

CHAPTER 1.7 - Discharges with Water Quality Additives

This chapter is designed to help calculate use restrictions and determine WET monitoring frequencies when additives are used. This guidance is intended to apply to discharges of noncontact cooling water, contact cooling water, boiler blowdown, or cooling tower blowdown that contain water quality additives.

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.

What is an “Additive”?

Biocides, additives, polymers, and sediment control products come in a wide variety of mixtures and forms, and are used in a wide variety of applications. They are often referred to as “water quality additives” and include things like: anti-fouling/anti-scaling compounds, biocides, corrosion inhibitors, clarifying agents, polymers, surfactant-based detergents, etc.

Research into the toxicity of additives has shown a great potential for toxicity by many of these compounds. Biocides are specifically designed to kill biological organisms and are usually of greatest concern. As with other chemical-specific compounds, the more additives present, the greater the potential for toxicity due to additive or synergistic effects. The vast majority of additives have not undergone sufficient aquatic toxicological study to develop water quality criteria, a component of a water quality standard under the Clean Water Act. To compensate for this, a process for developing “use restrictions” was developed to act as a surrogate toxicologically-based regulatory tool.

Approval of the use of additives is required from the WDNR prior to use when 1) the water quality additive is directly discharged to a water of the State without receiving treatment, or 2) the water quality additive is used in a treatment process that has the potential to be a source of effluent toxicity. The guidance given below outlines the process to be followed by WDNR staff when determining the need for use restrictions and WET testing related to water quality additives. Water quality additives are approved on a case-by-case basis; a blanket approval is not given. *This approach is for water applied products only, and does not include procedures for land applied erosion control products.* Separate water quality review guidance is available for land applied erosion control products.

Section NR 106.10, Wis. Adm. Code, exempts chlorine in non-contact cooling waters if it is not "intentionally" introduced into the discharge – i.e. present due to the water supply.

Are Use Restrictions Appropriate or Should I Use the WET Checklist?

The WET Checklist (described in Chapter 1.3) was designed to help Department staff make decisions regarding WET limits and monitoring frequencies for surface water discharges, based on their potential to exhibit toxicity. The Checklist assesses a discharge’s toxicity potential by asking questions relating to industry type (or industrial contributions, if municipal), treatment efficiency and operations, the presence of individual compounds measured in the wastewater, and other factors. Since many of these factors are usually absent in situations where the discharge does not contain process wastewaters (i.e., discharges made up solely of noncontact cooling water, contact cooling water, boiler blowdown, and/or cooling tower blowdown), the WET Checklist does not apply very well to many of those situations. However, since these discharges may have the potential to exhibit toxicity or exceed water quality standards, especially if water quality additives are present, another thought process is needed to determine whether it is necessary to limit the use of additives and/or use WET to control the discharge of potentially toxic effluents.

This chapter is intended to deal with situations that do not fit well into the Checklist, specifically those situations where use restrictions for additives and/or WET monitoring may be needed to control toxicity in discharges made up of noncontact cooling water, contact cooling water, boiler blowdown, or cooling tower blowdown. To clarify when this chapter should be used in the place of the WET Checklist, these discharges have been divided into two categories:

- Case 1:** Discharges made up of noncontact cooling water, contact cooling water, boiler blowdown, or cooling tower blowdown are Case 1 if any substance listed in ch. NR 105, Wis. Adm. Code, Tables 1-9, or Chapter 1.3, *Additional Compounds of Concern* ARE detected in the effluent. In most cases, the WET Checklist is appropriate and should be used to determine the need for WET limits and monitoring for Case 1 dischargers.
- Case 2:** Discharges made up of noncontact cooling water, contact cooling water, boiler blowdown, or cooling tower blowdown are Case 2 if any substance listed in ch. NR 105, Wis. Adm. Code, Tables 1-9, or Chapter 1.3, *Additional Compounds of Concern* ARE NOT detected in the effluent. The procedure contained in this chapter should be used to determine the need for use restrictions and WET monitoring frequency for Case 2 dischargers.

If a discharge is solely noncontact cooling water, contact cooling water, boiler blowdown, and/or cooling tower blowdown and no additives are used, then it is not necessary to complete the process described below or the WET Checklist - use restrictions and/or WET monitoring are usually not needed in those situations.

