CHAPTER 1.10 - Ammonia & Associated WET Requirements

The Department promulgated water quality standards for ammonia in s. NR 106.36, Wis. Adm. Code, on March 1, 2004, which adjusts WET requirements in certain situations. The following guidance is given in two parts:

Part One: The first part of this chapter provides guidance for Department staff, WET labs and permittees, regarding requirements in s. NR 106.36, Wis. Adm. Code, which allows effluent samples used in chronic fathead minnow WET tests to be modified to remove ammonia prior to testing when early life stage (ELS) - absent ammonia criteria are in effect.

Part Two: The second part of this chapter gives guidance for staff to use when making adjustments to WET requirements when a permittee has been granted a water quality standards variance for ammonia.

NOTICE: This document is intended solely as guidance, and does not contain any mandatory requirements except where requirements found in statute or administrative rule are referenced. This guidance does not establish or affect legal rights or obligations, and is not finally determinative of any of the issues addressed. This guidance does not create any rights enforceable by any party in litigation with the State of Wisconsin or the Department of Natural Resources. Any regulatory decisions made by the Department of Natural Resources in any matter addressed by this guidance will be made by applying the governing statutes and administrative rules to the relevant facts.

Part One: WET Sample Modification When ELS-Absent Criteria Are In Effect

USEPA's *1999 Update of Ambient WQC for Ammonia* contains a provision to adjust (relax) chronic water quality criteria (WQC) for ammonia when water temperatures are colder (< 15º C) and early life stages (ELS) are absent, in order to account for reduced sensitivity to ammonia by juvenile and adult fish at lower temperatures. In Wisconsin, this translates into higher (less stringent) limits for ammonia during winter months. Fathead minnow ELS were used, with other data, to develop the adjustment between ELS present and absent criteria, and the fathead minnow is known to be very sensitive to ammonia. Of the data used to develop WQC for ammonia, only *Hyalella* (an invertebrate), *Musculium* (a mussel), and *Lepomis* (blue gill) ELS were more sensitive to ammonia than the fathead minnow ELS. Like fathead minnow ELS, *Lepomis* ELS would not be expected in receiving waters during the ELS-absent period.

It has been pointed out that a conflict may exist between allowing this less stringent ammonia criteria during ELS-absent periods and requiring WET tests during those same periods, since chronic WET tests are conducted using fathead minnow ELS. Under this scenario, a situation could arise where the permittee is in compliance with its effluent limit for ammonia during an ELS-absent time period, but have a positive (failing) chronic fish WET test due to ammonia during that same period. Because of this, s. NR 106.36, Wis. Adm. Code, allows samples used in chronic fathead minnow WET tests to be modified to remove ammonia prior to testing when certain conditions are met (See Figure 1).

Permit Language When ELS-Absent Criteria Are Applied

The following standard language may be added to WPDES permits when WQBELs based on ELS-absent criteria are given:

> *"Effluent samples used in chronic fathead minnow tests may be modified to remove ammonia prior to testing, according to s. NR 106.36(2), Wis. Adm. Code, during periods when ammonia limits based on early life stage-absent criteria are in effect."*

Figure 1. NR 106.36 Alternative whole effluent toxicity monitoring for certain discharges of ammonia.

(1) In addition to water quality based effluent limitations for ammonia, the department may establish whole effluent toxicity testing requirements and limitations pursuant to ss. NR 106.08 and 106.09.

(2) Chronic fathead minnow whole effluent toxicity test samples may be modified to remove ammonia prior to testing when all of the following conditions are met:

(a) The whole effluent toxicity test is being conducted during a period when ammonia effluent limitations based on early life stage absent criteria are in effect.

(b) The permittee has demonstrated compliance with applicable acute and chronic water quality based effluent limitations for ammonia during the testing period.

(c) Total ammonia measured in whole effluent toxicity test effluent samples is less than the applicable chronic water quality based effluent limitation contained in the WPDES permit, but greater than the "ammonia threshold number", determined as follows:

1. Measure the pH of the whole effluent toxicity test effluent sample after the sample has been warmed to the test temperature.
2. Using the pH value of the sample as determined in subd.1., determine the value of the ammonia multiplier in Table 1 for the pH range corresponding to the effluent pH.
3. Divide 100 by the appropriate in–stream waste concentration, as a percentage, contained in the WPDES permit; then multiply the resulting value by the ammonia multiplier determined in subd. 2. to obtain the ammonia threshold number.

(3) If all of the criteria in sub. (2) have been met, ammonia may be removed from the test sample.

Table 1.

