CHAPTER 2.10 - Chlorides and WET Testing

This chapter supports s. NR 106.89, Wis. Adm. Code, providing guidance for making demonstrations that chloride is causing effluent toxicity.

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Why Is Chloride Treated Differently Than Other Toxic Compounds?

In most cases, the Department doesn't make a distinction about what causes whole effluent toxicity (WET) when determining permit requirements, because it is the permittee's responsibility to achieve and maintain WET compliance, regardless of the cause. The permittee is expected to identify the source of toxicity and fix it by whatever means necessary (e.g., source reduction, pretreatment, in-plant modifications). Chloride is unique, however, since it behaves conservatively and since wastewater treatment processes designed to remove it (e.g., reverse osmosis, ion exchange) have high capital equipment costs, operating & maintenance costs, high energy requirements, and produce large volumes of solid waste which make them undesirable environmental alternatives. So source reduction activities are more often the preferred approach for eliminating chloride from point source discharges to surface water.

WET-related Requirements in Wisconsin's Chloride Rule

Wisconsin chloride regulations are given in s. NR 106.80, Wis. Adm. Code, which spells out requirements for point sources that discharge wastewater containing chloride to surface waters of the state. The ultimate goal of that policy is for dischargers to comply with water quality-based effluent limits (WQBEL) for chloride. However, in recognition of the impracticality of end-of-pipe treatment for chloride, the rules allow permittees to request a source reduction based permit with a schedule to work towards the WQBEL, rather than a traditional permit which immediately imposes the WQBEL. When a source reduction based requirement is established in the WPDES permit, s. NR 106.89, Wis. Adm. Code, allows permittees to demonstrate that chloride is also responsible for WET failures. According to s. NR 106.89, Wis. Adm. Code, if chloride can be shown to be the sole cause of WET problems, chloride limits can be used in lieu of WET requirements until chloride source reduction measures are complete:

NR 106.89 Alternative whole effluent toxicity monitoring and limitations for dischargers of chloride.

(1) GENERAL. In addition to interim, target and calculated water quality-based effluent limitations and target values for chloride, the department may establish whole effluent toxicity testing requirements and limitations pursuant to ss. NR 106.08 and 106.09.

(2) FINDINGS. The department finds all of the following:

(a) Acute whole effluent toxicity limitations cannot be attained if the effluent concentration of chloride exceeds 2,500 mg/L;
(b) Chronic whole effluent toxicity limitations cannot be attained if the effluent concentration of chloride exceeds 2 times the calculated chronic water quality-based effluent limitation;
(c) Chloride limitations will be used in lieu of WET limitations to attain and maintain narrative criteria in ss. NR 102.04(1)(d) and NR 102.04(4)(d) in the cases where chloride is the sole source of acute or chronic whole effluent toxicity.
(3) **Chloride Limits in Lieu of Acute Wet Limits.** Chloride limitations shall be included in the WPDES permit in lieu of acute whole effluent toxicity testing requirements and acute whole effluent toxicity limitations until source reduction actions are completed if any of the following apply:

(a) The permittee can demonstrate to the satisfaction of the department that the effluent concentration of chloride exceeds 2,500 mg/L, or

(b) The permittee can demonstrate to the satisfaction of the department that the effluent concentration of chloride is less than 2,500 mg/L, but in excess of the calculated acute water quality-based effluent limitation, and additional data are submitted which demonstrate that chloride is the sole source of acute toxicity.

(4) **Chloride Limits in Lieu of Chronic Wet Limits.** Chloride limitations shall be included in the WPDES permit in lieu of chronic whole effluent toxicity testing requirements and chronic whole effluent toxicity limitations until source reduction actions are completed if either:

(a) The permittee can demonstrate to the satisfaction of the department that the effluent concentration of chloride exceeds 2 times the calculated chronic water quality-based effluent limitation, or

(b) The permittee can demonstrate to the satisfaction of the department that the effluent concentration of chloride is less than 2 times the calculated chronic water quality-based effluent limitation, but in excess of the calculated chronic water quality-based effluent limitation, and additional data are submitted which demonstrate that chloride is the sole source of chronic toxicity.

