

BUREAU OF WATER QUALITY BUREAU OF WATERSHED MANAGEMENT PROGRAM GUIDANCE

Wastewater Policy and Management Team
Water Resources Policy and Management Team
Runoff Management Policy and Management Team

Water Quality Review Procedures For Additives

Edition #3

December 2, 2022

EGAD Number: 3200-3400-3800-2022-02

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. 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.

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Introduction

This document describes the procedures for deriving secondary acute and secondary chronic values for additives that are used in the treatment of wastewater or stormwater runoff.

The federal Clean Water Act (CWA) requires states to develop water quality criteria for substances that may adversely impact the environment. If a product or substance has not undergone the rigorous toxicological testing required to develop water quality criteria for the protection of aquatic life, secondary acute and chronic values are derived following the methods in s. NR 105.05 and s. 105.06, Wis. Adm. Code. A secondary value is a concentration in surface water that protects aquatic life from adverse short-term and long-term effects. Secondary values are based on available data and account for the uncertainty of that data by using a safety factor. Once calculated, secondary values are converted into allowable usage rates or water-quality based effluent limits (WQBELs) as required in s. NR 106.10, Wis. Adm. Code, depending on the purpose of the additive.

Because the procedures for determining secondary values are the same regardless of the purpose of the additive, the steps in this document apply to both water-applied and landapplied additives. Additives are used in a number of applications and come in a variety of chemical formulations including, but not limited to, chemical salts, polymers, acids and bases, and organic chemicals. Examples of additives include biocides, boiler water treatments, clarifying agents, corrosion inhibitors, industrial process polymers, pH control, scale control, settling flocculent logs, soil stabilizers, erosion control products, and stormwater and frac sand process water clarification products.

Department Authority

This guidance supports the authority of s. 283.31(3)(d)1. and ss. 105.02(3), NR 105.05, NR 106.05(1)(b), and NR 106.10, Wis. Adm. Code, to protect Wisconsin's surface water resources from such products.

The procedures described in this guidance document are based on those in ss. NR 105.05(4) for secondary acute values and ss. 105.06(6) for secondary chronic values. These procedures are consistent with the methodology for deriving Tier II aquatic life criteria in the *Water Quality Guidance for the Great Lakes System* (40 CFR 132).

When is an additive review needed?

- 1) The additive may enter a surface water without receiving treatment
- 2) The additive is used in a treatment process, is not expected to be removed by wastewater treatment, and may contribute to effluent toxicity.
- 3) A new/modified product formulation or use is occurring.
- 4) The product was previously reviewed using methods that resulted in something other than a secondary value.

When is an additive review not needed?

- 1) A secondary value has been previously calculated for the product and the same application, product formulation, and usage conditions apply.
- 2) Other effluent limits will already be set to protect against adverse effects. Note: Staff should use best professional judgment to determine when these situations exist. For example, toxicity from chlorine and chlorine-containing products may be addressed with chlorine effluent limits, and acids or bases may be accounted for with pH limits.

Important considerations

- For discharges containing additives that occur <u>for more than 1 hour in any 24-hour period</u>,
 limits or usage rates should be based on acute secondary values.
- For discharges containing additives that occur <u>for 96 hours or more in a 7-day (168 hour)</u> period, limits or usage rates should also be based on chronic secondary values.
- Additives should be approved on a case-by-case basis; <u>blanket approvals should not be given.</u>
- Staff should pay attention to discharges that have a variance to water quality standards for an individual pollutant. In most cases, discharges with variances are attempting to minimize the use of products and sources containing that pollutant and/or maximize the removal of that pollutant to the extent practicable. Therefore, additives should be minimized to the extent practicable if they contain significant amounts of those pollutants for which there is a variance. Wherever possible, alternative additive products should be used that do not contain the pollutant for which a variance was granted.

To support consistent and efficient decision making across the state, the following WDNR staff are recommended to take the lead on these reviews and be able to adequately describe the process in this guidance.

- <u>Wastewater</u>: Requests for additive reviews will most often occur during either the permit application/reissuance process or during the permit term for additive changes that occur after the permit has been issued. Additive reviews that are needed at permit reissuance time should be conducted by limit calculators along with other effluent limit and WET determinations. Additive reviews that are requested by permittees during the permit term may be conducted by permit drafters since they are likely to be the ones that receive the request. If permit drafters need assistance, they can enlist the help of the limit calculator. Additive review reports should be attached to WQBEL recommendation memos and/or permit files and saved in the System for Wastewater Applications, Monitoring and Permits (SWAMP).
- Runoff Management: For runoff management, an additive review generally occurs when the product is proposed for sediment control, erosion control, and/or solids separation purposes, which include, but are not limited to: storm water clarification, sediment removal, manure lagoon clarification, and frac sand mining process water clarification. This guidance is used in conjunction with the appropriate conservation standard/additional guidance documents as detailed in Step 4C. Additive reviews that are requested for stormwater are conducted by Amy Minser (Amy.Minser@wisconsin.gov or 920-360-0913) and for CAFO are conducted by Bernie Michaud (Bernard.Michaud@wisconsin.gov or 608-266-5239).
- The Water Evaluation Section Toxicologist (Meghan Williams: meghanc3.williams@wisconsin.gov or 608-267-7654) can assist the staff listed above with questions.

The methods and procedures in this guidance document supersede those outlined in previous versions of this and related guidance including:

- WET Guidance, Ch 1.7 "Discharges with Water Quality Additives" (July 1, 2008),
- "Water Quality Review Procedures for Water Applied Biocides, Additives, Polymers & Erosion Control Products" Interim Final Guidance (December 4, 2006),
- "Water Quality Review Procedures for Land Applied Erosion Control Products" Interim Final Guidance (November 7, 2006), and
- Water Quality Review Procedures for Additive Guidance (April 23, 2015).
- Water Quality Review Procedures for Additive Guidance (October 1, 2019).

Useful Resources

In addition to creating this guidance document, DNR toxicologists have developed resources for staff and permittees to use when completing the additive review process. Electronic copies of this guidance document, the Secondary Value Calculator (Appendices A and B), and Additive Review Request Worksheet (Appendix C), along with other information can be found on the internet and intranet.

- An <u>intranet site</u> has been created to share additive-related guidance and other resources with staff.
- An internet site has been created to share this information with permittees, consultants, chemical suppliers, and others:
 https://dnr.wisconsin.gov/topic/Wastewater/Additives.html.
- A list of products that have previously undergone an additive review is provided internally for staff and on the internet for external use, to assist in determining whether a product has been previously reviewed by the department. This list is updated about once per quarter.
- Additionally, a <u>set of folders</u> has been created on the shared drive for staff use that
 contains secondary value spreadsheets, safety data sheets (SDS), toxicity test data,
 related emails, and other relevant information for each product that has been
 previously reviewed.
 - *Note:* To be keep this information up to date, staff will need to create a new folder in this location each time that they complete a review for a product that has not already been reviewed (folder naming convention: company name product name).

Determination of the Allowable Additive Usage Rate

This section of the guidance outlines the process to be followed by WDNR staff to assist with the timely and thorough evaluation of information related to additives. The additive review process consists of four general steps:

- Step 1) Additive review request
- Step 2) Secondary acute value (SAV) calculation
- Step 3) Secondary chronic value (SCV) calculation
- Step 4) Allowable usage rate determination

Each of these steps is described in more detail below. An excel template, the *Secondary Value Calculator*, was developed to assist with calculating secondary acute and secondary chronic values for additives. Instructions for using the *Secondary Value Calculator* can be found in Appendix A for Wastewater Staff and Appendix B for Runoff Management staff.

Step 1: Additive review request

- A. The permittee/applicant submits a request for the approval of an additive (i.e., the complete production formulation) to the WDNR staff responsible for their WPDES permitting or runoff management decisions.
- B. The WDNR staff member receiving information in Step 1 compiles all information and determines if the information package is complete. A complete request package should include general product information, product dosage/application information, official aquatic toxicity test (bioassay) results and parameters.
 - The Additive Review Request Worksheet (Appendix C) can be used by the permittee/applicant to obtain the proper information for the additive review from the product manufacturer/supplier.
 - Figure 1 provides details on the specific information needed from each of these categories.
 - Table 1 Acute and Chronic Test Types describes the toxicity test species, test types and results acceptable for use in performing an additive review.
 - Table 2 Test Parameter Summary describes the toxicity test parameters used to determine if the toxicity test results are acceptable for use in performing an additive review and the reasons why each parameter is needed.

Note: Certain additives, typically certain erosion control products, may not be soluble in water (e.g. wood chips). Because these products contain materials that are not soluble in water, the primary ecological concern is not for organisms that live in the water column (i.e., fish) but for organisms that live in or near the sediment (e.g., amphipods, crustaceans). Therefore, for these types of additives, the traditional water-column toxicological testing methods are not appropriate. Instead, toxicity testing methods that use sediment-dwelling species should be used (see Appendix D for more information).

