FINAL STAFF REPORT

PROPOSED AMENDMENT OF THE WATER QUALITY CONTROL PLAN – LOS ANGELES REGION – TO REVISE SALTWATER AMMONIA OBJECTIVES FOR INLAND SURFACE WATERS

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I. INTRODUCTION

Background

Ammonia is a pollutant routinely found in the wastewater effluent of Publicly Owned Treatment Works (POTWs), in landfill leachate, as well as in run-off from agricultural fields where commercial fertilizers and animal manure are applied.

Because ammonia has a known toxic effect to aquatic life, the United States Environmental Protection Agency (U.S. EPA) Office of Water has found that the control of ammonia discharges is necessary to protect aquatic life uses in surface waters of the United States.

Ammonia exists in two forms – un-ionized ammonia (NH3) and the ammonium ion (NH4+). Both forms are toxic, but the un-ionized form (NH3) is much more toxic. Un-ionized ammonia is much more toxic because it is a neutral molecule and able to diffuse across the epithelial membranes of aquatic organisms much more readily than the charged ammonium ion.

In brackish water and saltwater, the form of ammonia is dependent on pH, temperature, and to a lesser extent, salinity. Low pH and temperature leads to lower NH_3 and lower toxicity, while low salinity leads to higher NH_3 and toxicity.[1]

Proposed Action

[1] The two forms are in equilibrium according to the following equation:

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

$$K = \frac{[NH_3][H^+]}{[NH_4^+]}$$

The equilibrium constant K depends significantly on temperature; this relationship has been described by Whitfield (1974) for ammonia in saltwater with the following equation:

$$pK = 0.116 * i + 9.245$$

$$\text{where } pK = -\log_{10}K$$

Hampson's (1977) program for Whitfield's model has been used to calculate the un-ionized ammonia fraction of measured total ammonia concentrations. The equations for this model are:

$$\% NH_3 = 100 [1 + 10 \text{ ^ } (pK + 0.0324 (298-T) + 0.0415 P/T - pH)]^{-1}$$

where P = 1 atm
T = temperature (^oK)
$i = 19.9273 S (1000-1.005109 S)^{-1}$
where i = molal ionic strength of saltwater
S = salinity

The Regional Board staff proposes an amendment to the Basin Plan to update the ammonia water quality objectives for inland surface water not characteristic of freshwater (including enclosed bays, estuaries and wetlands). The proposed amendment would update the current objectives outlined in the Basin Plan for inland surface waters not characteristic of freshwater whose existing beneficial uses include those to protect aquatic life. The goal of this amendment is to reflect the criteria developed by U.S. EPA in the "Ambient Water Quality Criteria for Ammonia (Saltwater) - 1989". The 1989 guidance contains U.S. EPA's most recent saltwater aquatic life criteria for ammonia. The proposed amendment also includes language for implementing the revised objectives in the Los Angeles Region.

II. RATIONALE FOR BASIN PLAN AMENDMENT

The California Regional Water Quality Control Board, Los Angeles Region (Regional Board) has adopted a Water Quality Control Plan for the Los Angeles Region (Basin Plan). The existing Basin Plan establishes water quality objectives for ammonia in inland surface waters not characteristic of freshwater that are based on U.S. EPA's "Ambient Water Quality Criteria for Ammonia – 1984."

U.S. EPA's 1989 saltwater ammonia criteria constitute the agency's current recommended federal Clean Water Act (CWA) section 304(a) criteria, which States, Territories, and authorized Tribes may use as guidance in adopting water quality standards. Water quality standards developed from the section 304(a) criteria are designed to protect the beneficial uses identified for a particular water body. The water quality standards form the basis for establishing enforceable water quality-based effluent limitations in discharge permits.