(5) **Decision Documentation.** The department shall specify the decision to include chloride limitations in lieu of whole effluent toxicity limitations in the permit fact sheet.

(6) **Re-evaluation.** The department shall re-evaluate the need for whole effluent toxicity and chloride monitoring or limitations upon permit reissuance.

WET monitoring and limits may be excluded from permits if chloride limits are applied according to the procedures in s. NR 106.89, Wis. Adm. Code (when chloride is the sole source of toxicity). Standard permit language is provided in SWAMP and discussed in Chapter 1.14. Reasons for excluding WET requirements should be spelled out in the permit fact sheet. Once chloride source reduction is complete (i.e., WQBELs are being met), the need for WET monitoring and limits should be reevaluated. Monitoring may be necessary to show that all toxicity has been removed with the reduction of chloride.

### Allowing for Additional Data to be Collected

In some cases, there may be some question as to whether chloride is the sole source of toxicity when a permit is being reissued. If this happens, a compliance schedule may be given to allow time to make this demonstration. The WET limit and appropriate monitoring (based on the assumption that chloride is not the cause) should be placed in the permit, in the event that the permittee cannot successfully demonstrate that chloride is the sole source of toxicity. Below are some example schedules that may be used in these situations.

<table>
<thead>
<tr>
<th>Required Action</th>
<th>Date Due</th>
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<tbody>
<tr>
<td>Submit a study plan describing procedures to be used to demonstrate chloride is the sole source of effluent toxicity.</td>
<td>1-3 months (from permit issuance)</td>
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</tbody>
</table>
| Implement the study plan, make a reasonable attempt to identify the source of toxicity, and submit a report to the Department presenting the results of the evaluation. If the Department determines that chloride is the sole source of toxicity, the (acute/chronic) WET monitoring required in section (X) will not be required. If this demonstration is not successful, the permittee must complete the (acute/chronic) WET monitoring required in section (X). | 1 -1.5 yrs (from permit issuance)
If monitoring and WET limit recommended:

### Whole Effluent Toxicity Limit Compliance Schedule

<table>
<thead>
<tr>
<th>Required Action</th>
<th>Date Due</th>
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<tbody>
<tr>
<td>Submit a study plan describing procedures to be used to determine the cause of effluent toxicity.</td>
<td>1-3 months (from permit issuance)</td>
</tr>
<tr>
<td>Implement the study plan, make a reasonable attempt to identify the source of toxicity, and submit a report to the Department presenting the results of the evaluation. If the Department determines that chloride is the sole source of toxicity, the remainder of this schedule, (acute/chronic) WET monitoring in section (X), and the (acute/chronic) WET limit will not become effective. If this demonstration is not successful, the permittee must complete the remaining portions of this schedule and meet the WET limit in section (X).</td>
<td>1 - 1.5 yrs (from permit issuance)</td>
</tr>
<tr>
<td>Submit part two of the TRE Plan describing actions to be taken to reduce or eliminate the toxicity identified in part one of the TRE and the dates by which those actions will be implemented.</td>
<td>@ 1 month (from the end of step 2)</td>
</tr>
<tr>
<td>Submit a progress report identifying the actions taken to date to implement part two of the TRE plan.</td>
<td>about 1/2 way through part 2</td>
</tr>
<tr>
<td>Complete all actions identified in the TRE plan and achieve compliance with the effluent toxicity limitation.</td>
<td>1 - 1.5 yrs (from the end of step 2)</td>
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### What Additional Data Is Needed To Show That Chloride Is Causing Toxicity?

Section NR 106.89, Wis. Adm. Code, says the Department can place chloride limitations in the WPDES permit in lieu of WET monitoring and limits if either chloride is present at a preset level (2,500 mg/l for acute or 2x the WQBEL for chronic) or if effluent concentrations are above the WQBEL and additional data are submitted which demonstrate that chloride is the sole source of toxicity. So what is meant by "additional data"?

