Ammonia Dynamics on the Ocean Environment

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The Florida Department of Environmental Protection (FDEP) staff recently proposed a 0.035 mg/L as standard for unionized ammonia as a part of the triennial review process. If this standard were implemented as proposed, Florida would be the first state to apply an unionized ammonia standard to an open-ocean discharge. Two issues exist: the state of the science and the dynamics of the plumes in open-ocean waters as opposed to estuarine waters. A proposal was discussed that involved the following:

- Determine gaps in the science of ammonia toxicity.
- Determine what the typical ammonia concentrations are at the outfall wastewater treatment plants.
- Use the wastewater data to determine at what point in the plume the 0.035 mg/L as standard would be met.
- Determine the exposure time in the plume to get to 0.035 mg/L as (assuming only dilution).
- Compare that exposure time to the full life cycle and early life-stage bioassay test time, which is about 30 days.
- Determine what data support exists from other regulatory agencies for the difference in estuarine and open-ocean conditions.

State of the Science

The U.S. Environmental Protection Agency's (EPA's) *Ambient Water Quality Criteria for Ammonia (Saltwater) – 1989* document was relied upon in establishing the proposed unionized ammonia standard. This is the major work on marine effects of unionized ammonia. A peer-reviewed paper was written by the primary authors. The following were noted in developing the EPA's 1989 criteria document (EPA, 1989; Miller, et. al., 1990).

For Marine Acute Tests (30 days):

- Temperature appeared to make a limited impact on the toxicity (tested using sheepshead minnows and silverside larvae).
- pH had a mixed impact on toxicity – toxicity was greater at pH=7 and pH =9 than at pH=8 for the silverside larvae. Toxicity decreased log-linearly for *mysid* shrimp between pH = 7 and pH = 9.
- Salinity produced mixed results. For the silverside, salinity appeared to have limited impact; however, for the *mysids*, variation showed that toxicity was higher at lower salinity values.
- Maintaining constant pH conditions, particularly in the static renewal tests, was problematic and there were problems with the measurement of pH; hence, the unionized ammonia exposure concentrations may be incorrect.

For Marine Chronic Tests (30 days):

- *Mysid* full life-cycle test survival was found to be reduced at low unionized ammonia values (0.048 mg/L) but not at higher concentrations until the concentration reached 0.33 mg/L.
- The growth of silverside larvae was adversely impacted at low concentrations of unionized ammonia (0.074 mg/L).
- Miller, et. al. (1990), noted that they believed that equilibrium drift caused by formation of NH_4Cl in seawater might impact the results with pH.
- The measurement of pH and calculation of unionized ammonia exposure concentrations may be inaccurate.
- Using average concentrations may not accurately express test exposure.
- Differences in pH between the control and test solutions were up to 0.5 su.

Summarizing all tests suggests that:

- Temperature effects for marine species are much less than those for freshwater species.
- pH-related ammonia toxicity may not be uniform for saltwater species as a result of mixed results among species.
- Ammonia appears to be less toxic in marine waters than in freshwaters.
- The range of acute:chronic ratios tested was small using species sensitive to pH and was similar to freshwater species, although the exposure concentrations were greater.
- Some of the earlier test procedures may not comply with later guidance.
- The toxicity tests were focused on the simulation of estuarine conditions and did not consider open-ocean conditions.
- There was no consideration of the known environmental fate of nitrification and plant uptake in the ammonia criteria development.
- Confirming tests are needed, preferably with indigenous marine species.

Issues that were identified in the Ambient Water Quality Criteria for *Ammonia (Saltwater) – 1989* (EPA, 1989) as requiring more study include:

- The marine pH-toxicity relationships
- The test species sensitivity using additional acute, flow-through techniques with continuous pH control, both with and

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- without pH acclimation
- Confirmation of pH dependence
- The effects of water-quality variables on acute:chronic rations by conducting life-cycle and early life-stage tests with saltwater species
- Temperature effects of acute toxicity tests with species that can tolerate both high and low temperatures
- Effects of constant total ammonia exposure and cyclic water-quality changes to mimic tidal shifts in salinity and pH
- Effects of fluctuating and intermittent exposures to a variety of marine species
- Other variables (chlorine and DO were mentioned) for toxicity
- The contribution of ammonium to toxicity of aqueous ammonia to better resolve how the ammonia criterion should be expressed if dependence on pH continues to be demonstrated
- Confirmation of the study results. This was the first chronic early life-stage test for silversides and full life-cycle test for *mysids*, so only limited information is present for chronic toxicity for marine species.
- Influence of acclimation of marine animals in the flow-through tests
- Impact of life stage when exposed
- Improvements to pH measurements and calculations of unionized ammonia exposure concentrations
- Saltwater organism response – saltwater organisms do not respond in the same manner as freshwater organisms to unionized ammonia exposures.

