

Ammonia in Streams

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Ammonia in streams and rivers- In water, dissolved ammonia exists in equilibrium between free ammonia gas (NH_3 or un-ionized ammonia) and the solvated ammonium cation (NH_4^+). The $\text{NH}_3 - \text{NH}_4^+$ equilibrium is of profound importance to the biogeochemical cycling of ammonia. Over the pH range typical of most Iowa waters, NH_4^+ is the dominant species. The equilibrium is extremely dependent upon pH, and to a lesser extent on temperature. High pH favors the formation of the free gaseous NH_3 , with a sharp dissociation at a pH around 9. The NH_4^+ ion is nontoxic and is not of concern to organisms. However, un-ionized ammonia (NH_3) is harmful to aquatic life and may accumulate in the organism and cause alteration in metabolism or increases in body pH. Salmonids (cold-water species) and juvenile fish are especially sensitive to elevated concentrations of NH_3 . From a water-treatment standpoint, elevated concentration of NH_3 reduces the efficiency of chlorination schemes of treatment facilities by competitively reacting with the disinfectant agent produced in the chlorination process.

Iowa water quality criteria for ammonia – The state of Iowa has established both acute and chronic criteria for ammonia in Iowa streams designated for aquatic life uses (Class B waters, see attached tables 3a and 3b from Chapter 61, IAC). Iowa has no additional criteria for those waters designated as sources of potable water (Class C). Monitoring samples are analyzed using a method which assays for both $\text{NH}_4^+ + \text{NH}_3$, which is reported as “Nitrogen, ammonia as N”. Because it is the un-ionized NH_3 that is toxic to aquatic life, the criteria are indexed for specific pH and water temperature.

Comments specific to newspaper article - A challenge in newspaper articles such as the one published in the Des Moines Register is to report the nuances of the subject in a manner that is technically accurate, yet understandable to the lay reader. In my reading of the article, I find several points that may have been stated in a more “technically correct” manner. Following are two examples.

1. The article states that “An ammonia reading of more than 0.1 parts per million is considered damaging to fish and the tiny creatures and plants on which they feed.”

As shown in tables 3a and 3b from Chapter 61, IAC, and in the table 1 below, the lowest criterion concentration for ammonia for aquatic life uses is 0.179 mg/l as N. However, this criterion is the chronic criteria for a pH of 9 and 30°C, conditions that are encountered in only the most productive streams in the middle of the summer. A more accurate value for comparison monitoring results cited in the article would be in the range of 2.5 mg/l as N if we use stream conditions at the time of sample collection (pH of 7.5-8; temp of < 5°C). Acute criteria of ammonia streams classified as B(WW) under these conditions would be in the range of 8.4 mg/l as N (pH of 8; temp of < 5°C). The use of the incorrect criteria (“0.1 parts per million”) for comparison of monitoring values gives an inaccurate representation of conditions sampled.

Table 1. Summary of Lowest Concentrations to Meet Criterion for Ammonia in Iowa Streams. [Iowa Water Quality Standards (Chapter 61, IAC)]

Acute Criterion for Ammonia in Iowa Streams

- Class B(CW-1 and CW-2) - Nitrogen, ammonia as N ($\text{NH}_4^+ + \text{NH}_3$)
 - pH = 9, any temperature - Criteria = 0.885 mg/l as N
- Class B(WW-1), B(WW-2), B(WW-3) & B(LW) - Nitrogen, ammonia as N ($\text{NH}_4^+ + \text{NH}_3$)
 - pH = 9, any temperature - Criteria = 1.32 mg/l as N