Information Needed for Calculating Use Restrictions

The guidance given below is taken from “*Water Quality Review Procedures For Water Applied Biocides, Additives, Polymers, & Sediment Control Products*” (2006) which outlines a stepwise process to be followed by WDNR staff for ensuring timely and thorough evaluation of information related to water applied biocides, additives, polymers, and sediment control products. The following process should be followed for determining the appropriate permit requirements for Case 2 dischargers:

1. Requests approving the use of water quality additives should be sent to the appropriate WDNR staff responsible for WDPES permitting decisions. The request shall include, as a minimum, the following information:
 - a. Trade name of the product
 - b. Manufacturer of the product
 - c. Recommended application concentration/mixture and rate
 - d. Description of the conditions under which the product is to be used, including discharge conditions, how the product is to be applied, expected effectiveness, etc.
 - e. Any other information the permittee feels is relevant.
2. WDNR staff receiving the information in “Step 1” compile all information provided by the requestor and provides it to the appropriately designated staff in the Bureau of Watershed Management - Water Evaluation Section.
3. The Water Evaluation staff member determines if the information package is complete. Available information must address the “*whole product*” of the additive. The “whole product” is all active ingredients and any and all carriers, buffering agents, binding agents, and additional materials – the entire product as used. A complete information package will include the following:

- a. Trade name of the product
- b. Manufacturer of the product.
- c. Chemical name of the product (if applicable)
- d. Active ingredient(s) of the product (if applicable)
- e. Material Safety Data Sheet (MSDS) and/or official toxicity test results listing available aquatic life toxicity data for the whole product. Toxicity data for only the active ingredients is not acceptable for use in calculating a use restriction. The following types of data are acceptable. To calculate a use restriction it is necessary to have data from at least one of the Cladoceran species and at least one of the fish species.

<i>Species</i>	Endpoint of Concern
<i>Ceriodaphnia dubia</i> (Cladoceran)	48-hour LC ₅₀
<i>Daphnia magna</i> (Cladoceran)	48-hour LC ₅₀
<i>Lepomis macrochirus</i> (Bluegill Sunfish)	96-hour LC ₅₀
<i>Pimephales promelas</i> (Fathead Minnow)	96-hour LC ₅₀
<i>Oncorhynchus mykiss</i> (Rainbow Trout)	96-hour LC ₅₀

LC₅₀ = the estimated concentration of product that would cause 50% mortality to the test population following the given time period

- f. Complete listing of toxicity test conditions. Examples to follow include Tables 11 – 14 in Weber (1993).
- g. Standardized test methodology (name of a specific method & its reference may be listed for this, such as “Acute Toxicity Test Procedures for *Daphnia magna*” in Weber (1993)). If a modification to a standardized method was used, provide the reference of the specific method along with a specific listing of and reasons for the modifications.
- h. Any noted observations from the toxicity tests.

If this toxicological data and support material is not submitted, the WDNR staff informs the requestor that they must obtain the appropriate toxicological data and support material, and then resubmit their request.

If this toxicological data and support material is submitted, proceed to “Step 4”.

4. The Water Evaluation staff member reviews the toxicity test data for any anomalies or “red flags” (e.g. viscous solutions, test lengths, control mortalities, etc.).
5. Based on the information from “Step 3,” the Water Evaluation staff member calculates a use restriction for the requested product, as follows:
 - a. A use restriction can be calculated for a product *only* if the proper data identified in “Step 3” are available for at least one Cladoceran species (*Ceriodaphnia dubia* or *Daphnia magna*) and at least one of the following fish species: bluegill, fathead minnow, or rainbow trout.
 - b. If at least one 48-hour LC₅₀ value is available for *Ceriodaphnia dubia* or *Daphnia magna* and at least one 96-hour LC₅₀ value is available for either fathead minnow, bluegill sunfish, or rainbow trout, the mean* LC₅₀ for each of the represented species shall be calculated.

* = use a geometric mean when 3 or more data points are available for any single species

- c. The mean LC₅₀ calculated in “Step 5b” shall be divided by 5 if rainbow trout are represented in the dataset or divided by 10 if rainbow trout are not represented in the dataset.
- d. The use restriction shall be equal to the lowest value calculated according to “Step 5c.”

EXAMPLE. The following ecotoxicological data is available for Product XYZ:

Species	Test Type	LC ₅₀ (mg/L)	Geometric Mean (mg/L)
<i>Pimephales promelas</i>	96-hour LC ₅₀	0.29	0.54
<i>Pimephales promelas</i>	96-hour LC ₅₀	0.72	
<i>Pimephales promelas</i>	96-hour LC ₅₀	0.75	
<i>Oncorhynchus mykiss</i>	96-hour LC ₅₀	1.34	NA
<i>Daphnia magna</i>	48-hour LC ₅₀	0.13	NA

**The lowest LC₅₀ provided is 0.13 mg/L for *Daphnia magna*.
This value is divided by 5 since rainbow trout (*Oncorhynchus mykiss*) data is provided.
Thus the acute toxicity-based use restriction for Product XYZ is 0.026 mg/L (0.13 ÷ 5).**

6. The Water Evaluation staff member prepares a use restriction memo that summarizes information used to complete the review. The memo will include the following:
 - a. Information about the requestor,
 - b. Source and description of relevant toxicological information,
 - c. Factors considered in the calculation of the use restriction,
 - d. The calculated final use restriction value,
 - e. Any anomalies or “red flags” identified in the review.