Since 1989, the majority of work has focused on the freshwater species, including the EPA's *Ambient Water Quality Criteria for Ammonia – 1999* guidance manual; hence, the areas identified as requiring additional study remain unaddressed.

Bifurcation of Regulations by Coastal States

Surveys were conducted of all coastal states in the United States, plus each of the applicable EPA regional offices, to determine the current regulatory framework as perceived by the EPA and the regulatory agencies. The findings of this investigation indicated that ammonia toxicity is not perceived by other regulatory agencies to be an issue in the open ocean, but that in estuarine waters and fresh waters it was considered significant.

The basic contention from EPA regional and coastal state regulators was that dilution in the ocean was significant and rapid; therefore, there was less concern with nutrients and ammonia in the open-ocean environment as compared to estuarine conditions. The source of this belief is a series of studies performed 20–30 years ago by R.W. Eppley in the Pacific Ocean off the coast of California.

These studies indicated that the nutrients in the coastal ocean resulting from upwelling events far exceeded the total nutrients from ocean outfalls or run-off from terrestrial sources. Since the outfall also had significant dilution within the near-field (plume rise and buoyancy dominated fields, with dilutions generally 100 or more), it was decided that from a policy perspective, the outfalls were not major nutrient contributors. The exact definition of "open-ocean waters" is not used but is generally understood to be seaward from the beach in the California Ocean Plan.

The true source of the understanding of this delineation may be from the East Coast, where the major issues with outfalls arise only in Region I and the state of New York; all other outfalls in the ocean are comparatively small. Region I has used a delineation of "baseline" versus "non-baseline" systems to separate estuarine and open-ocean conditions. The source that defines this line is one map drawn over 20 years ago by the U.S. Department of Commerce for the near-shore limit of the 12-mile federal territorial waters.

In Region I, Region II, and New York, the open-ocean systems would be required to show what appropriate dilutions would be created in the near-field plume rise – typically 20-50:1 dilution, which is similar to that for the Florida open-ocean outfalls. This value would be used to grant mixing zones or "zones of initial dilution" in NPDES permits to meet any toxicity-based requirements.

Unless some readily identifiable impact from the discharge were noted, the regulatory agencies decided there was minimal potential for an impact in the open ocean. So far, none of these agencies has noted an open-ocean outfall discharge impact attributable to nutrients.

Physical Differences between Estuarine and Coastal Zones

Estuaries are a distinctive aquatic environment where the terrestrial freshwater meets the salt water of the sea. According to Reid and Wood, 1976, "The estuary is an ecotone" – a rather complex "buffer zone" sharing some characteristics of both types of aquatic ecosystems but identical to neither.

Estuaries have a number of unique factors and environmental conditions are highly variable. The hydraulic conditions are typically two opposing regimes: the unidirectional river-flow current and the oscillating tidal currents. These conditions have complicated effects on mixing sedimentation and other important physical characteristics.

The current reversal also allows a potential build-up of a plume under certain circumstances. The mixing of fresh and marine waters causes a variable chemical environment unlike either fresh or ocean water. To illustrate the differences, **Table 1** presents ranges of the parameters:

Table 1. Environmental Variables of Estuaries and Oceans Typical Range

Parameter	Estuaries	Ocean Waters
Solar Radiation	Exiction Coefficient 0.4-2.0	Less than 0.1
Color	Brown	Blue
Turbidity	Highly variable often high	Low
Thermal heat	Variable	Slowly variable
	Rainfall influence	
	Rapidly changeable	
Currents	Freshwater Flow	Coriolis driven
	Tidal Oscillations	Wave Action
	Wind Driven	Upwelling
	Large Flushing Times	
	Highly variable	
	Density gradient	
Dissolved	Highly variable	Relatively constant
Solids	0.5 to over 60%	33% to 38%
Dissolved	Variable	Relatively constant
Gases	Oxygen 0 – 100% sat.	At the 90 feet
	CO_2	Isopleth
pH	Variable	8.1 – 8.3
	6.5 to over 8	

Based on the information in Table 1, it is clear the estuarine waters are much more variable than the ocean waters.