Section 304(a)(1) of the Clean Water Act (33 U.S.C. 1314(a)(1)) directs U.S. EPA to publish and periodically update ambient water quality criteria. These criteria are to reflect the latest scientific knowledge on the identifiable effects of the pollutants on public health and welfare, aquatic life, and recreation. These criteria serve as guidance to States, Territories and authorized Tribes in adopting water quality standards under section 303(c) of the CWA that protect aquatic life from acute and chronic effects of ammonia. State and Tribal decision-makers retain the discretion to adopt water quality standards on a case-by-case basis that differ from this guidance when appropriate and where supported by local data.

In April of 2002, the Regional Board adopted a Basin Plan Amendment updating the freshwater ammonia objectives to reflect EPA's "1999 Update of Ambient Water Quality Criteria for Ammonia," December 1999. The Basin Plan Amendment became effective July 15, 2003. Although the Basin Plan Amendment updated the freshwater ammonia criteria for inland surface waters, it did not update the objectives for inland surface waters not characteristic of freshwater. At the April 2002 Board meeting, the Board directed staff to investigate and determine the most appropriate source of saltwater ammonia objectives for inland surface waters not characteristic of freshwater. As a placeholder, the Board retained the original ammonia objectives, based on U.S. EPA's "Ambient Water Quality Criteria for Ammonia – 1984," for inland surface waters not characteristic of freshwater.

III. EXISTING AMMONIA WATER QUALITY OBJECTIVES

The Basin Plan currently addresses ammonia in waters not characteristic of freshwater in the following manner:

For inland surface waters not characteristic of freshwater (as determined by the procedures in paragraph 1 of the Implementation Provisions below), concentrations of ammonia shall not exceed the values listed for the corresponding instream conditions in Tables 3-4 and 3-5.

IMPLEMENTATION

Implementation Provisions for the Application of Ammonia Objectives to Inland Surface Waters in the Los Angeles Region

1. Determination of Freshwater, Brackish Water or Saltwater Conditions[4]
(1) For inland surface waters in which the salinity is equal to or less than 1 part per thousand 95% or more of the time, the applicable objectives are the freshwater objectives, based on the US EPA "1999 Update of Ambient Water Quality Criteria for Ammonia." (2) For waters in which the salinity is equal to or greater than 10 parts per thousand 95% or more of the time, the applicable objectives are the inland surface water objectives in Tables 3-4 and 3-5. (3) For waters in which the salinity is between 1 and 10 parts per thousand, the applicable objectives are the inland surface water objectives in Tables 3-4 and 3-5.

[Existing Tables 3-4 and 3-5 are based on U.S. EPA's "Ambient Water Quality Criteria for Ammonia – 1984," for waters designated as warm water habitat]

IV. ANLAYSIS OF ALTERNATIVE OBJECTIVES

In order to determine the most appropriate saltwater objectives for inland surface waters, staff compared ammonia objectives in the 2001 California Ocean Plan and EPA's "Ambient Water Quality Criteria for Ammonia (Saltwater)-1989". A summary of the comparison is presented in Table 1 and in the text below.

Table 1. California Ocean Plan & US EPA Ammonia Saltwater Criteria Comparison

	California Ocean Plan	**US EPA Ammonia Saltwater Criteria**
Date of document	2001	1989
Date of data	1973 and earlier	1986 and earlier

[4] The procedure described in this section to determine which objectives should be applied is the same method employed in the California Toxics Rule (title 40, Code of Federal Regulations, § 131.38(c)(3)) .

	California Ocean Plan	US EPA Ammonia Saltwater Criteria
Number of toxicity studies considered	10 chronic saltwater [2] 30 acute freshwater[3] 9 acute saltwater	66 acute saltwater 22 chronic freshwater 2 chronic saltwater
Number of species considered	≈11 acute saltwater and freshwater	21 acute saltwater 10 chronic freshwater [4] 2 chronic saltwater
Limits	0.6 mg/L Total Ammonia (chronic)	0.233 mg NH_3/L acute (I-hr) 0.035 mg NH_3/L chronic (4-day)
Where native CA species considered? [5]	Acute – no Chronic – data unavailable	Acute – no Chronic - no
Methods for standards derivation	US EPA. 1972. "Water Quality Criteria".	US EPA. 1985. "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses".

