

Total and Un-ionized Ammonia Concentrations in the Upper San Francisco Estuary from 1974-2009: A Comparison of Ambient Data and Toxicity Thresholds

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1 The Concern

Concerns have been raised about whether direct ammonia toxicity is contributing to the Pelagic Organism Decline (POD) in the upper San Francisco Estuary. In water, ammonia primarily occurs as two forms: ammonium ion (NH₄⁺) and un-ionized ammonia (NH₃), which occur in the equilibrium:



(equilibrium depends on pH, temperature, salinity)

The un-ionized form (dissolved ammonia gas) is toxic to aquatic animals at concentrations which vary widely among taxa. Among the sources of ammonia in the upper SFE are wastewater treatment plant discharges, agricultural and urban runoff, atmospheric deposition, benthic fluxes, and N transformations in the water column (e.g., excretion, mineralization).

2 The Approach

- We compiled over 11,800 measurements of total and un-ionized ammonia from the Delta and Suisun Bay spanning 35 years.
- We compared total ammonia values to the USEPA Acute and Chronic Criterion calculated for each water sample.
- We compared ranked distributions of un-ionized ammonia concentrations to preliminary acute effects thresholds for Delta smelt.

3 The Data

All available co-occurring approx. monthly measurements of:

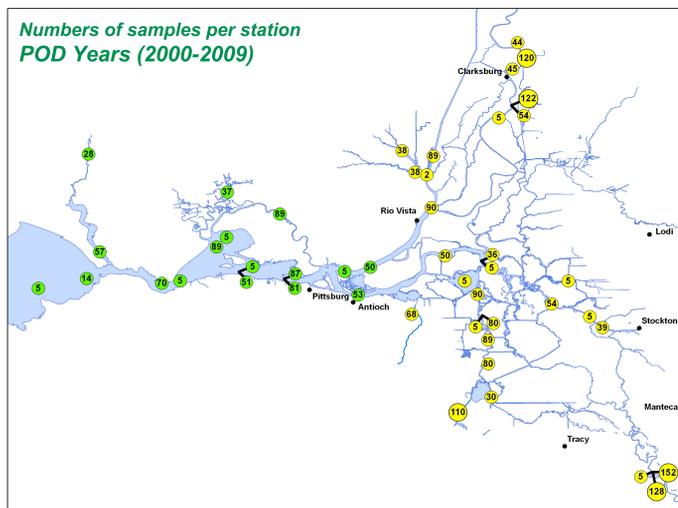
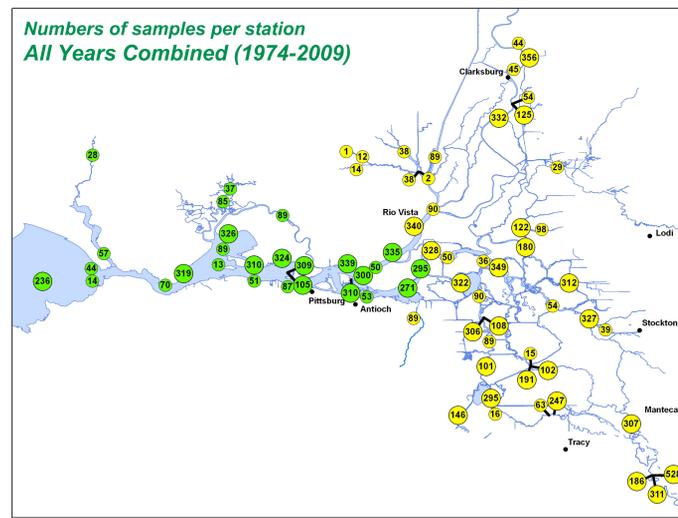
- Total ammonia
- pH
- Water temperature
- Salinity or Electrical Conductivity

Taken between 1974-2009 at **81 long-term monitoring stations** used by:

- DWR Municipal Water Quality Investigations
- IEP Environmental Monitoring Program
- USGS
- UC Davis ATL POD Project
- Sacramento Regional County Sanitation District (SRCSD) Coordinated Monitoring Program

The IEP EMP stopped measuring pH at many stations between 1995-2008, so there are fewer stations with data for POD years (2000-2009).