C. Once the request package is complete, it is forwarded to the DNR staff member responsible for calculating the allowable usage rate (Wastewater: limit calculators; Stormwater: <u>Amy.Minser@wisconsin.gov</u> or 920-360-0913; CAFO: <u>Bernard.Michaud@wisconsin.gov</u> or 608-266-5239).

Step 2: Secondary Acute Value (SAV) Calculation

- A. The DNR staff member checks the <u>internal list</u> of products that have previously undergone review to determine whether a review is needed. If the product has previously been reviewed and secondary values have been calculated, skip to Step 4C.
- B. If the product has not previously been reviewed and secondary values have not been calculated, the DNR staff member enters the permittee/applicant information and available product information into the "Secondary Value Report" in the Secondary Value Calculator.
- C. The DNR staff member enters all acute toxicity test results for the substance into the *Secondary Value Calculator*.

Note: If there is not at least one acceptable test result for a water flea species (i.e, Ceriodaphnia spp., Daphnia spp., or Simocephalus spp.), a secondary acute value (SAV) cannot be calculated. If this is the case, contact the Water Evaluation Section Toxicologist (Meghan Williams: meghanc3.williams@wisconsin.gov or 608-267-7654) for assistance.

- D. The DNR staff member determines if the toxicity test results are acceptable to use for the additive review (see Tables 1 and 2).
- E. The Secondary Value Calculator automatically calculates the Species Mean Acute Value (SMAV) by taking the geometric mean of all available toxicity test results for a given species and the Genus Mean Acute Value (GMAV) by taking the geometric mean of all SMAVs for a given genus.

General product information

- Permittee/Applicant contact information
- Product trade name & manufacturer (if available)
- Product chemical name (if available)
- Product active ingredient(s) including CAS # of product components (if available- CAS # may not be available if additives are not OSHA regulated)

Product dosage/ application Information

- Proposed application rate (runoff management applicants)
- Proposed dosage rate (WPDES permittees)
- Maximum discharge concentration (i.e., discharge concentration the represents worst case scenario –maximum additive dosage, minimum discharge flow, no degradation of additive; WPDES permittees).

Table 1 – Acute and Chronic Test Types describes the toxicity test species, test types and results acceptable for use in performing an additive review

• Table 2 – Test Parameter Summary describes the toxicity test parameters used to determine if the toxicity test results are acceptable for use in performing an additive review and the reasons why each parameter is needed

Official aquatic life toxicity (bioassay) test results

- Note (1): The toxicity information submitted must address the *commercial product formulation* in order to be applicable. The whole product is all active ingredients and any
 and all carriers, buffering agents, binding agents, and additional materials. Toxicity data for
 only the active ingredient(s) are not acceptable because they are not representative of
 what is actually being used.
- Note (2): In some instances, MSDS sheets provide a "no effects level" or 0% mortality value.
 If the discharger is using an additive at a substantially lower concentration than the no
 effect level, it is not necessary to calculate a SAV or SCV, or include limitations for this
 additive in the WPDES permit. It is important to verify that proper test methods were used
 to calculate a no effect level for an additive (see Appendix B).
- Test duration and endpoint
- · Test method
- Exposure format
- Control response

Official aquatic test parameters

- Additional parameters, if needed (see Appendix B)
- Note: The parameters listed above are necessary for completing the additive review. Material safety data sheets (MSDS) do not always contain the toxicity data needed to calculate secondary values and rarely contain the information necessary to determine if the available data is acceptable to use in calculating a secondary value. In these instances, the permittee/applicant can obtain additional toxicity test information from the chemical distributor and/or manufacturer (see Appendix B).

Figure 1. Information needed for a complete additive review request package

Table 1. Acute and Chronic Test Types

Acceptable acute and chronic test types and results for common test species

Test Type	Test Species	Acute Test Duration	Test Result	Method⁰	Chronic Test Duration#	Test Result	Method⁰
Water Column Tests	Ceriodaphnia dubia (Water flea)			EPA 2002.0			EPA 1002.0
	Ceriodaphnia reticulate (Water flea)			‡			‡
	Ceriodaphnia serrulatus (Water flea)		EC ₅₀	‡		LOAEL	‡
	Daphnia magna (Water flea)	48-hr	OR LC ₅₀	EPA 2021.0	Life-cycle	or NOAEL	‡
	Daphnia pulex (Water flea)						‡
	Simocephalus serrulatus (Water flea)			‡			‡
	Simocephalus vetulus (Water flea)			‡			‡
	Pimephales promelas (Fathead minnow)			EPA 2000.0	Early life stage		EPA 1000.0 or 1001.0
	Lepomis macrochirus (Bluegill)	96-hr	LC ₅₀	‡	OR Partial Life-	LOAEL or NOAEL	‡
	Oncorhynchus mykiss (Rainbow trout) Salvelinus fontinalis			EPA 2019.0	cycle OR		‡
	(Brook trout)				Life-cycle		‡
Whole Sediment Tests*	Ceriodaphnia dubia (Water flea) Daphnia magna (Water flea)	48-hr	NOAEL	ASTM E1706	N/A		
	Hyalella azteca (Amphipod)	N/A	71 .		10 day	NOAEL	ASTM E1706

^oApproved alternate test methods can be found at: https://dnr.wisconsin.gov/sites/default/files/topic/Wastewater/
ApprovedToxicityTestingMethodsForAdditiveReviews_May2021.pdf

Definitions:

Early life stage = used as predictors of life-cycle and partial life-cycle tests with the same species.

 EC_{50} = estimated concentration of product that would cause 50% effect (e.g., mortality, immobilization) to the test population following a given time period

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

Life-cycle = exposures of each of two or more groups of individuals of a species to a different concentration of the test material throughout a life cycle

LOAEL = lowest observable adverse effect level

NOAEL = no observable adverse effect level

Partial Life-cycle = exposures of each of two or more groups of individuals of a species of fish to a different concentration of the test material through most portions of a life cycle-allowed with fish species that require more than a year to reach sexual maturity, so that all major life stages can be exposed to the test material in less than 15 months

^{*}Certain additives, typically certain erosion control products, may not be soluble in water. For these types of additives, sediment testing should be conducted in place of water column testing (see Appendix D for more information).

[†] Consult with toxicologist to determine whether the test methods used meet acceptability requirements.

^{*}Chronic toxicity tests typically last 7 days or longer.

Table 2. Test Parameter Summary

Descriptions and reasons for determining if test results are acceptable for use in preforming an additive review

Test Parameter	Reason Why Test Parameter Is Important
REQUIRED TEST PARAI	METERS
Test method	Indicates which protocols were followed during the test
Exposure type	Indicates the manner in which organisms were exposed to the substance of concern.
Toxicity endpoint	The method for calculating secondary values is based on using these toxicity endpoints (LC $_{50}$, EC $_{50}$, etc.)
Control response	If a high number of control organisms die, other factors may be affecting the health of the organisms and the calculated secondary value may be artificially lower.
ADDITIONAL TEST PAR	AMETERS
Dilution water	The proper dilution water is necessary for organisms to function properly and minimizes concerns of contamination
Number of test	A large number of test concentrations provides consistency and helps reduce
concentrations	potential for an "all-or-nothing" response (i.e., either all organisms alive or all dead)
Dilution series	A stepwise dilution series (also called serial dilutions) provides consistency and helps reduce potential for an "all-or-nothing" response
Temperature	Higher or lower temperatures than those of the organism's optimal range can affect how the substance of concern is metabolized and, thus, impact toxicity
Test duration	The shorter an organism is exposed to a toxic substance, the higher the concentration needed to cause the effect. Therefore, improper test duration can result in inaccurate secondary values
Age of organisms prior to test	Organisms must all be undergoing the same developmental processes during the test for the results to be valid
Number of organisms per test chamber	
Number of chambers per concentration Number of organisms per concentration	The more organisms used, the higher the confidence we have that the results are accurate.

The Secondary Value Calculator automatically calculates the Secondary Acute Values (SAVs) for the appropriate designated use classification(s). The SAV equals the lowest GMAV divided by the Secondary Acute Factor (SAF); the SAF is automatically selected based on how many different organism classes are represented.

Table 3: Applicable Secondary Acute Factor (SAF)

Number of organism classes represented	SAF
1	21.9
2	13
3	8
4	7
5	6.1
6	5.2
7	4.3

Step 3: Secondary Chronic Value (SCV) calculation

A. The DNR staff member enters all chronic toxicity test results for the substance into the *Secondary Value Calculator*.

Note: The calculator uses a mathematical formula to generate Secondary Chronic Values (SCVs) even if no chronic toxicity test results are available.

B. The DNR staff member determines if the toxicity test results are acceptable to use for the additive review (see Step 2D for more details).

Note: Acceptable chronic endpoints (7+ day duration) for use when calculating secondary values are NOAELs or LOAELs. IC25s are <u>not</u> used to calculate secondary values, according to ch. NR 105, Wis. Adm. Code.

- C. The *Secondary Value Calculator* automatically calculates the Toxicity Test Acute-Chronic Ratio (TACR). The TACR is the Species Mean Acute Value (SMAV) divided by Species Mean Chronic Value (SMCV) for each species.
- D. The *Secondary Value Calculator* automatically calculates the Species Mean Acute-Chronic Ratio (SMACR). The SMACR is the geometric mean of all available TACRs for a given species.

Note: A SMACR is required for the following organism categories: fish, invertebrate, sensitive freshwater species. If no TACRs are available for a category, a default SMACR of 18 is used, as specified in s. NR 105.06 (7), Wis. Adm. Code.

- E. The Secondary Value Calculator automatically calculates the Secondary Acute-Chronic ratio (SACR). The SACR is the geometric mean of the Species Mean Acute Chronic Ratios (SMACRs) for at least one species (or default value) in each organism category.
- F. The Secondary Value Calculator automatically calculates the Secondary Chronic Values (SCVs) for the appropriate designated use classification(s). The SCV equals the Secondary Acute Value (SAV) divided by the Secondary Acute-Chronic Ratio (SACR).

Step 4: Allowable usage rate determination

- A. Once the *Secondary Value Calculator* is completed, the applicable secondary acute and chronic values are automatically populated into the "Secondary Value Report."
- B. The DNR staff member calculating the secondary value creates a new folder in \\central\water\WQWT PROJECTS\WY CP Additives\Additive Product Toxicity and includes all information containing secondary value spreadsheets, safety data sheets (SDS), toxicity test data, related emails, and other relevant information for the product

Note: Folder naming convention is "company name_product name"

C. The DNR staff member who received the request makes a final decision whether to approve or disapprove the use of the product as requested. If approved, the DNR staff member determines the allowable usage concentration (i.e., the level of the additive acceptable for use). Staff from different programs will follow the appropriate steps below:

i. Wastewater Permit staff

- Once the secondary acute and secondary chronic values are calculated, an allowable application/dosage rate is determined.
- To estimate the effluent concentration, the following are considered:
 - 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.

Note: No degradation of the additive is typically assumed.

In some instances, the water containing the additive may be mixed with other wastewater that dilutes the concentration prior to discharging. In these instances, the additive may be at the intended concentration where added but well below that concentration at the discharge point. Therefore, the estimated effluent concentration is typically compared to a water quality based effluent limitation (WQBEL) equal to the acute secondary value. Table 4 lists the typical approval conditions based on the comparison between the estimated effluent concentration and WQBEL.

Table 4. Decision Matrix for Additive Decisions

Estimated Average Effluent Concentration	Potential Outcome
Significantly less than the lowest calculated WQBEL (typically < 1/5 th of the limit)	Additive may be approved for use at the proposed application rate. WQBEL is not required, as long as application rate does not increase.*
Less than the lowest calculated WQBEL but greater than 1/5 th of the limit	Additive may be approved for use at the proposed application rate, but staff should use best professional judgment to determine if a WQBEL or use restriction should be included in the permit to ensure that additive use does not increase.*
Greater than the lowest calculated WQBEL	The additive is not approved for use at the proposed application rate.*

^{*} Staff should clearly document decisions about additive approvals (or denials) and/or the need for WQBELs in permit fact sheets accompanying reissued permits or in written correspondence to the permittee, if changes in additive use are being evaluated during the permit term.

ii. Runoff Management staff

- Once the Secondary Values have been calculated, Runoff Management staff calculate the allowable application rate for the product using the procedures detailed in the following documents:
 - Water Application for Sediment Control Additives DNR Conservation
 Standard 1051
 - <u>Land Application for Erosion Control Additives DNR Conservation Standard</u>
 1050
 - Water Application of Additives for Manure Sedimentation (in development)
- This final allowable application rate is compared to the proposed application rate to determine if the product can be used as requested.
- Runoff Management staff then prepare a letter to the applicant that states the application rate at which the product can be used in Wisconsin and whether or

not the product can be used as proposed. Department of Transportation staff are provided this information as necessary.

- D. Once a final decision is made on whether to approve or disapprove the use of the product as requested, Runoff Management staff should save a copy of the Secondary Value Report in the appropriate folder in https://www.ncentral/water/wqwt-projects/wy-cp-additives/Additive-product Toxicity-Information.
 - For <u>Wastewater additive reviews</u>, limit calculators include the additive review report in the official permit file and upload it into SWAMP. Associated permits, fact sheets, and/or approval letters, should reflect approval (or denial) decisions and should be added to SWAMP so that others can tell why decisions were made.
 - For <u>Runoff Management additive reviews</u>, the staff member responsible for calculating the allowable usage rate (Stormwater: <u>Amy.Minser@wisconsin.gov</u> or 920-360-0913; CAFO: <u>Bernard.Michaud@wisconsin.gov</u> or 608-266-5239).

Additional Information for Wastewater Reviews

Calculating Water Quality-Based Effluent Limits

Guidance related to the calculation of WQBELs based on secondary values and their implementation in wastewater permits is provided in Section 6.4 of the guidance document titled "Calculating Water Quality-Based Effluent Limitations for Surface Water Discharges".

Determining the Need for WET Testing

For wastewater dischargers, whole effluent toxicity (WET) tests may be needed to determine the potential for impacts to the receiving stream fish and aquatic life community from point source discharges. These tests may be needed in addition to secondary values.

The WET Checklist (described in Chapter 1.3 of the WET Guidance Document) is designed to help WDNR staff make decisions about WET monitoring frequencies and limits for wastewater effluents being discharged to surface waters, based on their potential to exhibit toxicity. The WET Checklist assesses toxicity potential by assigning points for factors such as industry type, wastewater treatment type and operations, etc., that increase the chances for toxicity. Since many of these factors are usually absent when there are no process wastewaters in the discharge, the WET Checklist may not apply well to those situations. The guidance in this document should be used instead of the WET Checklist in situations where process wastewaters

are not being discharged. Examples of this would be discharges that consist solely of cooling water, cooling tower blowdown, and/or boiler blowdown.

WET testing should be considered in addition to limits based on secondary values when any of the following conditions apply:

- When there is uncertainty regarding the amount of degradation or dilution that an additive undergoes before discharge.
- When historical or projected use of an additive suggests that the effective dose may exceed 1/5th of the calculated secondary value.
- When a discharge contains multiple additives that are likely to be discharged simultaneously.

If staff are unsure which process should be applied to a given situation, they should contact the Biomonitoring Coordinator (Kari Fleming: kari.fleming@wisconsin.gov or 608-400-2851).

The amount of WET monitoring that is needed in a given situation will be site-specific and depends on the number of additives used and the discharge conditions involved. The monitoring frequencies recommended below cover some, but not all, of the possible discharge scenarios that may call for WET testing.

Table 5. Recommended WET Monitoring For Effluents With Multiple Additives

Monitoring Fraguency	Number of Additives	WET test conducted on effluent that is likely to contain
Monitoring Frequency	Number of Additives	the:
Once a year	1	Additive or its residual*
Once a year for first 2 years	≥ 2 that are likely to be	Mixture or the residual of the mix
ioi iiist 2 years	discharged simultaneously	Mixture of the residual of the mix
Once every 3 months	> 2 that are not likely to be	Additive or its residual
for the first 9 months	discharged simultaneously	Additive of its residual
* This recommendation	applies independently to each	additive used unless otherwise noted.

Note: These recommendations represent the **minimum** frequencies recommended to evaluate the potential for additive-related impacts to receiving stream fish and aquatic life communities. These frequencies should be increased if there are case-specific reasons that warrant a further evaluation of this potential.

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 water chemistry (temperature, pH, etc.) on the toxicity of an additive, seasonal changes in the receiving water species composition, etc.

Wastewater Treatment Plant Product Trials

Wastewater permittees should contact their DNR compliance staff before moving forward with a pilot of a new treatment chemical or product at their wastewater treatment plant (WWTP). In order to ensure that proper operation and maintenance of the WWTP is taking place, as required in s. NR 205.07(j), Wis. Adm. Code, permittees should communicate with their compliance staff regarding the standard operating procedures for the operation and installation of their pilot. Wastewater compliance staff should review and approve the scope of the pilot before it begins. At a minimum, the following information should be included:

- Anticipated start date and the estimated timing of the pilot,
- Flow diagram of the WWTP with the location of the product addition,
- Calculations for amount of product used and contact time,
- SDS for the additive,
- Date of WET test(s) to be performed (where applicable), and
- Disposal plans for any leftover product or byproduct from the pilot (where applicable).