Discussion of US EPA Ammonia Saltwater Criteria

US EPA used genus mean acute values to calculate a final acute value for ammonia toxicity of 0.465 mg NH_3/L. The 1989 criteria guidance did not use a water quality dependent function to calculate the final acute value because there was insufficient data to determine the relationship between toxicity and pH, temperature, and salinity. The final acute value was based on the four most sensitive species - the species with LC_{50} values in the 95th percentile. The criteria maximum concentration of 0.233 mg NH_3/L was derived by dividing the final acute value by two, in accordance with the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" 1985. The resulting criteria maximum concentration is reasonably protective of the tested species and presumably, those species occurring in the environment.

To calculate a final chronic value, EPA used acute chronic ratios (ACRs) for two saltwater species and four of the most sensitive freshwater species. EPA then divided the final acute value by the geometric mean of the six ACRs (13.1) to calculate a final chronic value of 0.035 mg NH_3/L. The criteria maximum concentration is equal to the

[2] Only three of the ten data points were used to calculate the upper bound of the "logical range" of chronic toxicity values. The lower bound of this logical range was defined as the background seawater concentration of ammonia.
[3] According to the analysis used in developing the Ocean Plan objectives, no statistically significant difference existed between the sensitivities of freshwater and saltwater species.
[4] Only the acute chronic ratios for the most chronically sensitive species were used to determine chronic toxicity criteria: channel catfish, bluegill, rainbow trout, and fathead minnow. The same freshwater studies were used in EPA's 1989 saltwater criteria as were used in the 1984 freshwater criteria.
[5] According to the analysis used in developing the Ocean Plan objectives, no direct evidence was found of important systematic differences in sensitivities between resident California species and those found elsewhere.

final chronic value in accordance with the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" 1985.

Discussion of California Ocean Plan Ammonia Objectives

To arrive at the ammonia objectives in the Ocean Plan, State Board took the lowest 10th percentile of the LC_{50} data for 39 acute toxicity studies, then derived estimates of chronic toxicity by multiplying them by an application factor of 0.1, as recommended in "Water Quality Criteria 1972." The resulting water quality objective is 600 μg total ammonia/L for the six-month median. The daily maximum was calculated by multiplying the six-month median by four to obtain 2400 μg total ammonia/L, and the instantaneous maximum was calculated by multiplying the six-month median by ten to obtain 6000 μg total ammonia/L.

The chronic ammonia objective of 600 μg total ammonia/L was deemed acceptable since it was within the "logical range" of chronic toxicity values. The logical range was determined to lie between the average background seawater concentration of 5 μg total ammonia/L and the conservative chronic toxicity estimate of 4000 μg total ammonia/L. The conservative estimate of chronic toxicity was computed as the log mean of the lowest three chronic and sub-lethal concentrations reported in the studies reviewed. The average background seawater concentration was taken as the log mean of all available data.

Comparison of California Ocean Plan Objectives and US EPA Criteria

The use of Ocean Plan ammonia objectives for inland surface waters not characteristic of freshwater would be consistent with the Regional Board's use of Ocean Plan objectives for ocean waters and would simplify the Basin Plan objectives. In addition, the Ocean Plan objectives are more straightforward and potentially easier to implement than the EPA recommended criteria because they are based on one limit for total ammonia. The EPA criteria for un-ionized ammonia must be converted to total ammonia, which is dependent on temperature, pH and salinity, and may prove to be more difficult for compliance monitoring and reporting. Also of note is the fact that the EPA criteria are often less stringent than the Ocean Plan objectives, depending on pH, temperature, and salinity. However, the data and standards development method used in the EPA criteria are more current and are therefore the most appropriate source for the revised Basin Plan objectives.

