again to the west in San Pablo Bay, essentially a mirror image of the distribution of ammonia concentrations. These results are consistent with the earlier observations for Suisun Bay that ammonia concentrations suppress algal primary production and standing chlorophyll levels and appear to extend these findings to the freshwater Delta. However, caution should be exercised in interpreting the freshwater phytoplankton results until the peer reviewed manuscript is available for review by phytoplankton experts in both the Delta and San Francisco Bay. Additional validation experiments may be necessary to confirm the earlier results and estimate ammonia concentrations that do not suppress algal production in the Delta.

An additional complicating factor is that chlorophyll a concentrations decrease down the Sacramento River[4, 19]. The decline in chlorophyll appears to commence above the SRWTP. The average annual decline in pigment between Tower Bridge in the City of Sacramento and Isleton is about 60 percent. The cause of the decline is not known but does not appear to be caused by the SRWTP as the decrease commences above the plant. Decreases in algal biomass entering the Delta from the Sacramento watershed may also contribute to the low standing stock of phytoplankton available for the food chain and may exacerbate ammonia induced algal toxicity. Follow up studies are needed to identify the cause of the decline in chlorophyll down the River.

Shift in Algal Communities Dugdale *et al* hypothesize that larger algal cells (diatoms) are favored and grow faster in the nitrate-dominated river above the SRWTP while smaller phytoplankton species (flagellates and bluegreen) are competitively superior and grow faster at

[19] A. Parker, A. Machi, J. Davidson-Drexel, R. Dugdale, and F. Wilkerson. 2010. Effect of ammonium and wastewater effluent on riverine phytoplankton in the Sacramento River, CA. Final report to the State Water Resources Control Board, 73 p.

[20] A. Parker, R. Dugdale, F. Wilkerson, A. Marchi, 2010. Biogeochemical Processing of Anthropogenic Ammonium in the Sacramento River and the northern San Francisco Estuary: Consequences for Pelagic Organism Decline Species. Presented at the 6th Biennial Bay-Delta Science Conference held in Sacramento California on 27-29 September 2010.

the higher ammonia levels present below the SRWTP. A higher growth rate should cause the smaller sized cells to gradually replace the diatom-dominated community. In addition, Glibert hypothesizes that a change in ambient nitrogen to phosphorus ratios and in the oxidation state of the nitrogen species can also alter algal species composition[21]. Glibert has suggested that ambient nitrogen to phosphorus ratios in the Delta now favors blue-green algae and flagellates. Lehman and Brown have documented that the algal community in the Delta has changed from a diatom to a flagellate/blue-green algal dominated community consistent with the predictions of Dugdale *et al.* and Glibert[22]. Whether this is the result of changes in nutrient concentrations or their ratio or some other factor is not known. Diatoms are assumed to be more nutritious to primary consumers like zooplankton than flagellates and bluegreen algae. Changes in algal food availability and its quality or a "bottom up" effect is one factor hypothesized to contribute to the POD[9]. Follow up studies are needed to determine the ecological effect of the change in nutrient concentrations and ratios on the phytoplankton community and whether more stringent nutrient controls in the Central Valley might cause the algal community to revert back to a diatom based system.

In summary, evidence is accumulating that ammonia concentrations in the Sacramento River and Delta are at concentrations that may produce beneficial use impairments. The most robust evidence of impairment is the suppression of algal blooms in Suisun Bay. However, the observation that ammonia concentrations in the Delta may also suppress primary production and standing chlorophyll levels is important and, if validated by additional study, may help explain the low standing chlorophyll levels in the Delta and the recent POD. Follow up studies are needed to confirm the effect of ammonia on the phytoplankton community and determine why chlorophyll levels decline down the Sacramento River.

Next Steps One process issue and several areas for further investigation are identified below. The process issue involves the fact that at least some of the ammonia originates in the Central Valley while at least one of the impacts extends into the San Francisco Bay region. The involvement of two Regional Boards complicates both the science investigations and the ultimate regulation. There may need to be some formal process set up between the two Regional Boards to coordinate science, solicit input from Stakeholders, develop the regulatory program and determine who pays for the work. Advice from upper management and from both Boards may be helpful.

Two areas for immediate research are identified below. More work may also be required in other areas once all the final reports have been completed and reviewed by stakeholders.

The two areas for further immediate research are:

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[21] P. Glibert, 2010. Long-term changes in nutrient loading and stoichiometry and their relationships with change in the food web and dominant pelagic fish species in the San Francisco Estuary, California. Review in Fisheries Science (accepted).

[22] Lehman, P. 1998. Phytoplankton species composition, size structure, and biomass and their possible effect on copepod food availability in the low salinity zone of the San Francisco Bay/Delta and Suisun Bay. IEP technical report No 62. August 1998.

Lehman, P. 2000A The influence of climate on phytoplankton community biomass in San Francisco Bay Estuary. Limn and Ocean 45(3):580-590

Lehman, P. 2000B. Phtyoplankton biomass, cell diameter, and species composition in the low salinity zone of northern San Francisco Bay Estuary. Estuaries 23 (2):216-230.

Brown, T. 2010. Phytoplankton community comnposition: the rise of the flagellates. IEP Newsletter.

- First, conduct experiments in the Sacramento River above the City of Rio Vista to determine the primary processes responsible for the loss of phytoplankton down the river. The studies should include the Sacramento River above Tower Bridge.
- Second, continue to conduct experiments in the Sacramento River below the City of Rio Vista to determine the effect of ammonia and other nutrients on both primary production rates and algal species composition. Conduct experiments to determine whether more stringent nutrient controls in the Central Valley would increase algal standing biomass and revert the algal community to a diatom based system.