Stations were classified as **Freshwater** if salinity was less than 1 ppt 95% or more of the time (in accordance with the California Toxics Rule). At **Estuarine** stations, salinity was between 1-10 ppt 95% of the time.



4 Calculating Un-ionized Ammonia Fractions (f_{NH3})

Saltwater

$$f_{\text{NH}_3} = \frac{1}{1 + 10^{\left[\text{p}K_a + 0.0324(298-T) + \frac{(0.0415)P}{T} - \text{pH} \right]}}$$

$$\text{p}K_a = 9.245 + 0.116 \times I$$

$$I = \frac{19.9273 \times S}{1000 - 1.005109 \times S}$$

S = Salinity in ppt

T = water temperature

P = atmospheric pressure

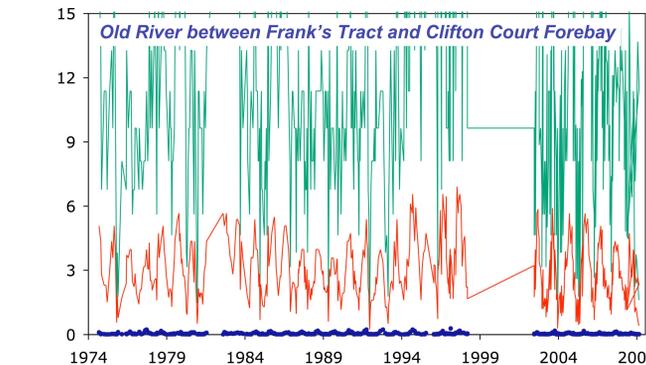
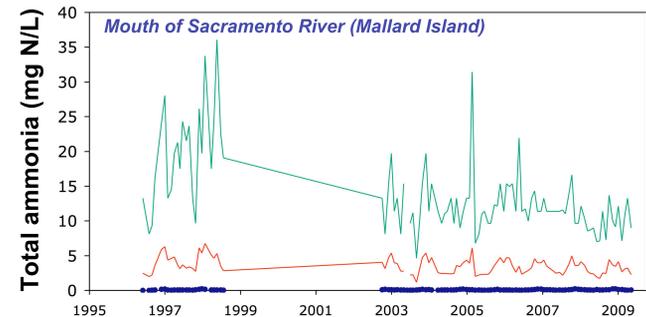
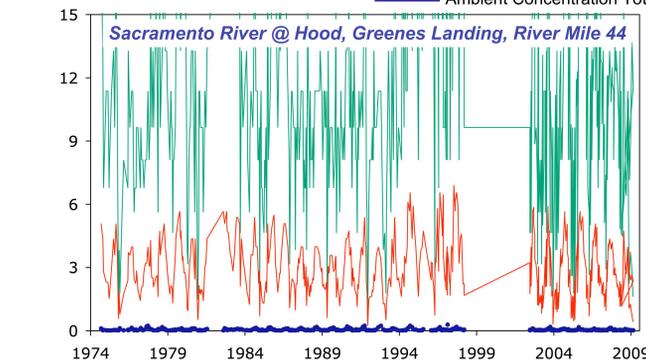
Freshwater

$$f_{\text{NH}_3} = \frac{1}{1 + 10^{\text{p}K - \text{pH}}}$$

$$\text{p}K = 0.09018 + \frac{2729.92}{273.2 + T}$$

Selected Time Series

- Acute Criterion - salmonids present
- Chronic Criterion - early life stages present
- Ambient Concentration Total Ammonia



5 US EPA Ammonia Criteria

- The Criteria are designed to protect the most sensitive fish and aquatic invertebrate species for which acceptable test results are available.
- Criteria are revised periodically when new data become available and are vetted by the EPA. Criteria are different for saltwater and freshwater.
- In the current EPA data set, the most sensitive freshwater species is rainbow trout, and the most sensitive saltwater species is winter flounder.
- Recent acute toxicity tests (L. Werner, UC Davis, unpublished data) indicate that Delta smelt are about as sensitive to ammonia as rainbow trout.
- Normally chronic criteria apply to 4-day (saltwater) or 30-day (freshwater) averaging periods -- not monthly grabs.