Note: The memo may simply state that a use restriction could not be calculated due to insufficient or improper data submittal.

7. The Water Evaluation staff member sends the memo to the DNR staff who requested the toxicological review in “Step 2.”
8. Permits staff reviews the use restriction to make a final decision whether to approve or reject the use of the product as requested, considering site-specific parameters provided by the requesting party (from “Step 1”).
 - a. Typically in industrial and municipal processes, the water containing the “water quality additive” is mixed with other wastewater that dilutes the concentration prior to discharging. Since the use restriction is applied at the point of discharge to a water of the state, it is necessary to consider these and other factors that may influence the concentration of the “water quality additive” between the point where it is applied at its effective concentration and the point of discharge. The following are considered in calculating either an acceptable application rate based on the use restriction, or alternatively, a final effluent concentration based on the proposed effective application rate/concentration:

- the maximum proposed application/dosage rate
- any dilution that would be expected to occur with other effluent streams prior to discharging
- using low flow conditions as conservative estimates
- no degradation of the “water quality additive” is considered

If the calculated acceptable application rate is below that proposed to be effective at the plant, the “water quality additive” is not approved for use. Alternatively, if the proposed calculated effluent concentration is significantly less than the use restriction (1/5 of the use restriction, as a general guideline), the “water quality additive” is “approved” for use at the proposed concentration, and a use restriction is not required in a Wisconsin pollution discharge elimination system (WPDES) permit. If the additive concentration is less than the use restriction, but greater than 1/5 of the use restriction value, consideration should be given to including the use restriction in the next permit reissuance. In the interim, the additive approval letter is an adequate permit action, and a permit modification is unnecessary. If the proposed effluent concentration is greater than the use restriction, the “water quality additive” is not approved for use.

Permit staff will make the appropriate calculations noted above, approve or reject use of the proposed “water quality additive”, modify or issue a permit as necessary, and notify the requestor in “Step 1.”

9. The Water Evaluation staff member maintains all use restriction files and related toxicological information, and updates the relevant information in the biocides, additives, polymers, and erosion and sediment control products database.

REFERENCES:

- Weber, C. 1993. *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 4th Edition*. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH. EPA/600/4-90/027F.
- Wenholz, Mike. November 7, 2006. “*Water Quality Review Procedures For Water Applied Biocides, Additives, Polymers, & Sediment Control Products, Interim Final*”, Bureau of Watershed Management, WDNR.

Determining the Need for Whole Effluent Toxicity (WET) Testing

WET tests should be utilized to determine the potential for impacts to the receiving stream fish and aquatic life community under any of the following discharge conditions:

- When the toxicity data required above are not made available to the WDNR.
- When historical or projected use of an additive suggests that the dosage necessary to be effective in production or treatment exceeds 1/5 of the daily maximum limitation calculated as suggested above.
- Whenever a discharge contains two or more additives that may be discharged simultaneously.

Any discharger who uses additives may opt to conduct WET tests in lieu of having end-of-pipe limitations placed in a permit. The permittee should notify the WDNR in writing prior to or during the public-notice period that this is the preferred method of compliance.

The need for acute and/or chronic WET monitoring should be decided based on the following dilution scenarios:

If $Q_{7,10}:Q_e > 1000:1$, no WET testing is recommended, since dilution is high and the potential for impacts due to toxicity are lower. Department staff may, in certain circumstances, determine that testing is necessary despite high dilution, but this decision should be clearly documented in the permit file, so others can tell why decisions were made.

If $Q_{7,10}:Q_e \leq 1000:1$ & $> 100:1$, only acute testing is recommended, since dilution is high and the potential for impacts due to

chronic toxicity are lower. Staff may, in some instances, determine that chronic testing is necessary despite high dilution, but this decision should be clearly documented in the permit file, so others can tell why decisions were made.

If $Q_{7,10}:Q_e \leq 100:1$, both acute and chronic WET testing is recommended.