Effluent pH (s.u., after warming)	Ammonia multiplier (mg/l total ammonia)
6.0 – 6.5	30
6.6 – 7.0	25
7.1 – 7.5	15
7.6 – 8.0	5
8.1 – 9.0	1

Modification of WET Samples During ELS-Absent Periods

As outlined above, it may be appropriate to conduct the fathead minnow portion of the chronic WET test on effluent samples that have been treated to remove ammonia prior to testing. When those conditions are met, effluent samples may be treated with zeolite resin prior to testing. Samples should be treated daily, before use in WET tests, rather than batch treated for multiple day usage. Ammonia, pH, hardness, and alkalinity should be measured prior to and after zeolite treatment. A blank (an extra negative control) should also be run through zeolite, to account for toxic artifacts due to the zeolite treatment. Samples used for fathead minnow chronic tests should not be modified in any way other than ammonia removal with the zeolite resin. Samples used in concurrent acute tests (fathead minnow and *Ceriodaphnia dubia*) and chronic tests with *C. dubia* are not to be modified prior to testing.

Decisions regarding WET monitoring frequencies and scheduling should be made according to guidance in Chapter 1.3 (http://dnr.wi.gov/topic/wastewater/WETguidance.html) and acute and chronic WET tests should be required during ELS-absent periods, when recommended by the guidance found there. Continued WET testing during winter months is important, when possible, because wastewater treatment (and, therefore, effluent toxicity) can be significantly different during colder weather. Chronic fathead minnow WET tests conducted during periods when ELS-absent ammonia criteria are in effect will still be used to assess whether toxicity is present due to other compounds. Toxicity due to ammonia and other compounds will also be assessed with acute WET tests and the *C. dubia* chronic test during these periods.

Can This Be Applied To Other Pollutants?

It is important to note that this is not just a matter of passing a chemical-specific limit for a toxicant and failing a WET test that identifies that chemical as the toxicant. This is a special case only for ammonia because this provision to adjust the chronic criteria during periods of the year when water temperatures are colder and fish ELS are absent is unique to ammonia. Ammonia is the only chemical for which data showing a difference in sensitivity between ELS and adult fish has been used to allow for an adjustment in the WQC in the absence of fish ELS. This approach is believed to be appropriate for ammonia because the early life stage used in the chronic fathead minnow WET test, and other early life stages that the fathead minnow is being used as a surrogate for, are not found in receiving waters during ELS-absent periods. Therefore, it is believed that a positive chronic fathead minnow WET test result caused by ammonia toxicity would not likely be indicative of negative effects in the receiving water because the life stages that experience those toxic effects would not be present. In addition, any significant chronic toxicity due to ammonia that may be harmful to other non-fish species present in the receiving water during colder periods should be indicated by *C. dubia* chronic tests.

Will Zeolite Remove More Than Ammonia?

Zeolite is composed of natural or synthetically created crystalline, hydrated alkali-aluminum silicates. When zeolite is exposed to an aqueous solution (such as an effluent), the positively charged resin removes cations from the solution. Since it is an effective ion exchange resin, zeolite has frequently been used in toxicity identification work (*Methods for Aquatic Toxicity Identification: Phase II TIE Procedures*, EPA/600/R-92/080), specifically to remove the ammonium ion (NH_4^+) from effluent samples. However, because of its ion exchange properties, it may also remove other cations such as heavy metals. In addition, although the primary action of zeolite is chemical (ion exchange), the physical manipulation of filtration also occurs during the process. Removal of compounds via filtration through zeolite may include surfactants and polymers. Changes in the ionic balance of the sample caused by the zeolite treatment may also cause chemicals that would not have caused toxic effects before zeolite treatment to be rendered biologically available.

While it is true that modification of samples with zeolite can remove substances other than ammonia and may modify the sample in other ways, the potential for this method to reduce the ability of the WET test to detect toxicity due to other substances should be small in most cases. In addition, substances other than ammonia that may be removed by zeolite, especially heavy metals, are typically more toxic to *C. dubia* than the fathead minnow. Since samples used in the *C. dubia* test are not being modified, that toxicity should still be detected. Additionally, since the presence of ammonia in a sample may mask toxicity caused by other substances, the removal of ammonia could allow for the detection of substances that may have been missed had ammonia been present.

Historical WET Data From Previous ELS-Absent Periods

In some cases, a permittee may have collected WET data during previous years when ELS-absent ammonia criteria would have been applicable. The question arises then of how to consider WET tests conducted under these conditions, when making permit-related decisions. The results of a fathead minnow chronic test completed during ELS-absent periods should not be used when assessing reasonable potential or choosing the WET monitoring frequency (i.e., in the WET Checklist process) if all of the following are true: 1) the test appears to have failed due to ammonia toxicity, 2) concurrent acute tests and chronic *C. dubia* tests did not show toxicity, and 3) the conditions listed in s. NR 106.36, Wis. Adm. Code (shown in Figure 1 above), are met.