V. PROPOSED AMMONIA OBJECTIVES

The proposed objectives are based on "Ambient Water Quality Criteria for Ammonia (Saltwater)-1989" and reflect research and data analyzed specific to saltwater. The criteria are for un-ionized ammonia. The proposed amendment includes an implementation procedure to convert un-ionized ammonia objectives to total ammonia effluent limits. This procedure is included because sampling and lab methods are not available to analyze for un-ionized ammonia. In addition, in order to attain a fixed un-ionized concentration, a discharge with a higher total ammonia concentration is allowable at low temperatures. Furthermore, a discharge with a low pH can have a high total ammonia concentration because the equilibrium favors the ionized form at low pH.

However, when the discharge reaches the receiving water, it will equilibrate to the receiving water pH, which if higher, could cause much of the ionized ammonia to convert to the toxic un-ionized form. Therefore, the effluent limits must be based on total ammonia. The implementation provisions also include a "Receiving Water Compliance Determination" section that specifies which ammonia objectives (freshwater or saltwater) shall apply when determining compliance.

Finally, specific steps for deriving effluent concentration allowances where mixing zones have been approved by the Regional Board were deleted from the existing implementation provisions. This is because the existing procedure was based on upstream and downstream flows, which do not apply to inland surface waters such as enclosed bays, estuaries, and harbors. Instead, to simplify and generalize the implementation provision for all inland surface waters, if a mixing zone has been authorized by the Regional Board, the amendment specifies that effluent concentration allowances shall be derived using established procedures in the SIP or other appropriate methodologies approved by the Regional Board. Existing Steps 3 through 5, which describe how to determine the long-term average discharge condition and how to calculate maximum daily and average monthly effluent limitations, remain unchanged.

The proposed objectives will apply only to inland surface waters not characteristic of freshwater (including enclosed bays, estuaries and wetlands) and do not impact the Ammonia Water Quality Objectives for ocean waters contained in the California Ocean Plan.

Staff proposes the following changes to the existing Basin Plan language:

[Insert after paragraph 4 under Ammonia subheading:]

The objectives for inland surface waters not characteristic of freshwater are based on US EPA Ambient Water Quality Criteria for Ammonia (Saltwater) -1989. Both the one-hour average and 4-day average objectives are fixed concentrations for un-ionized ammonia, independent of pH, temperature, or salinity.

[Replace existing paragraph 5 with the following text:]

For inland surface waters not characteristic of freshwater (as determined by the procedures in paragraph 1 of the Implementation Provisions below), the four-day average concentration of un-ionized ammonia shall not exceed 0.035 mg/L and the one-hour average concentration shall not exceed 0.233 mg/L. ~~*concentrations of ammonia shall not exceed the values listed for the corresponding instream conditions in Tables 3-4 and 3-5*~~.

[Delete existing Tables 3-4 and 3-5.]

IMPLEMENTATION

Implementation Provisions for the Application of Ammonia Objectives to Inland Surface Waters in the Los Angeles Region

[Replace existing implementation provision No. 1 with the following text:]

1. Determination of Freshwater, Brackish Water or Saltwater Conditions[4]
For inland surface waters in which the salinity is equal to or less than 1 part per thousand 95% or more of the time, the applicable objectives are the freshwater objectives, based on the US EPA "1999 Update of Ambient Water Quality Criteria for Ammonia." (2) For waters in which the salinity is equal to or greater than 10 parts per thousand 95% or more of the time, the applicable objectives are a 4-day average concentration of 0.035 mg un-ionized NH_3/L and a one-hour average concentration of 0.233 mg un-ionized NH_3/L. (3) For waters in which the salinity is greater than 1 but less than 10 parts per thousand, the applicable objectives are ~~the inland surface water objectives in Tables 3-4 and 3-5.~~ the more stringent of the freshwater or saltwater objectives. (a) However, the Regional Board may by adoption of a resolution approve the use of either freshwater or saltwater objectives for an enclosed bay, wetland or estuary with findings that scientifically defensible information and data demonstrate that on a site-specific basis the biology of the water body is dominated by freshwater aquatic life and that freshwater objectives are more appropriate; or conversely, the biology of the water body is dominated by saltwater aquatic life and that saltwater objectives are more appropriate. When determining the biotic dominance of a water body, the following factors shall be considered: the nature of the conditions causing the dominance (e.g., natural vs. anthropogenic), the historical conditions of the water body, and the reversibility of the existing conditions.

[Insert after implementation provision No. 4:]

5. Translation of Objectives into Effluent Limits[6]

If the Regional Board determines that water quality based effluent limitations are necessary to control ammonia in a discharge, the permit shall contain effluent limitations for ammonia using one of the following methods:

1. *Use the following procedure based on a steady-state model:*

   Step 1: Identify the applicable water quality objectives for ammonia for the receiving water immediately downstream of the discharge.

   Step 2a: For each water quality objective, calculate the effluent concentration allowance (ECA) using the following steady-state mass balance model:

[4] The procedure described in this section to determine which objectives should be applied is the same method employed in the California Toxics Rule (title 40, Code of Federal Regulations, § 131.38(c)(3)) .

[6] The method whereby objectives are translated to effluent limits is similar to the method contained in the "Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California" (2000). The method is also consistent with that outlined in the U.S. EPA "Technical Support Document for Water Quality-based Toxics Control (1991).

If a mixing zone has not been authorized by the Regional Board, or when WQO ≤ B:

ECA = WQO

If a mixing zone has been authorized by the Regional Board:[7]

ECA = WQO + D (WQO - B) when WQO > B

Where: WQO = water quality objective (adjusted as described in Step 2b, if necessary, for temperature, pH, and salinity.)

D = dilution credit
B = ambient background concentration

The dilution credit (D) shall be derived taking into account water body characteristics and the type of discharge (i.e. completely-mixed or incompletely-mixed with the receiving water), using established procedures in the "Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California" (2000) or other appropriate U.S. EPA approved methodologies. The resulting dilution credit must be approved by the Executive Officer.

The ambient background concentration shall be the observed maximum as determined in accordance with procedures in the "Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California" (2000) or other appropriate U.S. EPA approved methodologies. The resulting ambient background concentration must be approved by the Executive Officer.

Step 2b: In order to adjust the un-ionized saltwater ammonia objective to an ECA expressed as total ammonia, the following equation shall be used:

$$[NH_4^+]+[NH_3] = [NH_3] + [NH_3]*10 \text{ ^ } (pK_a^S + 0.0324\ (298-T) + 0.0415\ P/T - pH)$$

Where:
P = 1 atm
T = temperature (^oK)
*pK_a^S = 0.116 * i + 9.245, the stoichiometric acid hydrolysis constant of ammonium ions in saltwater based on i*
i = 19.9273 S (1000-1.005109 S) $^{-1}$, the molal ionic strength of saltwater based on S
S = salinity

(Per U.S. EPA Ambient Water Quality Criteria for Ammonia (Saltwater)-1989)

[7] Mixing zones may be authorized on a discharge-by-discharge basis per the mixing zone provision in Chapter 4 of the Basin Plan.

[Insert after implementation provision No. 5:]

6. Receiving Water Compliance Determination
Per Implementation Provision No. 1, the following methods for determining compliance with proposed objectives shall be used:

If salinity sampled at a particular receiving water station indicates saline conditions (equal to or greater than 10 ppt), then saltwater objectives shall apply.

If salinity sampled at a particular receiving water station indicates freshwater conditions (equal to or less than 1 ppt), then freswater objectives shall apply.

If salinity sampled at a particular receiving water station indicates brackish conditions (greater than 1 but less than 10 ppt), then the more stringent of the freshwater or saltwater objectives shall apply except where the Regional Board, by adoption of a resolution, approves the use of either freshwater or saltwater objectives per Implementation Provision 1(3)(a).

VI. COMPARISION OF EXISTING OBJECTIVES AND PROPOSED OBJECTIVES

The proposed Basin Plan Amendment will result in chronic ammonia objectives that are less stringent than existing chronic objectives at pH values less than 7.75 and temperatures less than 15 ^{o} C. The proposed acute objectives will be less stringent than existing acute objectives at pH values less than 8 and temperatures less than 20 ^{o} C. Above pH values of 7.75 and temperatures greater than 15 ^{o} C, the existing chronic objective for un-ionized ammonia ranges from 0.036 mg/L to .059 mg/L. The proposed un-ionized acute objective is 0.035 mg/L. Above pH values of 8 and temperatures greater than 20 ^{o} C, the existing acute objective for un-ionized ammonia is 0.26 mg/L. The proposed un-ionized acute objective is 0.233 mg/L.

VII. OTHER CONSIDERATIONS

The California Water Code (CWC), section 13241, specifies that Regional Boards shall establish water quality objectives that in its judgement will ensure the reasonable protection of beneficial uses and the prevention of nuisances. Factors to be considered by a Regional Board when establishing water quality objectives shall include, but not necessarily be limited to, all of the following:

1. Past, present and probable future beneficial uses of water.

2. Environmental characteristics of the hydrographic unit under consideration including the quality of the water available thereto.

3. Water quality conditions that could reasonably be achieved through coordinated control of all factors, which affect water quality in the area.

The "Beneficial Uses" and "Water Quality Objectives" chapters of the Basin Plan (Water Quality Control Plan for the Los Angeles Region) are incorporated by reference to address the above three factors.

4. Economic considerations.
   The Regional Board has considered the costs of implementing the amendment, and other factors, as required by the California Water Code, section 13241. Because the proposed objectives are generally less stringent than the existing objectives, the economic burden on the regulated community posed by the proposed objectives will not be significantly greater than the burden resulting from the existing objectives.

5. The need for developing housing within the region.
   These objectives should not affect the housing market as the proposed objectives are generally less stringent than those that they replace.

6. The need to develop and use recycled water.
   Increasing the levels of ammonia should not alter the development or use of recycled water because this amendment only applies to surface water discharges to brackish or saltwater.

VIII. ALTERNATIVES

1. **No action**. To maintain the existing objectives would be to ignore the latest, peer-reviewed scientific data. The current saltwater ammonia objectives for inland surface waters are based on U.S. EPA's "Ambient Water Quality Criteria for Ammonia – 1984," which contains criteria for protection of freshwater aquatic life. These objectives were only retained as a placeholder until staff could investigate more appropriate ammonia objectives for inland surface waters not characteristic of freshwater.

2. **Adopt 1989 EPA saltwater ammonia criteria.** Although they are more complicated to implement and are generally less stringent than the California Ocean Plan objectives, the EPA criteria are based on the most recently available data and most current standards derivation methods. They are therefore the most appropriate standards to include in the Basin Plan.

3. **Adopt 2001 California Ocean Plan objectives.** While the objectives in the California Ocean Plan are more straightforward, total ammonia-based limits, they are based on older data and an older standards derivation method.

IX. RECOMMENDED ALTERNATIVE

Alternative #2: Adopt 1989 EPA saltwater ammonia criteria

Regional Board staff is recommending the application of EPA's 1989 saltwater criteria to inland surface waters not characteristic of freshwater. The EPA criteria are based on the most recently available data and the most current standards derivation method. The

proposed objectives will apply only to inland surface waters not characteristic of freshwater (including enclosed bays, estuaries and wetlands) and do not impact the Ammonia Water Quality Objectives contained in the California Ocean Plan for ocean waters.

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