Normally, when an effluent has shown repeated toxicity, a permittee is required to perform a Toxicity Reduction Evaluation (TRE) to identify and fix the source(s) of toxicity. In toxicity identification steps, effluent samples may be manipulated to remove suspect chemicals (e.g., metals, organics) and then re-tested to see if toxicity remains. If a specific effluent manipulation removes toxicity, then the researcher has a clue about the source of toxicity. However, chloride is a unique substance that is not easily altered by chemical reactions, therefore traditional investigation methods do not work well for identifying chloride as the cause of toxicity. However, other information can be used to help determine if chloride is responsible for toxicity.

### Most Sensitive Species.

As shown in Table 1 (below), there is a significant difference in the sensitivities of WET test organisms to chloride, and that difference can provide useful information when determining whether chloride is the sole cause of toxicity. *Ceriodaphnia dubia* is the most sensitive to chloride (as NaCl), with an average acute critical concentration (LC$_{50}$) of about 2,500 mg/l and an average chronic critical concentration (IC$_{25}$) of about 720 mg/l. The algae species is less sensitive with an average IC$_{50}$ of about 2,200 mg/l. The fathead minnow is the least sensitive of these 3 species, with an average LC$_{50}$ more than twice as high as that for *C. dubia* and an IC$_{25}$ more than four times as high. This relative sensitivity pattern is useful as a first step towards determining whether chloride is a significant source of toxicity. If the LC$_{50}$ for the fathead minnow is lower than that for *C. dubia*, it is safe to rule out chloride as the primary toxicant. If the situation is reversed and chloride levels are near levels of concern, further data may be needed to verify whether chloride is the primary toxicant in the effluent.
### TABLE 1. CHLORIDE TOXICITY VALUES (mg/l)

<table>
<thead>
<tr>
<th></th>
<th>Acute</th>
<th>Chronic</th>
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</thead>
<tbody>
<tr>
<td><strong>Water Quality Criteria</strong> (according to ch. NR 105, Table 1 &amp; Table 5)</td>
<td>757</td>
<td>395</td>
</tr>
<tr>
<td><strong>Water Quality Based Effluent Limits (WQBEL)</strong> (according to ss. NR 106.06(3) and (4)).</td>
<td>1514</td>
<td>((395)(Q_s+(1-f)Q_e)-(Q_s-fQ_e)(C_s))/(Q_e)</td>
</tr>
<tr>
<td><strong>Reference toxicant information (NaCl)</strong> (average of data from 5 labs, except algae data which represents SLH data only); (Acute = LC50; chronic = IC25)</td>
<td>2500 (C. dubia)</td>
<td>720 (C. dubia)</td>
</tr>
<tr>
<td></td>
<td>5830 (fhm)</td>
<td>2220 (algae)</td>
</tr>
<tr>
<td></td>
<td>3080 (fhm)</td>
<td></td>
</tr>
</tbody>
</table>

1. Range of last 20 LC50 values from reference toxicant tests using sodium chloride (NaCl) from all certified labs in 2014 was 1,710 – 3,540 mg/l.
2. Range of last 20 IC50 values from reference toxicant tests using NaCl from all certified labs in 2014 was 210 – 1,730 mg/l.

- **Q_s** = receiving water flow (usu. \(Q_{7,10}/4\)); **Q_e** = effluent design flow (municipal) or average annual effluent flow (industrial); **f** = fraction of the effluent withdrawn from the receiving water; **C_s** = background concentration of the substance.
- **fhm** = fathead minnow (Pimephales promelas)

### Effluent Chloride Concentration

Additional insight can be obtained by determining the chloride concentration in the effluent. As a general rule, if chloride levels are near or above the reference toxicant values shown in Table 1, the concentration may be high enough to adversely affect WET test species. If effluent levels are significantly lower than these values, chloride may not be the primary source of toxicity.

### Phase I TIEs

Additional information can be obtained by conducting a toxicity identification evaluation (TIE). If Phase I TIE manipulations on effluent with high chloride levels indicate that toxicity cannot be eliminated or significantly reduced by any of the treatment steps, the chloride concentration in the effluent may be responsible for toxicity and should be further evaluated. Since the toxicity of chloride may be masked or affected by associated ions (see below), it may be necessary to include a determination of specific ion concentrations in the effluent before and after each step of the Phase I TIE protocol. (See Chapter 2.2 for more discussion of Phase I TIEs.)