Summary of Findings Using Plume Models

A question raised concerning unionized ammonia exposure was the length of time that a free-floating marine species could remain in contact with the plume while the concentration of unionized ammonia exceeded the proposed 0.035 mg/L as proposed standard, which is below the noobservable-effect-concentration (NOEC). To determine the exposure time, the near-field and far-field plume characteristics must be related to time. Also, ammonia was considered conservative with neither oxidation to nitrate nor uptake by phytoplankton.

As the plume rises in the near-field, then moves with the current to the far-field, dilution increases. Meanwhile, the pH increases, causing the unionized ammoniafraction of total ammonia to increase, meaning the two forces fight one another. Plotting the dilution curves allowed for translation to the time of exposure.

Dynamics of the plume can be characterized by series of equations based on measured field data. The plume characteristics can be defined by near- and far-field regimes. The near-field regime is defined as the area where the effluent leaves the pipe, rises to the surface, dissipates any residual buoyancy, and merges with the ambient ocean current. The near-field dilution typically occurs in 20 minutes or less. Beyond that point is the far-field regime, which is dominated by the ambient currents.

The near-field effects are controlled in part by the outfall design, while the far-field dilution is fully controlled by currents and natural processes. Information required to determine the characteristics are the specifics of each outfall, the quantity of flow, effluent concentrations, and current regime. For the current regime, the value used was the 10th percentile velocity during rotary currents (12 cm/s), which is conservative. These are shown in **Table 2** for each of the open-ocean outfalls in Southeast Florida. Background ammonia was assumed to be zero for this evaluation.

Table 2 shows the details for the six outfalls. **Table 3** shows the measured concentrations for the average (C50), 95th percentile (C95), 99th percentile (C99), and total ammonia (TA) for each outfall (SCRWTP is estimated because data was not available). The C50 and C99 percentile concentrations were plotted using these equations and assuming a current speed (the 10th-percentile velocity during rotary current events as incorporated in the recent rule change to FAC 62-4.244) is 0.12 meters/second.

Table 4 shows the dilution characteristics for each outfall using the 0.12 m/s value and summarizes the results when using the program. The dilution required at effluent average ammonia concentrations to reach 0.035 mg/L of is not met in the near-field in any of the outfalls, but occurs within 30 minutes in all but two of the outfalls. Those two, Broward County and Miami-Dade Central, achieve the target dilution within a matter of hours.

Table 5 shows the results for CORMIX runs for each outfall and compares them to the previously calculated dilution values.

Table 2. Outfall Characteristics and Permitted Flow Rate

Outfall	Discharge Depth (m)	Terminis Distance Offshore (m)	Number	Diameter (m)	Port Spacing (m)	Total Flow (MGD)
Miami-Dade - Central	28.2	5730	5	1.22	9.8	143
Miami-Dade - North	29	3350	12	0.61	12.2	112
Hollywood	28.5	3050	1	1.52	n/a	42
Broward County	32.5	2130	1	1.37	n/a	66
Boca Raton	29	1600	1	0.76	n/a	17.5
SCRWWTP	27.3	1515	1	0.91	n/a	23

Table 3 .Total Ammonia Concentrations and Dilution Requirements
C50 = Concentration of 50th percentile

Outfall	C50 mg/L	C95 mg/L	C99 mg/L	Dilution to 0.035 mg/L N*	Dilution to 0.035 NH3*
Miami-Dade - Central	17.5	23.7	25	47.2	57.3
Miami-Dade - North	18.6	30.4	83.5	50.2	60.9
Hollywood	7.1	10.6	11.5	19.1	23.3
Broward County	22.3	29.6	32.1	60.1	73.0
Boca Raton	16.8	24.5	26.8	45.3	55.0
SCRWWTP	20	n/a	30	53.9	65.5

* Dilution assumes background ammonia is zero.

Table 4. Summary of Dilution Modeling Results
Using SEFLOE II Based Equations

Outfall	Initial Dilution*	Dilution Required UIA	Lb (m)	Time to 0.035 mg/L as NH^3	Farfield Time
Miami-Dade - Central	16.7	57.3	n/a	<250 min	166.67
Miami-Dade - North	39.3	60.9	n/a	<10 min	50.00
Hollywood	19.4	23.3	270	<10 min	16.67
Broward County	15.8	73.0	429	<500 min	383.33
Boca Raton	41.5	55.0	114	<10 min	83.33
SCRWWTB	35.8	65.5	149	<25 min	166.67

*Centerline Dilution
Lb is length scale for edge of nearfield

CORMIX is the standard program used by regulatory agencies for determining mixing-zone configurations and is accepted by the EPA; however, CORMIX was not the model used for characterization of the outfalls during SEFLOE. Instead, Huang, et al 1998, calibrated the SEFLOE results to their equation; however, in running the latest version of CORMIX, it appears that some consideration of this change was included, since the four single-port outfalls track well with the analytical model results conducted herein.