If staff have questions related to the potential for toxicity impacts from new or unique chemical applications or wastewater treatment technologies, they should contact the Biomonitoring Coordinator (Kari Fleming: kari.fleming@wisconsin.gov or 608-400-2851).

Glossary

- **Additive**: any substance, typically a commercial product, that has the potential to be directly discharged to a surface water and may cause toxicity to fish and aquatic organisms.
- Acute Toxicity Criterion: maximum daily concentration of a substance which ensures
 adequate protection of sensitive species of aquatic life from the acute toxicity of that
 substance and will adequately protect the designated fish and aquatic life use of the surface
 water if not exceeded more than once every 3 years.
- **Biocide**: a chemical substance (e.g., pesticide, herbicide, fungicide) or microorganism which is used to deter or kill living organisms through chemical or biological means.
- **CAS number**: unique numerical identifier assigned by Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature.
- Chronic Toxicity Criterion: the maximum 4–day concentration of a substance which ensures adequate protection of sensitive species of aquatic life from the chronic toxicity of that substance and will adequately protect the designated fish and aquatic use of the surface water if not exceeded more than once every 3 years.
- **Clarifying agent**: chemicals that are used to remove suspended particles from liquids by inducing flocculation.
- Effective Concentration 50% (EC₅₀): the concentration of a toxic substance which causes an adverse effect, including mortality, in 50% of the exposed organisms in a given time period.
- **Flocculent log**: a block made of polymers and/or other additives used reduce and prevent fine and colloidal particles from entering stormwater.
- Frac sand: quartz sand used in hydraulic fracturing (i.e., fracking) to produce oil, natural gas, or other petroleum-based materials.
- **Genus Mean Acute Value (GMAV)**: the geometric mean of the all species mean acute values (SMAVs) for a given genus.
- **IC25**: The inhibition concentration (IC) is a statistical analysis used to estimate sublethal effects in chronic toxicity tests. An IC₂₅ is an estimate of the concentration that causes a 25% reduction in a nonlethal endpoint, such as reproduction or growth.
- Lethal Concentration 50% (LC₅₀): the concentration of a toxic substance which is lethal to 50% of the exposed organisms in a given time period.
- Lowest observable adverse effect level (LOAEL): the lowest tested concentration that caused an adverse effect in comparison with a control when all higher test concentrations caused the same effect.
- Material safety data sheet (MSDS): see Safety Data Sheet below.
- No observable adverse effect level (NOAEL): highest tested concentration that did not cause an adverse effect in comparison with a control when no lower test concentration caused an adverse effect.
- **Polymer**: natural or synthetic materials that have a chain of carbon molecules that are identical, repeating units.

- Safety Data Sheet (SDS): a document that outlines chemical information and procedures for handling and working with the chemical; typically include physical and chemical property information, potential hazard information, emergency procedures, and manufacturer contact information. Formerly known as a Material Safety Data Sheet (MSDS).
- Secondary Acute Factor (SAF): a safety factor used in the calculation of Secondary Acute
 Values to account for uncertainty in adverse effects across untested organism classes. SAFs
 are based on how many different organism classes are represented in the available data
 (fewer classes = higher SAF).
- Secondary Acute Value (SAV): a temporary value that represents the concentration of a substance which ensures adequate protection of a sensitive species of aquatic life to adverse effects from acute exposure to that substance; equal to the lowest genus mean acute value divided by the appropriate secondary acute factor for a given fish and aquatic life designated use subclassification.
- **Secondary Acute-Chronic Ratio (SACR):** the geometric mean of at least one Species Mean Acute-Chronic Ratio (SMACR) for each of the following categories. Used when a final acute-chronic ratio FACR cannot be calculated because all of the required data is not available.
- Secondary Chronic Value (SCV): a temporary value that represents the concentration of a
 substance which ensures adequate protection of a sensitive species of aquatic life to
 adverse effects from acute exposure to that substance; equal to the appropriate secondary
 acute value (SAV) divided by the secondary acute-chronic ratio (SACR) for a given fish and
 aquatic life designated use subclassification.
- **Species mean acute value (SMAV):** the geometric mean of all acceptable acute toxicity values for a given species.
- Species Mean Acute-Chronic Ratio (SMACR): the geometric mean of all available TACRs for a given species. A SMACR is required for the following organism categories: fish, invertebrate, sensitive freshwater species.
- **Species Mean Chronic Value (SMCV):** the geometric mean of all acceptable chronic toxicity values for a given species.
- System for Wastewater Applications, Monitoring and Permits (SWAMP): a computer system designed to assist with management of the WPDES Permit Program.
- **Toxicity Test Acute-Chronic Ratio (TACR)**: the Species Mean Acute Value (SMAV) divided by Species Mean Chronic Value (SMCV) for toxicity test available for each species.
- Water quality based effluent limits (WQBEL): effluent limitations established by the department to meet applicable water quality standards.
- Whole Effluent Toxicity (WET): toxicological testing conducted on point-source end-of-pipe effluent to measure, predict, and control the discharge of materials that may be harmful to aquatic life.
- Wisconsin Department of Transportation (WisDOT): state agency responsible for addressing transportation erosion.

• Wisconsin Pollution Discharge Elimination System (WPDES): as authorized by the Clean Water Act, the National Pollutant Discharge Elimination System (NPDES) permit program controls water pollution by regulating point sources that discharge pollutants into waters of the United States. In most cases, the NPDES permit program is administered by delegated states. The Wisconsin DNR administers the Wisconsin Pollutant Discharge Elimination System (WPDES) permit program for discharges to waters of the state.

References

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Wisconsin Department of Natural Resources. 2004. State of Wisconsin Aquatic Life Toxicity Testing Methods Manual, 2nd edition.

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Wisconsin Department of Natural Resources. Whole Effluent Toxicity Program Guidance Document. (http://dnr.wi.gov/topic/wastewater/WETguidance.html)

Appendix A: Using the Secondary Value Calculator for Wastewater Reviews

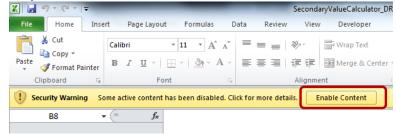
GENERAL TIPS

- **Save Before Changing-** Save the additive review spreadsheet under a new name before making edits to the spreadsheet.
- Locked Cells- This spreadsheet has locked cells to avoid editing the wrong features, unlocked cells that can be edited by WDNR staff are highlighted in blue.
- **Copy and Paste** To copy and paste text into highlighted cells double click the appropriate cell first, so the text cursor appears in the cell. You cannot simply click the cell and paste text without being in the "text" mode.
- Watch for "red flags"- Red flags are comment features in excel, and provide additional information for the person filling out the spreadsheet.
- **Deleting Selection** To delete dropdown information, click the incorrect cell and press the backspace or delete key.

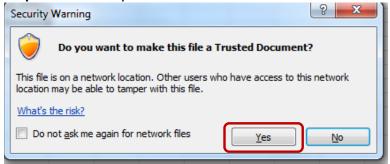
SECONDARY VALUES REPORT

This is the first sheet that should come up when you open the spreadsheet.

Step 1: In the "Macros has been disabled" box, select "Enable Content".



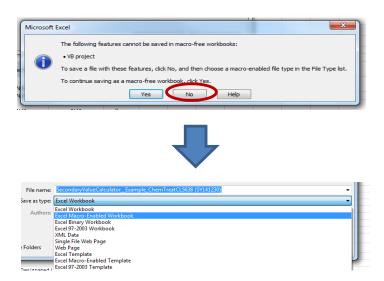
Step 2: If the "Do you want to make this file a Trusted Document?" box appears, select "Yes".



Step 3: Create a new folder in \\central\water\\WQWT PROJECTS\\WY CP Additives\\Additive \\Product Toxicity Information\\ and save the spreadsheet in there.

Note: Folder naming convention is "company name_product name" and spreadsheet naming convention is : "Year_Product Name_Initials".

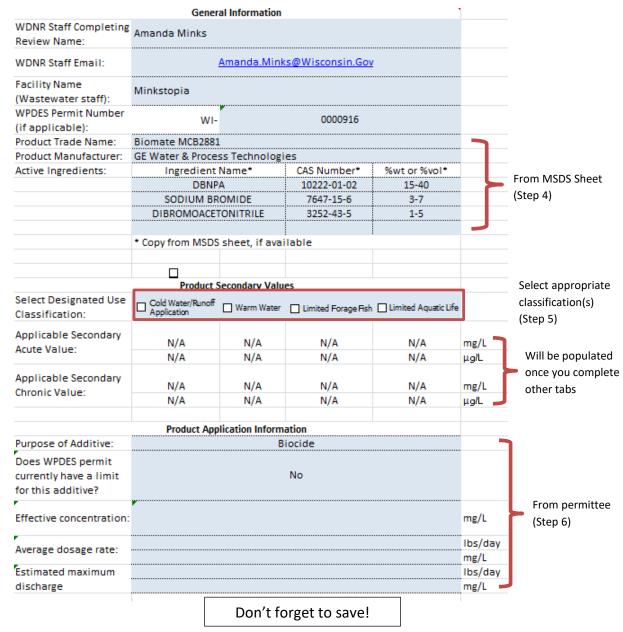
Tip: If you get an error when trying to save (see box below), click "No" and select "Excel Macro-Enabled Workbook" under "Save as Type".



Step 4: In the "General Information" section, fill in all highlighted cells for which you have data. You will likely need to refer to previous permit documents, SWAMP data, and SDS sheets to complete this tab.

Step 5: For "Designated Use Classification", select the appropriate box(es). **Note:** The applicable secondary acute and chronic value rows (Rows 19 and 20) will automatically fill-in with the correct data once you fill out the rest of the spreadsheet.

Step 6: In the "Product Application" section, fill in all highlighted cells for which you have data. You will likely need to refer to previous permit documents, SWAMP data, and SDS sheets to complete this tab.



A (ACUTE)

Step 7: Use the dropdown menus to fill in the toxicity information provided from the SDS sheet(s) and/or lab sheet(s). This should also include test method data provided by the lab.

Tip: Test method data may be available via lab reports or through lab correspondence. Work with the permittee to ascertain these data.

Tip: Contact the Water Evaluation Toxicologist if toxicity data are provided for species other than those listed in A (Acute) tab.

Tip: Only 48-hour and 96-hour toxicity endpoints should be used in this tab.

Step 8: Review the spreadsheet, in particular the "Acceptable?" column (Column L), to determine if data can be used to calculate secondary values. Column L will automatically be labeled "Yes" if data are acceptable. In some cases, data is not flagged as acceptable because "Other" was selected as the "Test Method" (Column H). If this is the case, go to Step 9 in B (Acute-Optional) tab to determine if this data can be used in the calculation.



Only data from rows labeled "Yes" is included in the calculation

If Test Method is "Other", go to Tab B (Acute-Optional).

B (ACUTE-OPTIONAL)

This tab is used for data that for which "Other" was selected as the "Test Method" (see step 8).

Step 9 (optional): Use the dropdown menus to select the test parameters used to generate the toxicity endpoint. All fields must be filled in before the data can be considered acceptable. Contact the Water Evaluation Toxicologist with questions. Once completed, go to C (Acute) tab.

Tanisian Tank Bananatan		Water flea		Fathead Minnow	Bluegill	Rainbow Trout
Toxicity Test Parameters	(Ceriodaphnia spp.)	(Daphnia spp.)	(Simocephalus spp.)	(Pimephales promelas)	(Lepomis macrochirus)	(Oncorhynchus mykiss)
Temperature:		25±1 °C	▼			
Dilution water:	20±1 ° 25±1 ° Other					
Number of test concentrations:		≥ 5 + control				
Dilution series setup:		≥0.5 dilution series				
Age of test organisms:		< 24 h				
Number of organisms/test chamber:		≥5				
Number of replicate chambers per concentration:		≥ 4				
Number of organisms per concentration:		≥ 20				
Data acceptable?	No	Yes	No	No	No	No

Don't forget to save!

C (ACUTE)

Step 10: No action is necessary in this tab. DNR staff may wish to review to verify findings. All information is automatically entered into tab and a SAV is calculated. The final SAVs are highlighted in orange.

Taxa Category	Genus	Species	Common Name	Test Result	SMAV	GMAV	Designated Use Classification				
axa category	Genus	эренез	Common Name	mg/L	mg/L	mg/L	cw	ww	LFF	LAL	
		dubia	Water flea		N/A						
	Ceriodaphnia	reticulata	Water flea		N/A	N/A	x	х	x	x	
		serrulatus	Water flea		N/A						
Planktonic Crustacean		magna	Water flea	3.30	3.30						
	Daphnia	pulex	Water flea		N/A	3.30	х	X	X	X	
Simoce		serrulatus	Water flea		N/A				,		
	Simocephalus	vetulus	Water flea		N/A	N/A	Х	Х	Х		
Non-Salmonid	Pimephales	promelas	Fathead minnow	8.70	8.70	8.70	x	x	x		
Fish	Lepomis	Macrochirus	Bluegill	6.50	6.50	6.50	х	х	х		
	Oncorhynchus	mykiss	Rainbow trout	2.30	2.30	2.30	x				
Salmonid Fish	Salvelinus	fontinalis	Brook trout		N/A	N/A	х				
					SA	AF:	8				
					Lowest	GMAV:	2.30	3.30	3.30	3.30	
					Calculat	ed SAV:	0.29	0.41	0.41	0.41	
					Selecti	ed SAV:	0.288 287.5	_	0.413 412.5		

D (CHRONIC)

Step 11: Determine whether chronic data (test duration ≥ 7 days) have been submitted to DNR for review. If chronic data have been submitted, proceed to Step 12. If no chronic data is submitted, go to Step 16 ("Secondary Values Report" Tab). A secondary chronic value will be calculated using default parameters.

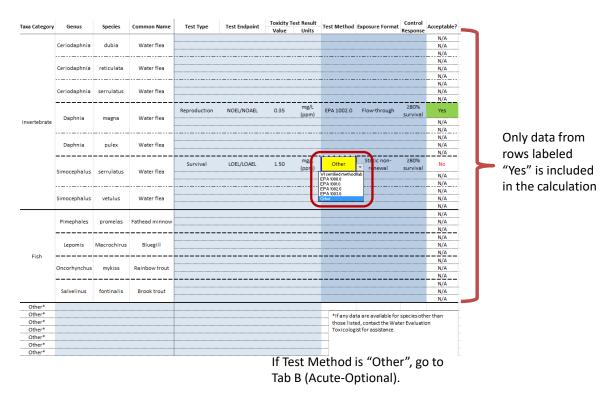
Step 12: Use the dropdown menus to fill in the toxicity information provided from the SDS sheet(s) and/or lab sheet(s). This should also include test method data provided by the lab.

Tip: Test method data may be available via lab reports or through lab correspondence. Work with the permittee to ascertain these data.

Tip: Contact the Water Evaluation Toxicologist if toxicity data are provided for species other than those listed in D (Chronic) tab.

Tip: Only long-term toxicity endpoints (e.g., NOAEL, LOAEL) should be used in this tab. <u>Do</u> not enter information from IC25s here.

Step 13: Review the spreadsheet, in particular the "Acceptable?" column (Column M), to determine if data can be used to calculate secondary values. Column M will automatically be labeled "Yes" if data are acceptable. In some cases, data is not flagged as acceptable because "Other" was selected as the "Test Method" (Column I). If this is the case, go to Step 14 in E (Chronic-Optional) tab to determine if this data can be used in the calculation.



Don't forget to save!

E (CHRONIC-OPTIONAL)

This tab is used for data that for which "Other" was selected as the "Test Method" (see step 13).

Step 14 (optional): Use dropdown menus to select the test parameters used to generate the toxicity endpoint. All fields must be filled in before the data will be considered acceptable. Contact the Water Evaluation Toxicologist with questions. Once completed, go to F (Chronic) tab.

Total de Total Dominion		Fathead Minnow		
Toxicity Test Parameters	(Ceriodaphnia spp.)	(Daphnia spp.)	(Simocephalus spp.)	(Pimephales promelas)
Test duration:	≤ 8 days			
Temperature:	20±1 °C			
Dilution water:	Synthetic water			
Number of test concentrations:	≥ 5 + control			
Dilution series setup:	≥0.5 dilution series			
Age of test organisms:	< 24 h	-		
Number of organisms/te < 24 h Other chamber:				
Number of replicate chambers per concentration:	≥ 10			
Number of organisms per concentration:	≥ 10		_	
Data acceptable?	Yes	No	No	No

F (CHRONIC)

Step 15: *No action is necessary in this tab.* DNR staff may wish to review to verify findings. All information is automatically entered into tab and a SCV is calculated. The final SCVs are highlighted in orange.