It is important to keep in mind that this exclusion applies only to ammonia because it is the only water quality criterion that has an adjustment for the presence or absence of fish ELS. Any WET tests which showed toxicity in an acute test or a *C. dubia* chronic test, or in a fathead minnow chronic test due to any toxicant other than ammonia should not be excluded from WET determinations. Results generated by acute tests and *C. dubia* chronic tests conducted during

periods when ELS-absent ammonia criteria are in effect are still applicable for assessing effluent toxicity from all toxicants, including ammonia. If staff have questions regarding WET data collected during ELS-absent periods, they should contact the Biomonitoring Coordinator (Kari.Fleming@wisconsin.gov; 608-267-7663).

Part Two: WET Monitoring When an Ammonia Variance Has Been Granted

WET testing has been conducted on effluents from municipal and industrial point sources where toxicity potential was thought to be present since the late 1980s. Ammonia has been shown to be a common toxicant found in wastewater effluents and has been regulated accordingly in the WET program. WET test failures caused by ammonia are treated the same way as those caused by other toxicants. Ammonia-related WET failures occur most often during the winter months, especially in cases where stabilization ponds and aerated lagoons are used, because wastewater treatment is less effective (or ineffective) in colder temperatures. In most cases, higher ammonia levels will occur in wastewater during the months of December through May.

Permittees may be granted a variance to the ammonia water quality standard (WQS) as allowed in s. 283.15, Wis. Stats., due to socio-economic impacts or other factors. (See http://dnr.wi.gov/topic/wastewater/variances.html for more information on WQS variances.) As a condition of the variance, permittees may be given higher (less stringent) ammonia limits during the term of the variance. In these cases, it may be necessary to also adjust WET monitoring schedules to account for periods when levels of ammonia in the effluent are allowed to be present above water quality-based effluent limits that were applicable before the variance was granted.

Depending on the level of ammonia present in the effluent, toxicity may occur in acute and chronic tests and to one or all of the tested species. It is generally accepted that the fathead minnow will experience acute toxicity if ammonia is present at levels above 30 mg/l (at pH $\leq$ 7.5) and chronic toxicity if ammonia > 15 mg/l (at pH $\leq$ 7.5 and 100% IWC). *C. dubia*, on the other hand, would not be expected to show acute toxicity until ammonia is above 60 mg/l (at pH $\leq$ 7.5) and chronic *C. dubia* toxicity wouldn't be expected until levels are > 50 mg/l (at pH $\leq$ 7.5 and 100% IWC).

Depending on the level of ammonia expected to be present in the effluent, staff may determine that it is appropriate to not require WET testing at certain times of the year or to require that only *C. dubia* be tested. For example, if the maximum daily amount of ammonia present in the effluent is expected to stay above 15 mg/l, but below 50 mg/l in December through May, the permit could require that chronic WET tests be conducted at other times of the year (June – November). If it is desirable to collect WET data during the months of December – May in this same case, staff could require that testing be done using *C. dubia* only.

If it has been determined that the permittee should be granted (or has previously been granted) a variance for ammonia, staff should make decisions on whether or not to use previously collected WET data using the same logic as described above. If WET tests were collected under conditions that are being excluded for testing in the future, then it may be appropriate to remove those data from WET limit and monitoring determinations. WET test results that indicate toxicity is due to substances other than ammonia should still be used when making WET determinations.

Ammonia Toxicity and pH Drift

Natural processes which act to regulate the pH of natural waters also occur in mixtures of natural surface waters and effluents. With the exception of lagoon systems, effluent pH values are often lower than those in receiving waters, due to the presence of excess carbon dioxide resulting from the artificially high rates of respiration of microorganisms in wastewater treatment plants. When the effluent is discharged to surface waters (or mixed with receiving waters in laboratory settings), respiration rates fall to "natural" levels and excess carbon dioxide is stripped, causing a pH rise or drift upwards. Significant pH drift can sometimes occur in WET tests, due to the static conditions present in the test. This can

impact how much toxicity is expressed due to ammonia in these WET tests, since higher pHs result in more ammonia toxicity. Extra care should be taken in tests where ammonia is at or near toxic levels. Chapter 2.8 (http://dnr.wi.gov/topic/wastewater/WETguidance.html) discusses the use of CO2 entrapment methods to control pH drift and when it is required in permit-required WET tests.

Questions regarding WET test design, data interpretation, or the applicability of historical data should be directed to the Biomonitoring Coordinator (Kari.Fleming@wisconsin.gov; 608-267-7663).