CORMIX 4.1 does not work for the plume at Miami-Dade North because of its geometry. CORMIX treats the diffusers as single ports; clearly they overlap, which CORMIX does not accommodate. The analytical model results were used and the jet mixing confirmed the analytical model results. Likewise, the jet-mixing results confirmed the analytical findings for the jet influence and the Miami-Dade Central facility.

Table 5 also shows a comparison between methods: CORMIX version 4.1 and the SEFLOE II (1994) calculated method from Chin (2000), Huang (1998), and Okobu (1971). Based on the comparative times, these two methods appear to confirm one another fairly well. As a result, is seems reasonable to assume that the exposure is less than eight hours for all outfalls, under the 10th-percentile velocity and the average ammonia concentration. For four of the out-

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Table 5. Comparison of CORMIX and Calculated Results

Outfall	Dilution	CORMIX		SEFLOE II Calculated	
	Required [1]	Init. Dilu.	0.035 mg/L	Init. Dilu.	0.035 mg NH_3/L
			Time		Time
Miami-Dade - Central	57.3	16.6*	n/a	16.7	<250 min
Miami-Dade - North	60.9	39*	n/a	66.5	<10 min
Hollywood	23.3	22.3	~ 10 min	23.1	<10 min
Broward County	73.0	23.4	>200 min	19.8	<500 min
Boca Raton	55.0	40.9	< 6 min	53.5	<10 min
SCRWWTP	65.5	35.8	<60 min	41.6	<25 min

*Model not stable
1 Assumes background ammonia is zero.

Table 6. Comparison of Time of Exposure to 0.035 mg/L as NH_3

Outfall	Time over 0.035, mg NH_3/L UIA min	Percent of Long Term Chronic Tests
Miami-Dade C	<250	0.6%
Miami-Dade N	<10	0.02%
Hollywood	<10	0.02%
Broward County	<500	1.2%
Boca Raton	<10	0.02%
SCRWWTB	<60	0.14%

1. Based on C50 concentrations
As can be seen, the UIA is reduced to proposed marine standards in less than 2 percent of the exposure time of the long-term chronic test.

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falls, the exposure was less than 30 minutes. These are conservative exposure results, as there is no consideration for ammonia oxidation or phytoplankton uptake.

Comparing the time of exposure to the full life-cycle test (invertebrate) and the early life-stage tests of 30 days, the results are presented in **Table 6**.

Conclusions

The FDEP staff has raised several issues to be studied involving ocean outfalls and unionized ammonia. These are:

- Determine what the typical ammonia concentrations are at the outfall wastewater treatment plants.
- Use this data to determine at what point in the plume the 0.035 mg/L as standard would be met.
- Determine the exposure time in the plume to get to 0.035 mg/L as (assuming only dilution).
- Compare that time to the full life-cycle and early life-stage bioassay test time.
- Determine what data support exists from other regulatory agencies for the difference in estuarine and open-ocean conditions.

The conclusions of this investigation are:

- Average, 95th percentile, and 99th percentile values were determined for five of the six outfalls based on existing data (see Table 3). Hollywood had the lowest total ammonia – 7.1 mg/L.
- The South Florida outfalls have a limited exposure, in all cases less than 500 minutes to reach the proposed 0.035 mg/L as standard. Four are under an hour. These dilutions were based on the conservative assumption of the 10th-percentile velocity during rotary currents
- Table 6 presents the field exposure for each outfall as a percent of the full life-cycle bioassay tests. The percent is minimal in all cases. Because the early life-stage bioassay test organisms are not defined, a comparison of time is not possible. Only the Broward outfall would appear to have even limited potential effects on early life-stage bioassay tests.
- The West Coast regulators rely upon studies conducted in the 1970s indicating that terrestrial nutrients are of lesser quantities than those in deep waters.
- The East Coast regulators rely on findings of identified impacts from outfalls and plume models. There are no identified East Coast impacts implicating open-ocean outfalls.
- Estuaries are defined differently from open-ocean waters with regard to dilution, currents, nutrient loading, and other factors.

Based on these results, and based on the minimal percentage of the total area in the Florida Current the plume actually impacts, it would appear that the potential effects of unionized ammonia as a toxic chemical on the ocean surface from treated effluent plumes does not warrant further regulation until further investigation is undertaken.

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