Chronic Criterion for Ammonia in Iowa Streams – Early Life Stages Present

- All classes
 - pH = 9, Temp = 30 °C - Criteria = 0.179 mg/l as N

1. The acute criteria represent the level of protection necessary to prevent acute toxicity to aquatic life. Instream concentrations above the acute criteria will be allowed only within the boundaries of the zone of initial dilution.
 2. The chronic criteria represent the level of protection necessary to prevent chronic toxicity to aquatic life. Excursions above the chronic criteria will be allowed only inside of mixing zones or only for short-term periods outside of mixing zones; however, these excursions cannot exceed the acute criteria shown in Tables 1 and 3. The chronic criteria will be met as short-term average conditions at all times the flow equals or exceeds either the design flows noted in subrule 61.2(5) or any site-specific low flow established under the provisions of subrule 61.2(5).
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2. The article states that “In February and March, readings ranged up to 2.6 parts per million in major Iowa streams, and several times that in tributaries. Some of the highest readings were found on the West Nishnabotna near Malvern, the East Nishnabotna near Shenandoah, the Boyer River near Missouri Valley and the Floyd River near Sioux City. Readings spiked in rivers almost everywhere, including near Ames, Iowa City, Cedar Rapids, Boone, Oskaloosa, Fort Dodge, Ottumwa, Marshalltown, Mason City and Waterloo. Only in far northeastern Iowa did top readings stay below 0.1 parts per million.”

Similar to comment #1 above, these comments incorrectly compares the monitoring values at these sites to applicable numeric criteria for ammonia as established in Chapter 61, IAC. Monitoring values for the months of February and March for these rivers are provided in Table 2 and compared to applicable criteria. None of these rivers exceeded either the acute or chronic criteria, and were, in fact, well below these thresholds in most cases.

Table 2. Ambient monitoring data for ammonia from rivers identified in Des Moines Register article. [Data from Iowa DNR STORET]

| | Nitrogen, ammonia as N | pH | Temp | Acute Criteria | Chronic Criteria |
|----------------------|--|-----|------|--|---------------------|
| | (NH ₄ ⁺ + NH ₃) mg L ⁻¹ as N | | °C | (NH ₄ ⁺ + NH ₃) mg L ⁻¹ as N | |
| West Nish (2/4/08) | 1 | 8 | 0.2 | 8.4 | 2.43 |
| West Nish (3/4/08) | 2.6 | 7.8 | 0.8 | 12.1 | 3.18 |
| East Nish (2/4/08) | 0.97 | 7.8 | 0.3 | 12.1 | 3.18 |
| East Nish (3/4/08) | 2.2 | 7.7 | 0.4 | 14.4 | 3.58 |
| S. Raccoon (2/14/08) | 0.5 | 7.6 | 1.0 | 17.0 | 3.98 |
| S. Raccoon (3/3/08) | 1.4 | 7.9 | 0.8 | 10.1 | 2.80 |
| Boyer (2/5/08) | 0.25 | 8.1 | 0 | 6.95 | 2.10 |
| Boyer (3/5/08) | 1.7 | 7.9 | 0.3 | 10.1 | 2.80 |
| Floyd (2/5/08) | 0.13 | 8.1 | 0 | 6.95 | 2.10 |
| Floyd (3/5/08) | 1.4 | 8.1 | 0.1 | 6.95 | 2.10 |

Temporal pattern of ammonia in Iowa streams and rivers – The Des Moines Register article leaves the reader with the impression that the ammonia concentrations found in the IDNR ambient monitoring are uncharacteristically high compared to past seasonal patterns. Attached at the end of this document is a figure portraying “Nitrogen, ammonia as N” (NH₄⁺ + NH₃) values for the months of January – March from all ambient stream sites for the period between 2000 and 2008 (figure provided by IDNR). This analysis demonstrates that, while highly variable, ammonia concentrations are consistently higher during these months than other times of the year. While levels found in 2008 were among the higher recorded over this time, the range and variation was consistent with several past years, likely under similar hydrologic conditions. Such inter-annual variability would seem to indicate that any attempt to ascribe patterns of ammonia concentrations to short-term land management activities may lead to spurious conclusions. As with all such relationships, the interactions are complex, and it is difficult to separate the effects of land management from the overriding impacts of climate and hydrology.

Other entities, such as the Des Moines Waterworks and the Des Moines River Water Quality Network also observed high total ammonia levels during the same time period of 2008. Such findings illustrate the need for increased monitoring to understand the relative magnitude of the potential sources and to direct effective management.

TABLE 3a. Acute Criterion for Ammonia in Iowa Streams

| Acute Criterion, mg/l as N (or Criterion Maximum Concentration, CMC) | | |
|---|--|-----------------------|
| pH | Class B(WW-1), B(WW-2), B(WW-3) & B(LW) | Class B(CW1) & B(CW2) |
| 6.5 | 48.8 | 32.6 |
| 6.6 | 46.8 | 31.3 |
| 6.7 | 44.6 | 29.8 |
| 6.8 | 42.0 | 28.0 |
| 6.9 | 39.1 | 26.1 |
| 7.0 | 36.1 | 24.1 |
| 7.1 | 32.8 | 21.9 |
| 7.2 | 29.5 | 19.7 |
| 7.3 | 26.2 | 17.5 |
| 7.4 | 23.0 | 15.3 |
| 7.5 | 19.9 | 13.3 |
| 7.6 | 17.0 | 11.4 |
| 7.7 | 14.4 | 9.64 |
| 7.8 | 12.1 | 8.11 |
| 7.9 | 10.1 | 6.77 |
| 8.0 | 8.40 | 5.62 |
| 8.1 | 6.95 | 4.64 |
| 8.2 | 5.72 | 3.83 |
| 8.3 | 4.71 | 3.15 |
| 8.4 | 3.88 | 2.59 |
| 8.5 | 3.20 | 2.14 |
| 8.6 | 2.65 | 1.77 |
| 8.7 | 2.20 | 1.47 |
| 8.8 | 1.84 | 1.23 |
| 8.9 | 1.56 | 1.04 |
| 9.0 | 1.32 | 0.885 |

TABLE 3b. Chronic Criterion for Ammonia in Iowa Streams - Early Life Stages Present

| Chronic Criterion – Early Life Stages Present, mg/l as N (or Criterion Continuous Concentration, CCC) | | | | | | | | | | |
|--|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| pH | Temperature, °C | | | | | | | | | |
| | 0 | 14 | 16 | 18 | 20 | 22 | 24 | 26 | 28 | 30 |
| 6.5 | 6.67 | 6.67 | 6.06 | 5.33 | 4.68 | 4.12 | 3.62 | 3.18 | 2.80 | 2.46 |
| 6.6 | 6.57 | 6.57 | 5.97 | 5.25 | 4.61 | 4.05 | 3.56 | 3.13 | 2.75 | 2.42 |
| 6.7 | 6.44 | 6.44 | 5.86 | 5.15 | 4.52 | 3.98 | 3.50 | 3.07 | 2.70 | 2.37 |
| 6.8 | 6.29 | 6.29 | 5.72 | 5.03 | 4.42 | 3.89 | 3.42 | 3.00 | 2.64 | 2.32 |
| 6.9 | 6.12 | 6.12 | 5.56 | 4.89 | 4.30 | 3.78 | 3.32 | 2.92 | 2.57 | 2.25 |
| 7.0 | 5.91 | 5.91 | 5.37 | 4.72 | 4.15 | 3.65 | 3.21 | 2.82 | 2.48 | 2.18 |
| 7.1 | 5.67 | 5.67 | 5.15 | 4.53 | 3.98 | 3.50 | 3.08 | 2.70 | 2.38 | 2.09 |
| 7.2 | 5.39 | 5.39 | 4.90 | 4.31 | 3.78 | 3.33 | 2.92 | 2.57 | 2.26 | 1.99 |
| 7.3 | 5.08 | 5.08 | 4.61 | 4.06 | 3.57 | 3.13 | 2.76 | 2.42 | 2.13 | 1.87 |
| 7.4 | 4.73 | 4.73 | 4.30 | 3.78 | 3.32 | 2.92 | 2.57 | 2.26 | 1.98 | 1.74 |
| 7.5 | 4.36 | 4.36 | 3.97 | 3.49 | 3.06 | 2.69 | 2.37 | 2.08 | 1.83 | 1.61 |
| 7.6 | 3.98 | 3.98 | 3.61 | 3.18 | 2.79 | 2.45 | 2.16 | 1.90 | 1.67 | 1.47 |
| 7.7 | 3.58 | 3.58 | 3.25 | 2.86 | 2.51 | 2.21 | 1.94 | 1.71 | 1.50 | 1.32 |
| 7.8 | 3.18 | 3.18 | 2.89 | 2.54 | 2.23 | 1.96 | 1.73 | 1.52 | 1.33 | 1.17 |
| 7.9 | 2.8 | 2.8 | 2.54 | 2.24 | 1.96 | 1.73 | 1.52 | 1.33 | 1.17 | 1.03 |
| 8.0 | 2.43 | 2.43 | 2.21 | 1.94 | 1.71 | 1.50 | 1.32 | 1.16 | 1.02 | 0.897 |
| 8.1 | 2.10 | 2.10 | 1.91 | 1.68 | 1.47 | 1.29 | 1.14 | 1.00 | 0.879 | 0.773 |
| 8.2 | 1.79 | 1.79 | 1.63 | 1.43 | 1.26 | 1.11 | 0.973 | 0.855 | 0.752 | 0.661 |
| 8.3 | 1.52 | 1.52 | 1.39 | 1.22 | 1.07 | 0.941 | 0.827 | 0.727 | 0.639 | 0.562 |
| 8.4 | 1.29 | 1.29 | 1.17 | 1.03 | 0.906 | 0.796 | 0.700 | 0.615 | 0.541 | 0.475 |
| 8.5 | 1.09 | 1.09 | 0.990 | 0.870 | 0.765 | 0.672 | 0.591 | 0.520 | 0.457 | 0.401 |
| 8.6 | 0.920 | 0.920 | 0.836 | 0.735 | 0.646 | 0.568 | 0.499 | 0.439 | 0.386 | 0.339 |
| 8.7 | 0.778 | 0.778 | 0.707 | 0.622 | 0.547 | 0.480 | 0.422 | 0.371 | 0.326 | 0.287 |
| 8.8 | 0.661 | 0.661 | 0.601 | 0.528 | 0.464 | 0.408 | 0.359 | 0.315 | 0.277 | 0.244 |
| 8.9 | 0.565 | 0.565 | 0.513 | 0.451 | 0.397 | 0.349 | 0.306 | 0.269 | 0.237 | 0.208 |
| 9.0 | 0.486 | 0.486 | 0.442 | 0.389 | 0.342 | 0.300 | 0.264 | 0.232 | 0.204 | 0.179 |

TABLE 3c. Chronic Criterion for Ammonia in Iowa Streams - Early Life Stages Absent