Following the procedure used in the California Toxics Rule for other toxicants...

at Estuarine Stations, **both** Freshwater and Saltwater Criteria were calculated for every sample,

and

the stricter criterion (Freshwater or Saltwater) was compared to the ambient concentration

$$\text{Freshwater Acute Criterion (salmonids present)} = \frac{0.275}{1 + 10^{7.204 - \text{pH}}} + \frac{39.0}{1 + 10^{\text{pH} - 7.204}}$$

$$\text{Freshwater Chronic Criterion (early life stages present)} = \left(\frac{0.0577}{1 + 10^{7.688 - \text{pH}}} + \frac{2.487}{1 + 10^{\text{pH} - 7.688}} \right) \times \text{MIN} \left(2.85, 1.45 \times 10^{0.028(25 - T)} \right)$$

$$\text{Saltwater Acute Criterion} = \frac{0.233}{f_{\text{NH}_3}}$$

$$\text{Saltwater Chronic Criterion} = \frac{0.035}{f_{\text{NH}_3}}$$

6 Results

Screening using US EPA Criteria

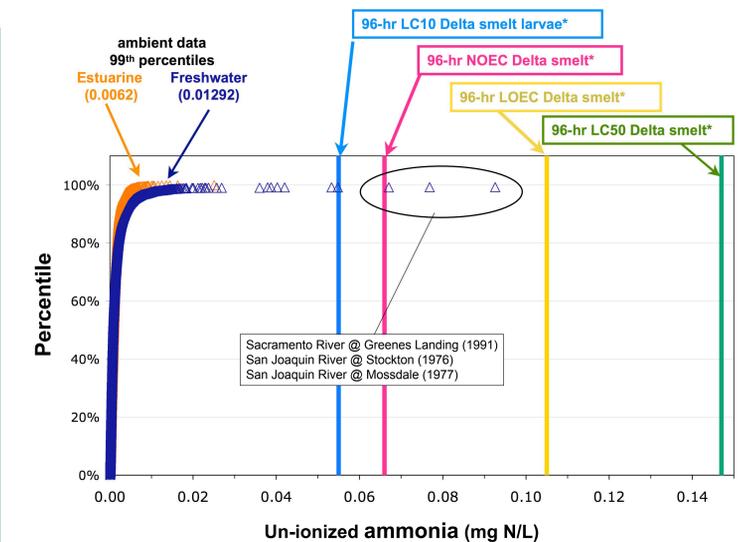
- 7192 samples from Freshwater Stations were screened (1687 from POD years)
- 4641 samples from Estuarine Stations were screened (800 from POD years)
- In this large data set, 0 values exceeded the Acute Criterion, and only 2 values exceeded the Chronic Criterion:

Sacramento River @ Greenes Landing - 1991
San Joaquin River @ Stockton - 1976
- None of the ammonia measurements from POD years exceed US EPA criteria.
- The average Margin of Safety using the Chronic Criterion, (CCC/ambient NH₃), was 70 for Freshwater stations and 50 for Estuarine stations.

Ranked Distribution of Un-ionized Ammonia Values

- Un-ionized ammonia was calculated for 7153 samples from freshwater stations and 4638 samples from estuarine stations.
- No measurements of un-ionized ammonia in this data set (N=11,791) exceeded the currently estimated LC50 for juvenile Delta smelt.
- Only 3 freshwater samples exceeded any of the other estimated effects-thresholds for Delta smelt, and these samples were not from POD years (2000-2009).

Ranked Distributions of Un-ionized Ammonia Concentrations



* (L. Werner, UC Davis Aquatic Toxicology Laboratory, unpublished data)

7 Conclusions

- Ambient ammonia levels in the upper San Francisco Estuary meet US EPA Acute and Chronic criteria by a comfortable margin of safety. Over a 35 year period, ambient ammonia concentrations have been on average 50 and 70 times lower than the US EPA chronic criterion at estuarine and freshwater sites, respectively.
- Ammonia levels in the upper estuary are not acutely toxic to Delta smelt. No measurements of un-ionized ammonia have exceeded the currently estimated LC50 for juvenile Delta smelt, which is higher than the 99th percentiles for un-ionized ammonia by over an order of magnitude.

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