Taxa Category	C	Species	Common Name	SMAV	Chronic Test Value	SMCV	SMACR	Designated Use Classification				
axa Category	Genus	Species	Common Name	mg/L	mg/L	SIVICV	SIVIACK	CW	ww	LFF	LAL	
	Ceriodaphnia	dubia	Water flea					x	x	x	X	
	Ceriodaphnia	reticulata	Water flea					х	х	х	х	
	Ceriodaphnia	serrulatus	Water flea					х	х	х	х	
nvertebrate	Daphnia	magna	Water flea	3	FALSE			х	х	×	х	
	Daphnia	pulex	Water flea					х	х	х	х	
	Simocephalus	serrulatus	Water flea		1.500	1.50		х	х	х	х	
	Simocephalus	vetulus	Water flea					х	х	х	х	
					Invertebra	te SMACR:	18.00	(default)				
	Pimephales	promelas	Fathead minnow	8.7				х	х	х		
Fish	Lepomis	Macrochirus	Bluegill	6.5				х	х			
FISH	Oncorhynchus	mykiss	Rainbow trout	2.3				х				
	Salvelinus	fontinalis	Brook trout					х				
					Fit	sh SMACR:	18.00	(default)				
				Sens	sitive Freshwater Speci							_
						SA		13.027	14.510	14.510	13.027	
						Selecte Calculat		0.288	0.413	0.413	0.413	
						Calculat	eu SCV:	0.022	0.028	0.028	0.032	ma/I
						Selecte	d SCV:	22.1	28.4	28.4	31.7	mg/L μg/L

Don't forget to save!

SECONDARY VALUES REPORT

Step 16: Return to "Secondary Values Report" Tab. The appropriate final secondary acute and chronic values are highlighted in orange.

Note: If the SAV/SCV is greater than 0.1 mg/L (100 μ g/L), the value with units of mg/L will be highlighted. If the SAV/SCV is less than 0.1 mg/L (100 μ g/L), the value with units of μ g/L will be highlighted.

	Product 5	Secondary Valu	es		
Select Designated Use Classification:	Cold Water/Runoff Application	✓ Warm Water	Limited Forage Fish	Limited Aquatic Life	
Applicable Secondary Acute Value:	N/A	0.413	N/A	N/A	mg/L
Acute Value.	N/A	413	N/A	N/A	μдгь
Applicable Secondary Chronic Value:	N/A	0.03	N/A	N/A	mg/L
cilionic value.	N/A	28.4	N/A	$\frac{N/A}{}$	μg/L

Step 17: Use the SAV and SCV to derive water-quality based effluent limits (WQBEL) using the procedures described in ss. NR 106, Wis. Adm. Code.

Appendix B: Using the Secondary Value Calculator for Runoff Management Reviews

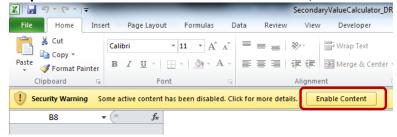
GENERAL TIPS

- **Save Before Changing-** Save the additive review spreadsheet under a new name before making edits to the spreadsheet.
- Locked Cells- This spreadsheet has locked cells to avoid editing the wrong features, unlocked cells to be edited by the WDNR staff are highlighted in blue.
- **Copy and Paste** To copy and paste text into highlighted cells double click the appropriate cell first, so the text cursor appears in the cell. You cannot simply click the cell and paste text without being in the "text" mode.
- Watch for "red flags" Red flags are comment features in Excel, and provide additional information for the person filling out the spreadsheet.
- **Deleting Selection** To delete dropdown information, click the incorrect cell and press the backspace or delete key.

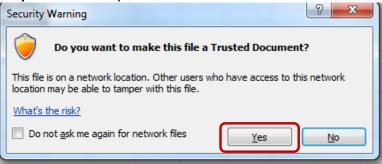
SECONDARY VALUES REPORT

This is the first sheet that should come up when you open the spreadsheet.

Step 1: In the "Macros has been disabled" box, select "Enable Content".



Step 2: If the "Do you want to make this file a Trusted Document?" box appears, select "Yes".

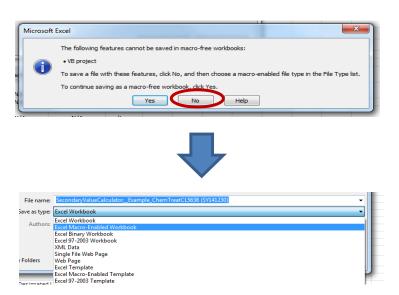


Step 3:

Create a new folder in \\central\water\WQWT PROJECTS\WY CP Additives\Additive Product Toxicity Information\\ and save the spreadsheet in there.

Note: Folder naming convention is "company name_product name" and spreadsheet naming convention is: "Year Product Name Initials".

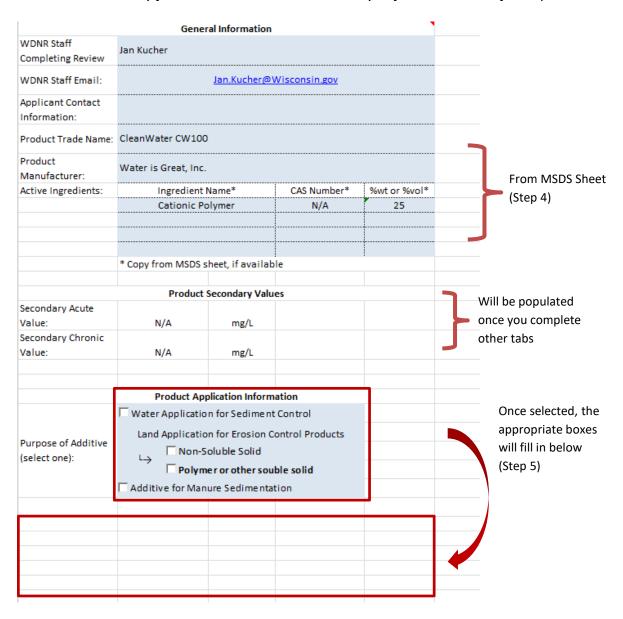
Tip: If you get an error when trying to save (see box below), click "No" and select "Excel Macro-Enabled Workbook" under "Save as Type".



Step 4: In the "General Information" section, fill in all highlighted cells for which you have data. You will likely need to refer to SDS sheets and product technical documents to complete this tab.

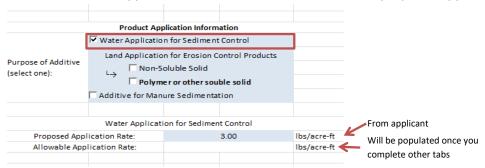
Step 5: For "Purpose of Additive", select the appropriate box. Once selected, additional rows will appear.

Note: The applicable secondary acute and chronic value rows (Rows 15 and 16) will automatically fill-in with the correct data once you fill out the rest of the spreadsheet.

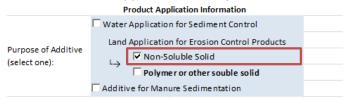


Step 6: In the "Product Application" section, fill in all highlighted cells

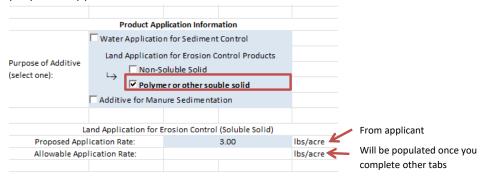
iii. For Water Application for Sediment Control, enter the proposed application rate.



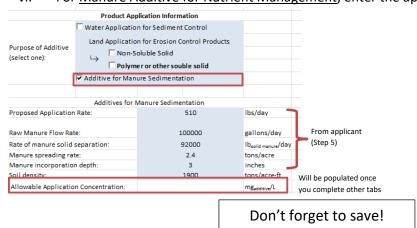
iv. For <u>Land Application for Erosion Control Products—Non-Soluble Solid</u>, a different process is used (see Appendix D for steps).



v. For <u>Land Application for Erosion Control Products—Polymer or other soluble solid</u>, enter the proposed application rate.



vi. For Manure Additive for Nutrient Management, enter the appropriate information



A (ACUTE)

Step 7: Use the dropdown menus to fill in the toxicity information provided from the SDS sheet(s) and/or lab sheet(s). This should also include test method data provided by the lab.

Tip: Test method data may be available via lab reports or through lab correspondence. Work with the applicant to ascertain these data.

Tip: Contact the Water Evaluation Toxicologist if toxicity data are provided for species other than those listed in A (Acute) tab.

Tip: Only 48-hour and 96-hour toxicity endpoints should be used in this tab.

Step 8: Review the spreadsheet, in particular the "Acceptable?" column (Column L), to determine if data can be used to calculate secondary values. Column L will automatically be labeled "Yes" if data are acceptable. In some cases, data is not flagged as acceptable because "Other" was selected as the "Test Method" (Column H). If this is the case, go to Step 9 in B (Acute-Optional) tab to determine if this data can be used in the calculation.



Only data from rows labeled "Yes" is included in the calculation

If Test Method is "Other", go to Tab B (Acute-Optional).

B (ACUTE-OPTIONAL)

This tab is used for data that for which "Other" was selected as the "Test Method" (see step 8).

Step 9 (optional): Use the dropdown menus to select the test parameters used to generate the toxicity endpoint. All fields must be filled in before the data can be considered acceptable. Contact the Water Evaluation Toxicologist with questions. Once completed, go to C (Acute) tab.

Taulaitu Taut Bauranatau		Water flea		Fathead Minnow	Bluegill	Rainbow Trout
Toxicity Test Parameters	(Ceriodaphnia spp.)	(Daphnia spp.)	(Simocephalus spp.)	(Pimephales promelas)	(Lepomis macrochirus)	(Oncorhynchus mykiss)
Temperature:		25±1 °C	▼			
Dilution water:	20±1 ° 25±1 ° Other					
Number of test concentrations:		≥ 5 + control				
Dilution series setup:		≥0.5 dilution series				
Age of test organisms:		< 24 h				
Number of organisms/test chamber:		≥5				
Number of replicate chambers per concentration:		≥ 4				
Number of organisms per concentration:		≥ 20				
Data acceptable?	No	Yes	No	No	No	No

Don't forget to save!

C (ACUTE)

Step 10: *No action is necessary in this tab.* DNR staff may wish to review to verify findings. All information is automatically entered into tab and a SAV is calculated. The applicable final SAV is highlighted in orange.

Taxa Category		Sanda Sanda Nama	Common Name	Test Result		GMAV	Designated Use Classification			1	
laxa Category	Genus	Species	Common Name	mg/L	mg/L	mg/L	cw	ww	LFF	LAL	
	Ceriodaphnia	reticulata	Water flea		N/A	N/A	x	x	x	x	
		serrulatus	Water flea		N/A						
Planktonic Crustacean		magna	Water flea	3.30	3.30						
	Daphnia	pulex	Water flea		N/A	- 3.30	X	х	х	Х	
	Simocephalus	serrulatus	Water flea		N/A	- N/A X	х	x	x		
		vetulus	Water flea		N/A				^		
Non-Salmonid	Pimephales	promelas	Fathead minnow	8.70	8.70	8.70	x	x	x		
Fish	Lepomis	Macrochirus	Bluegill	6.50	6.50	6.50	x	x	х		
	Oncorhynchus	mykiss	Rainbow trout	2.30	2.30	2.30	x				
Salmonid Fish	Salvelinus	fontinalis	Brook trout		N/A	N/A	x				
					SA	AF:	8				
						GMAV:	2.30	3.30	3.30	3.30	
						ted SAV:	0.29	0.41	0.41	0.41	
					Selecti	ed SAV:	0.288	0.41	0.41	0.41	mg/L

D (CHRONIC)

Step 11: Determine whether chronic data (test duration ≥ 7 days) have been submitted to DNR for review. If chronic data have been submitted, proceed to Step 12. If no chronic data is submitted, go to Step 16 ("Secondary Values Report" Tab). A secondary chronic value will be calculated using default parameters.

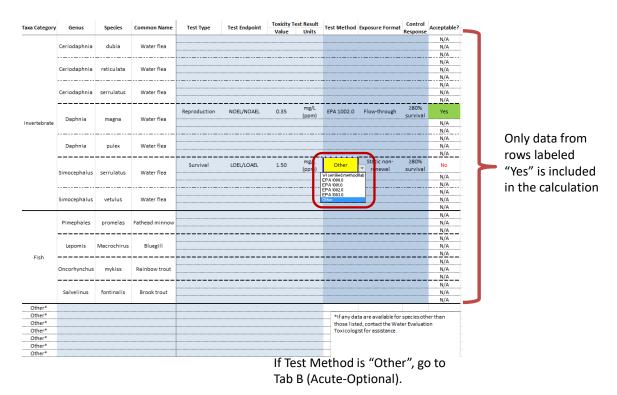
Step 12: Use the dropdown menus to fill in the toxicity information provided from the SDS sheet(s) and/or lab sheet(s). This should also include test method data provided by the lab.

Tip: Test method data may be available via lab reports or through lab correspondence. Work with the applicant to ascertain these data.

Tip: Contact the Water Evaluation Toxicologist if toxicity data are provided for species other than those listed in D (Chronic) tab.

Tip: Only long-term toxicity endpoints (e.g., NOAEL, LOAEL) should be used in this tab. <u>Do not</u> enter information from IC25s here.

Step 13: Review the spreadsheet, in particular the "Acceptable?" column (Column M), to determine if data can be used to calculate secondary values. Column M will automatically be labeled "Yes" if data are acceptable. In some cases, data is not flagged as acceptable because "Other" was selected as the "Test Method" (Column I). If this is the case, go to Step 14 in E (Chronic-Optional) tab to determine if this data can be used in the calculation.



Don't forget to save!

E (CHRONIC-OPTIONAL)

This tab is used for data that for which "Other" was selected as the "Test Method" (see step 13).

Step 14 (optional): Use dropdown menus to select the test parameters used to generate the toxicity endpoint. All fields must be filled in before the data will be considered acceptable. Contact the Water Evaluation Toxicologist with questions. Once completed, go to F (Chronic) tab.

Tanisity Tast Barranatan		Water flea		Fathead Minnow
Toxicity Test Parameters	(Ceriodaphnia spp.)	(Daphnia spp.)	(Simocephalus spp.)	(Pimephales promelas)
Test duration:	≤ 8 days			
Temperature:	20±1 °C			
Dilution water:	Synthetic water			
Number of test concentrations:	≥ 5 + control			
Dilution series setup:	≥0.5 dilution series			
Age of test organisms:	< 24 h	-		
Number of organisms/te < 24 h Other chamber:				
Number of replicate chambers per concentration:	≥ 10			
Number of organisms per concentration:	≥ 10			
Data acceptable?	Yes	No	No	No

F (CHRONIC)

Step 15: *No action is necessary in this tab.* DNR staff may wish to review to verify findings. All information is automatically entered into tab and a SCV is calculated.

axa Category	Genus	Species	Common Name	SMAV	Chronic Test Value	SMCV SMACE	CMACD	Designated Use Classification				
axa Category	Ty delius species common in	Common Name	mg/L mg/L	SIVICV	SIVIACK	CW	ww	LFF	LAL			
	Ceriodaphni a	dubia	Water flea					x	x	x	x	
	Ceriodaphni a	reticulata	Water flea					х	x	х	х	
	Ceriodaphni a	serrulatus	Water flea					х	х	х	x	
nvertebrate	Daphnia	magna	Water flea	3	FALSE			х	х	х	х	
	Daphnia	pulex	Water flea					х	х	х	х	
	Simocephalu s	serrulatus	Water flea		2.500	2.50		х	х	х	х	
	Simocephalu s	vetulus	Water flea					х	х	х	x	
					Invertebrat	e SMACR:	18.00	(default)				
	Pimephales	promelas	Fathead minnow	8.7				х	х	х		
Fish	Lepomis	Macrochiru s	Bluegill	6.5				х	х			
11511	Oncorhynchu s	mykiss	Rainbow trout	2.3				x				
	Salvelinus	fontinalis	Brook trout					x				
					Fis	h SMACR:	18.00	(default)				
				Sensi	tive Freshwater Specie							
						SA		13.027	14.510	14.510	13.027	
							d SAV:	0.288	0.413	0.413	0.413	
						Calculat		0.022	0.028	0.028	0.032	
						Selecte	d SCV:	0.02	0.03	0.03	0.03	mg/L

Don't forget to save!

SECONDARY VALUES REPORT

Step 16: Return to "Secondary Values Report" Tab. The appropriate final secondary acute and chronic values are highlighted in orange.

	Product S	Secondary Va	lues	
Secondary Acute Value:	0.288	mg/L	←	Used to calculate allowable application rate
Secondary Chronic Value:	0.02	mg/L		

Step 17: The SAV is used to calculate an application rate using the appropriate conversion factors. Compare the allowable application rate to the proposed application rate to determine if the product can be used as proposed.

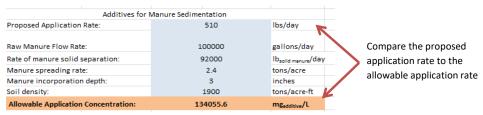
- Water Application Products for Sediment Control

Water Applicati	Compare the proposed		
Proposed Application Rate:	3.00	lbs/acre-ft	application rate to the
Allowable Application Rate:	0.388	lbs/acre-ft	allowable application rate
			anowabic application rate

- Land Application Products for Erosion Control

Land Application for E	Compare the proposed			
Proposed Application Rate:	3.00	lbs/acre		
Allowable Application Rate:	0.200	lbs/acre	application rate to the	
			allowable application rate	

Additives for Manure Sedimentation



Appendix C: Additive Review Request Worksheet

Additive Review Worksheet

This worksheet summarizes the information to be submitted to the WDNR for review of additives. This information is required because additives are approved on a case-by-case basis.