One can also assess the cause(s) of toxicity by evaluating the concentration of major ions that compose the effluent's total dissolved solids (TDS). Measured concentrations of ions can be compared to literature or to laboratory-derived effect concentrations to determine if ion concentrations are above effect concentrations. Chemical fractionation schemes can provide additional information on whether inorganic toxic constituents are contributing to toxicity. Chromatographic columns containing cation and anion exchange resins have also been successfully used by researchers to help determine if inorganic salts are playing a role in toxicity.

### Ionic Composition vs. Toxicity

TDS, conductivity, and salinity are often used as measures for ions in effluents. However, the correlation between increasing TDS or conductivity and toxicity may vary with ionic composition and therefore may not be the best predictor of toxicity due to chloride. Because chloride is not usually present as individual constituents but rather in combination with other ions, the toxicity of chloride may be masked or affected by associated ions. Therefore, it may be necessary to understand the effects of the various ions alone and to consider those caused by the combination of ions in the effluent.

For example, in one study, the effects of more than 2,900 ion solutions on *C. dubia*, *D. magna*, and the fathead minnow (*P. promelas*) were studied (Mount, et al, 1997). The relative ion toxicity was found to be \(K^+ > HCO_3 > Mg^{2+} > Cl > SO_4^{2-}\). For all of the salts tested, *C. dubia* was found to be the most sensitive species, when compared to *D. magna* and *P. promelas*. For certain salts, such as CaSO_4, toxicity to the three species was found to be similar, whereas for others (i.e., NaCl), the difference was great. In addition, the toxicity of Na\(^+\) and Ca\(^{2+}\) salts was primarily attributable to the corresponding anion. For *C. dubia* and *D. magna*, the toxicity of chloride was sometimes reduced in solutions that were enriched with more than one cation.
**Synthetic Effluents.** Synthetic or "mock" effluents, which mimic the major ions in the effluent under evaluation, have also proven useful for the assessment of TDS toxicity. In this procedure, aliquots of the effluent are mixed with various amounts of synthetic effluent (based on chemical evaluation of the effluent for the major ions) in an effort to determine if the concentration of the measured anions and cations cause toxicity to the test organism. The hypothesis of this procedure is that if the effluent is diluted with various amounts of synthetic effluent that contain only the salts found in the effluent, then any unknown toxicants potentially in the effluent will also be diluted, resulting in a lessened acute or chronic toxicity response of the test organism. However, if TDS is the toxicant of concern in the wastewater, the corresponding acute or chronic toxicity responses would be similar.

In Summary, Chloride Toxicity May Be Indicated If:

- There is greater sensitivity by *Ceriodaphnia dubia* compared to *Daphnia magna*, *Selenastrum capricornutum* (algae), and the fathead minnow, together with high conductivity and/or chloride measurements.

- Phase I TIE manipulations show that: 1) pH adjustments don’t remove toxicity and a precipitate is not visible in the pH adjustment test, pH adjustment and filtration test, or pH adjustment and aeration test; 2) there is no loss of toxicity in the post C18 SPE column tests, or a partial loss of toxicity, but no or little change in conductivity; 3) there is no change in toxicity with the EDTA addition test, sodium thiosulfate addition test, or the graduated pH test; 4) toxicity is not removed or reduced by passing the effluent over activated carbon; and 5) toxicity is removed or reduced by ion exchange resin.

- A mock effluent prepared with the same ions as the effluent exhibits similar toxicity as the effluent.

The above approaches can be used individually or together in a weight-of-evidence approach to demonstrate the part that chloride plays in effluent toxicity. Because of the differences between production and treatment processes and wastewater effluents, flexibility in the design of these studies is essential and approaches used are often facility specific. The guidance provided here is intended to describe general approaches which may be used to identify chloride as the primary cause of toxicity. It is up to the permittee, with help from their WET lab or consultant, to develop a study plan and to determine what is necessary to determine the cause of toxicity. Communication/cooperation between the permittee and the Department is essential in plan development and implementation and will help ensure achievement of the study objectives.

REFERENCES:
