# CHAPTER 2.10 - Chlorides and WET Testing

## This chapter supplements the "Implementation Plan for the Chloride Rule" (1/00), providing guidance for making demonstrations that chloride is causing effluent toxicity.

*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.*

### Why Is Chloride Treated Differently Than Other Toxic Compounds?

The Department doesn't usually make a distinction between causes of whole effluent toxicity (WET), because it's the permittee's responsibility to maintain compliance, regardless of the cause. The permittee is usually expected to remove toxicity by whatever means necessary (e.g., source reduction, pretreatment, in-plant modifications). According to NR 106, Wis. Adm. Code, permittees are responsible for effluent toxicity, whatever the cause.

Chloride is considered unique, however, since it behaves conservatively (i.e., its concentration in water is not altered by chemical/biological reactions and only dilution dictates its concentration) and since treatment processes designed to remove it (e.g., reverse osmosis, ion exchange) have high capital equipment, operating & maintenance costs, high energy requirements, and produce large volumes of waste which make them undesirable alternatives. Therefore, source control (which is less costly and more environmentally friendly) is the recommended chloride reduction alternative.

### Wisconsin's Chloride Rule

In February 2000, Wisconsin's new chloride rules became effective. Toxicity criteria was added to NR 105, Wis. Adm. Code, and implementation language was added to NR 106, Wis. Adm. Code. The ultimate goal of the 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 permittee gets a source reduction based permit, NR 106.89, Wis. Adm. Code, allows permittees to demonstrate chloride is the source of WET. If chloride is the sole cause of WET, the Department may hold WET testing/limits in abeyance until source reduction measures are complete:

> *"**NR 106.89 Alternative whole effluent toxicity monitoring and limits for dischargers of chloride.** (1) In addition to interim, target and calculated water quality-based effluent limits and target values for chloride, the department may establish whole effluent toxicity testing requirements and limits pursuant to ss. NR 106.08 and 106.09.*
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> *(2) Acute whole effluent toxicity testing requirements and acute whole effluent toxicity limits may be held in abeyance by the department until source reduction actions are completed if either:*
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> *(a) The permittee can demonstrate to the satisfaction of the department that the concentration of chloride exceeds 2,500 mg/L, or*
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> *(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 limit, and additional data are submitted which demonstrate that chloride is the sole source of acute toxicity.*
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> *(3) Chronic whole effluent toxicity testing requirements and chronic whole effluent toxicity limits may be held in abeyance by the department until source reduction actions are completed if either:*
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> *(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 limit, 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 limit, but in excess of the calculated chronic water quality-based effluent limit, and additional data are submitted which demonstrate that chloride is the sole source of chronic toxicity.*

*(4) Following the completion of source reduction activities, the department shall evaluate the need for whole effluent toxicity monitoring and limits."*

Monitoring & limits that are held in abeyance will not appear in permits. Once source reduction is complete, WET testing should be done to demonstrate that toxicity has been removed with the reduction of chloride.

## Permits Reissued Before "Additional Data" Can Be Collected

In some situations, permits may expire before it can be demonstrated that chloride is the cause of toxicity. If this is true (i.e., source reduction measures are required, WET failures exist, and "additional data" is needed to demonstrate chloride is causing toxicity), a compliance schedule may be given to allow time to make this demonstration. The WET limit and monitoring should be placed in the reissued permit, with a reference to the compliance schedule, in the event that the permittee cannot successfully demonstrate that chloride is the sole source of toxicity. Below are example schedules that may be used in these situations:

**If the reasonable potential factor (RPF) is <0.3 and the WET Checklist recommends monitoring only** (see Ch1.3 for a discussion of the RPF and WET Checklist)**:**

**Whole Effluent Toxicity Compliance Schedule**

| Required Action | Date Due |
|---|---|
| Submit a study plan describing procedures to be used to demonstrate chloride is the sole source of effluent toxicity. | 1-3 months (from permit issuance) |
| 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 it has been successfully demonstrated that chloride is the sole source of toxicity, **(acute/chronic)** WET monitoring will not be required. If this demonstration is not successful, the permittee must complete the **(acute/chronic)** WET monitoring required on page **( )**. | 1 -1.5 yrs (from permit issuance) |

**If the RPF is ≥0.3 and the WET Checklist recommends a WET limit & monitoring:**

**Whole Effluent Toxicity Limit Compliance Schedule**

| Required Action | Date Due |
|---|---|
| Submit a study plan describing procedures to be used to demonstrate chloride is the sole source of effluent toxicity. | 1-3 months (from permit issuance) |
| 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 it has been successfully demonstrated that chloride is the sole source of toxicity, the remainder of this schedule, **(acute/chronic)** WET monitoring, 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 on page **( )**. | 1 -1.5 yrs (from permit issuance) |
| 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. | @ 1 month (from the end of step 2) |
| Submit a progress report identifying the actions taken to date to implement part two of the TRE plan. | about 1/2 way through part 2 |
| Complete all actions identified in the TRE plan and achieve compliance with the effluent toxicity limitation. | 1 -1.5 yrs (from the end of step 2) |

## What "Additional Data" Is Needed To Show That Chloride Is Causing Toxicity?

NR 106.89, Wis. Adm. Code, says the Department may hold WET monitoring/limits in abeyance if chloride is "*in excess of the water quality-based effluent limit, 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 may be required to perform a Toxicity Identification Evaluation (TIE) to characterize and identify the compound(s) causing toxicity. In a Phase I TIE, effluent samples are manipulated to remove suspect chemicals (e.g., metals, organics, etc.) 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, as mentioned above, chloride is a unique substance in that it is not easily altered by chemical reactions, therefore traditional TIE methods do not work well for identifying chloride as the cause of toxicity. However, other methods in addition to Phase I TIE procedures can help determine if chloride is responsible for effluent toxicity:

**Most Sensitive Species.** As shown in Table 2.10A, there is a significant difference in the sensitivities of WET test organisms to chloride, and that difference can often provide useful information when determining whether chloride is the sole cause of toxicity. *C. dubia* is the most sensitive to chloride (as NaCl), with an average $LC_{50}$ of about 2500 mg/l and an average $IC_{25}$ of 840 mg/l. The algae species (*R. subcapitata*) is less sensitive with an average $IC_{25}$ of about 2200 mg/l. The fathead minnow is the least sensitive of these 3 species, with an average $LC_{50}$ about twice as high as that for *C. dubia* (~5800 mg/l) and an $IC_{25}$ almost four times as high (~3100 mg/l). This relative sensitivity pattern is useful as a first step towards determining whether chloride is a significant source of toxicity. For example, if the $LC_{50}$ for *P. promelas* is lower than the *C. dubia* $LC_{50}$, it is safe to rule out chloride as the primary toxicant. If the situation is reversed and chloride levels are high in the effluent, further data may be needed to verify whether chloride is the primary toxicant in the effluent.

**TABLE 2.10A. CHLORIDE TOXICITY VALUES (mg/l)**

| | **Acute** | **Chronic** |
|---|---|---|
| **Water Quality Criteria** (according to NR 105, Table 1 & Table 5) | 757 | 395 |
| **Water Quality Based Effluent Limits (WQBEL)** (according to NR 106.06(3) and (4)). | 1514 | $\frac{(395)(Q_s+(1-f)Q_e) - (Q_s-fQ_e)(C_s)}{Q_e}$ |
| **Reference toxicant information (NaCl)** (average of data from 5 labs, except algae data which represents SLH data only); (Acute = $LC_{50}$; chronic = $IC_{25}$) | 2500 (*C. dubia*)<br>5830 (fhm) | 840 (*C. dubia*)<br>2220 (algae)<br>3080 (fhm) |

- $Q_s$= 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 2.10A, 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 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.

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 the associated ion. 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, compared with *D. magna* and *P. promelas.* For certain salts, such as $CaSO_4$, toxicity to the three species was found to be very 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 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. For example, treatment groups might include the following proportions: 100% effluent from the facility under evaluation; 75% effluent and 25% synthetic effluent; 50% each of effluent and synthetic effluent; 25% effluent and 75% synthetic effluent; and 100% synthetic effluent. 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:**

- 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.

- There is greater sensitivity by *C. dubia* compared to *D. magna, R. subcapitata,* and the fathead minnow, together with high conductivity and/or chloride measurements.

- 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 biomonitoring 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:

Goodfellow, et al. "Major Ion Toxicity In Effluents: A Review With Permitting Recommendations"; *Environmental Toxicology and Chemistry:* Vol. 19, No. 1, pp. 175–182.

Mount, et al. "Statistical Models to Predict Toxicity of Major Ions to *C. dubia, D. magna*, and fathead minnows"; *Environmental Toxicology and Chemistry:* Vol. 16, pp. 2009-2019.