Frequency of WET Testing

The frequency of WET testing discussed in this section represents the **minimum** recommended to evaluate the reasonable potential for additive-related impacts to the receiving stream fish and aquatic life community. These recommended frequencies may be increased if there are case-specific reasons that warrant a further evaluation of the reasonable potential. For example:

- When an additive is discharged independently and isn't likely to be mixed with other additives, a discharger should be required to conduct a WET test on effluent that is likely to contain that additive or its residual at least once per year for the first two years following permit issuance. This recommendation applies independently to each additive used unless otherwise noted.
- When two or more additives are used such that there is a chance that they are discharged simultaneously, a discharger should be required to conduct a WET test on effluent that is likely to contain that mixture or the residual of the mix at least once per year for the first two years following permit issuance.
- When > 2 additives are used and there is little chance that they are discharged simultaneously, a discharger should be required to conduct a WET test on the effluent at least once every three months for the first eighteen months following permit issuance. Effluent samples should be collected at a time when it is likely that an additive or its residual may be present in the effluent.
- Best professional judgment should be used to determine if any unusual circumstances exist that may warrant additional testing. Examples of discharge/additive-specific circumstances that may require additional testing include: known effects of temperature on the toxicity of an additive, changes in the receiving stream species composition on a seasonal basis, etc.

When To Require WET Limits

WET limits are required according to ch. NR 106, Wis. Adm. Code., whenever “...the RPF calculated according to par. (b) exceeds 0.3. Whole effluent toxicity limits may be imposed, on a case-by-case basis, whenever facility-specific whole effluent toxicity test data indicate toxicity to aquatic life as determined in s. NR 106.09. Whole effluent toxicity limits may also be imposed in the absence of facility-specific whole effluent toxicity test data, on a case by-case-basis, whenever facility-specific or site-specific data or conditions indicate toxicity to aquatic life that is attributable to the discharger.”

Noncontact cooling water, contact cooling water, boiler blowdown, and/or cooling tower blowdown discharges are subject to the same reasonable potential determinations and should be given WET limitations when available data suggests they are necessary. Staff should evaluate these discharges using the same logical process as that described in Chapter 1.3 to determine whether WET limits are necessary. Although the WET Checklist may not apply directly to these discharges, staff should use other guidance in Chapter 1.3 and their best professional judgement to determine which data is representative of the discharge and appropriate for use in calculating the reasonable potential factor (RPF). If the RPF ≥ 0.3 , a WET limit is required, according to s. NR 106.08, Wis. Adm. Code, and should be placed in the permit along with a compliance schedule and WET monitoring (usually quarterly monitoring after the limit has become effective).

ATTACHMENT 1

Information Needed For WDNR Review of Water Quality Additives

Whenever an additive is used, the following information listed in (a) - (h) below should be submitted for each additive, in order for the WDNR to determine if an effluent limitation or use restriction is warranted at the time of permit (re)issuance.

- a. Manufacturer of the additive.
- b. Chemical name of the additive.
- c. Active Ingredient(s) (if not proprietary information).
- d. CAS #(s) of the additive and/or active ingredients.
- e. Material Safety Data Sheet (MSDS) and/or official toxicity test results listing available aquatic life toxicity data for the WHOLE PRODUCT. Toxicity data for active ingredients is not acceptable for use in calculating a use restriction. The following types of data are acceptable:

Species	Endpoint of Concern
<i>Ceriodaphnia dubia</i> (Cladoceran)	48-hour LC ₅₀ or EC ₅₀ /IC ₂₅
<i>Daphnia magna</i> (Cladoceran)	48-hour LC ₅₀ or EC ₅₀ /IC ₂₅
<i>Lepomis macrochirus</i> (Bluegill Sunfish)	96-hour LC ₅₀ or EC ₅₀ /IC ₂₅
<i>Pimephales promelas</i> (Fathead Minnow)	96-hour LC ₅₀ or EC ₅₀ /IC ₂₅
<i>Oncorhynchus mykiss</i> (Rainbow Trout)	96-hour LC ₅₀ or EC ₅₀ /IC ₂₅

LC₅₀ = the estimated concentration of additive that would cause 50% mortality to the test population following the given time period

EC₅₀ = the estimated concentration of additive that would cause a given effect in 50% of the test population following a given time period

IC₂₅ = the estimated concentration of additive that would cause a 25% reduction in some biological measurement of the test population following a given time period

NOTE: To calculate a use restriction it is necessary to have data from at least one of the cladoceran species and at least one of the fish species (according to s. NR 106.10(1), Wis. Adm. Code).

- f. Complete list of toxicity test conditions. Examples to follow include Tables 11 – 14 in Weber (1993).
- g. Standardized test methodology (name of a specific method & its reference may be listed for this, such as “Acute Toxicity Test Procedures for *Daphnia magna*” in Weber (1993). If a modification to a standardized method was used, provide the reference of the specific method along with a specific listing of and reasons for the modifications).
- h. Any noted observations from the toxicity tests.

Toxicity test information on water quality additives should be submitted to the Water Quality Standards Section, WDNR, 101 South Webster Street, P.O. Box 7921, Madison, WI 53707-7921.

Reference:

Weber, C. 1993. *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 4th Edition*. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH. EPA/600/4-90/027F.