| Chronic Criterion – Early Life Stages Absent, mg/l as N (or Criterion Continuous Concentration, CCC) | | | | | | | | | | |
|---|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| pH | Temperature, °C | | | | | | | | | |
| | 0-7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15* | 16* |
| 6.5 | 10.8 | 10.1 | 9.51 | 8.92 | 8.36 | 7.84 | 7.35 | 6.89 | 6.46 | 6.06 |
| 6.6 | 10.7 | 9.99 | 9.37 | 8.79 | 8.24 | 7.72 | 7.24 | 6.79 | 6.36 | 5.97 |
| 6.7 | 10.5 | 9.81 | 9.20 | 8.62 | 8.08 | 7.58 | 7.11 | 6.66 | 6.25 | 5.86 |
| 6.8 | 10.2 | 9.58 | 8.98 | 8.42 | 7.90 | 7.40 | 6.94 | 6.51 | 6.10 | 5.72 |
| 6.9 | 9.93 | 9.31 | 8.73 | 8.19 | 7.68 | 7.20 | 6.75 | 6.33 | 5.93 | 5.56 |
| 7.0 | 9.60 | 9.00 | 8.43 | 7.91 | 7.41 | 6.95 | 6.52 | 6.11 | 5.73 | 5.37 |
| 7.1 | 9.20 | 8.63 | 8.09 | 7.58 | 7.11 | 6.67 | 6.25 | 5.86 | 5.49 | 5.15 |
| 7.2 | 8.75 | 8.20 | 7.69 | 7.21 | 6.76 | 6.34 | 5.94 | 5.57 | 5.22 | 4.90 |
| 7.3 | 8.24 | 7.73 | 7.25 | 6.79 | 6.37 | 5.97 | 5.60 | 5.25 | 4.92 | 4.61 |
| 7.4 | 7.69 | 7.21 | 6.76 | 6.33 | 5.94 | 5.57 | 5.22 | 4.89 | 4.59 | 4.30 |
| 7.5 | 7.09 | 6.64 | 6.23 | 5.84 | 5.48 | 5.13 | 4.81 | 4.51 | 4.23 | 3.97 |
| 7.6 | 6.46 | 6.05 | 5.67 | 5.32 | 4.99 | 4.68 | 4.38 | 4.11 | 3.85 | 3.61 |
| 7.7 | 5.81 | 5.45 | 5.11 | 4.79 | 4.49 | 4.21 | 3.95 | 3.70 | 3.47 | 3.25 |
| 7.8 | 5.17 | 4.84 | 4.54 | 4.26 | 3.99 | 3.74 | 3.51 | 3.29 | 3.09 | 2.89 |
| 7.9 | 4.54 | 4.26 | 3.99 | 3.74 | 3.51 | 3.29 | 3.09 | 2.89 | 2.71 | 2.54 |
| 8.0 | 3.95 | 3.70 | 3.47 | 3.26 | 3.05 | 2.86 | 2.68 | 2.52 | 2.36 | 2.21 |
| 8.1 | 3.41 | 3.19 | 2.99 | 2.81 | 2.63 | 2.47 | 2.31 | 2.17 | 2.03 | 1.91 |
| 8.2 | 2.91 | 2.73 | 2.56 | 2.40 | 2.25 | 2.11 | 1.98 | 1.85 | 1.74 | 1.63 |
| 8.3 | 2.47 | 2.32 | 2.18 | 2.04 | 1.91 | 1.79 | 1.68 | 1.58 | 1.48 | 1.39 |
| 8.4 | 2.09 | 1.96 | 1.84 | 1.73 | 1.62 | 1.52 | 1.42 | 1.33 | 1.25 | 1.17 |
| 8.5 | 1.77 | 1.66 | 1.55 | 1.46 | 1.37 | 1.28 | 1.20 | 1.13 | 1.06 | 0.99 |
| 8.6 | 1.49 | 1.40 | 1.31 | 1.23 | 1.15 | 1.08 | 1.01 | 0.951 | 0.892 | 0.836 |
| 8.7 | 1.26 | 1.18 | 1.11 | 1.04 | 0.976 | 0.915 | 0.858 | 0.805 | 0.754 | 0.707 |
| 8.8 | 1.07 | 1.01 | 0.944 | 0.885 | 0.829 | 0.778 | 0.729 | 0.684 | 0.641 | 0.601 |
| 8.9 | 0.917 | 0.860 | 0.806 | 0.756 | 0.709 | 0.664 | 0.623 | 0.584 | 0.548 | 0.513 |
| 9.0 | 0.790 | 0.740 | 0.694 | 0.651 | 0.610 | 0.572 | 0.536 | 0.503 | 0.471 | 0.442 |

*At 15°C and above, the criterion for fish early life stage (ELS) absent is the same as the criterion for fish ELS present.

Ambient Stream Sites