The fields highlighted in orange are required for all additive reviews and are NOT typically found on a safety data sheet (SDS).

The fields highlighted in blue are required for all additive reviews and are typically found on a SDS.

Part D needs to be completed **for each species** (e.g. Daphnia - water flea; Pimephales (fathead minnow), etc.) for which a toxicity test is conducted.

The fields highlighted in green are NOT typically found on a SDS and are required for toxicity tests conducted when "Other" is selected for Test Method in Part D-1.

If all of the needed information is not provided on the SDS, it is recommended that you contact the chemical distributor and/or manufacturer to obtain the required information. You do not need to conduct the toxicity test if the toxicity information is available on SDS or from the supplier/manufacturer. If the required toxicity data is not provided to the Department, the additive product may not be approved for use.

Note: Toxicity test results must address the *commercial product formulation*. The commercial product formulation is all active ingredients and any and all carriers, buffering agents, binding agents, and additional materials – the entire product as used. Information related to active ingredient alone is not sufficient.

For more information on the additive review process, see the "<u>Water Quality Review</u> <u>Procedures for Additives</u>" guidance document.

An electronic copy of this worksheet is also available in the <u>Forms Catalog</u> by searching for Form 3400-213.

A. General Production Information

Date of Request:	Click here to enter a date.	
Permittee Facility Name:	enter text here	WPDES Permitting
Applicant Contact Information:	enter text here	Runoff Management
Product Trade Name:	enter text here	
Product Manufacturer:	enter text here	
A att a transatta ata		

Active Ingredients:

Ingredient Name*	CAS Number**	%wt or % vol		
enter text here	enter text here	enter text here		
enter text here	enter text here	enter text here		
enter text here	enter text here	enter text here		
enter text here	enter text here	enter text here		
* Must be provided unless noted to be proprietary information				
** If available				

Is this product replacing another additive (if yes, include product name)?

□Yes □No

Current Product Name: enter text here

B. Dosage or Application Information

Purpose of additive:	enter text here		
Proposed application rate	enter text here	lb/acre	Runoff management
(expressed in lb/acre for land and			applicants
lbs/acre-ft for water applications):	enter text here	lb/acre-ft	applicants
Proposed dosage rate:	enter text here	lbs/day	
Proposed dosage rate.	enter text here	mg/L	Wastewater
Estimated maximum discharge	enter text here	lbs/day	permittees
concentration:	enter text here	mg/L	

C. Toxicity Test Results

Test Species	Toxicity Value Type	Toxicity Value	Toxicity Value Units
Select from list	Select from list	enter text here	Select from list
Select from list	Select from list	enter text here	Select from list
Select from list	Select from list	enter text here	Select from list
Select from list	Select from list	enter text here	Select from list

D. Toxicity Test Parameters (Sp	ecies: Select from list)				
1. Parameters needed for A	LL reviews				
	☐ WI certified WET testing lab/method				
Test method:	☐ EPA method (Method: Select from list)				
	☐ Other (additional information needed; see part D2)				
	☐ Static non-renewal				
Test type:	☐ Static-renewal				
	☐ Flow-through				
Cambridge	□ ≥ 90% survival				
Control response:	☐Other (Note: if this is selected, this data cannot be used)				
2. Parameters needed wher	using "other" test methods				
	☐Moderately hard synthetic water				
	□Synthetic water				
Dilution water:	☐Receiving water				
	☐Ground water				
	□Other (Specify: enter text here)				
Number of test concentrations:	enter text here				
Dilution series:	□ ≥ 0.5				
Dilution series.	☐ Other (Specify: enter text here)				
	□рН				
Water chemistry analyses	☐ Conductivity				
(check all that apply):	☐ Hardness				
	☐ Alkalinity				
Temperature:	Choose an item. (If other, specify enter text here:)				
Number of organisms per test	enter text here				
chamber:	Cited text field				
Number of replicate chambers	enter text here				
per concentration:					
Number of organisms per	enter text here				
concentration: Method for calculating the					
response endpoint:	enter text here				
response enuponit.					

If additional species have been tested, copy the above table (Part D) and paste on a separate page.

Appendix D: Additive Review for Non-Soluble Additives

1. Introduction

Some additives, typically erosion control products, are composed of solid materials that are not soluble in water. Examples may include, but are not limited to, bonded fiber matrices (e.g. wood chips), certain flocculating agents, and certain soil stabilizers. Because these products contain materials that are not soluble in water, the primary ecological concern is not for organisms that live in the water column (i.e., fish) but for organisms that live in or near the sediment (e.g., amphipods, crustaceans). Therefore, the traditional, water-column toxicological testing methods are not appropriate for these types of additives. Instead, toxicity testing methods with sediment-dwelling species should be used.

2. Acceptable Toxicity Tests

Table 1 lists the recommended test organisms, test type, test result, endpoint type, and test method for "non-soluble solid" additives.

Table 1. Acceptable whole sediment testing methods for common test species

Test Organism	Test Type	Test Result	Endpoint Type	Test Method
Ceriodaphnia dubia (Water flea) Daphnia magna (Water flea)	48-hr	NOAEL*	Survival	ASTM E1706
Hyalella azteca (Amphipod)	10-day	NOAEL*	Survival and/or Growth	ASTM E1706

^{*}NOAEL = no observable adverse effect level

In these tests, the erosion control product is used in place of the "whole sediment", since this is a close surrogate of how the product would exist in an aquatic environment.

Note: toxicity tests are to be conducted on the "commercial product formulation", which is all active ingredients and any and all carriers, buffering agents, binding agents, non-soluble solids, and additional materials (i.e., the entire product as used). Toxicological information related to "active ingredient" alone is not sufficient.

For these products, a secondary value is not derived. Instead, the highest test concentration that causes no mortality (i.e., the no observable adverse effect level-NOAEL) is used as the acceptable maximum application concentration.

Note: To determine the highest concentration that causes no mortality, several concentrations may need to be tested. It is recommended to start with the maximum proposed application concentration and use a 0.5 dilution factor to select other concentrations if necessary.

Runoff Management staff then calculate the allowable application rate for the product using the procedures detailed in the Land Application for Erosion Control Additives - DNR Conservation Standard 1050:

https://dnr.wisconsin.gov/sites/default/files/topic/Stormwater/1050LandApplAdditives.pdf

This final allowable application rate is compared to the proposed application rate to determine if the product can be used as requested. Runoff management staff then prepare a letter to the applicant that states the application rate at which the product can be used in Wisconsin and whether or not the product can be used as proposed. Department of Transportation staff are provided this information as necessary.

3. Specific Toxicity Test Process

At least two toxicity tests should be run, each with appropriate controls. Therefore, a sufficient amount of land applied erosion control product should be prepared to be used in:

- At least one 10-day acute Hyalella azteca whole sediment test, and/or
- At least one 2-day acute overlying water test with Ceriodaphnia dubia, and/or
- At least one 2-day acute overlying water test with Daphnia magna.

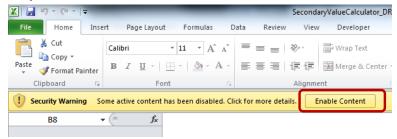
Additional considerations:

- Replace any reference to "sediment" in any of the methods above with the erosion control product.
- For the water flea tests, slight modifications of the methods can be used to get the erosion control product into the test chamber (e.g., chamber size, use of syringe to dispense product, etc.). However, the 1:4 sediment to water ratio should be maintained. If a modification is used, what was changed and how should be noted and included into the toxicity test results submitted to the DNR.
- Immobility of test organisms in the test treatments due to the physical nature of the product (such as in viscous polymer) shall be considered as equivalent to death for the purpose of these tests.

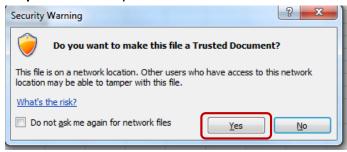
4. Instructions for Using the Secondary Value Calculator for Non-Soluble Additives

SECONDARY VALUES REPORT

Step 1: In the "Macros has been disabled" box, select "Enable Content".

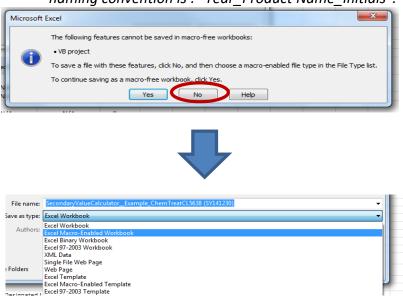


Step 2: If the "Do you want to make this file a Trusted Document?" box appears, select "Yes".



Step 3: Create a new folder in \\central\water\WQWT PROJECTS\WY CP Additives\Additive \\Product Toxicity Information\\\ and save the spreadsheet in there.

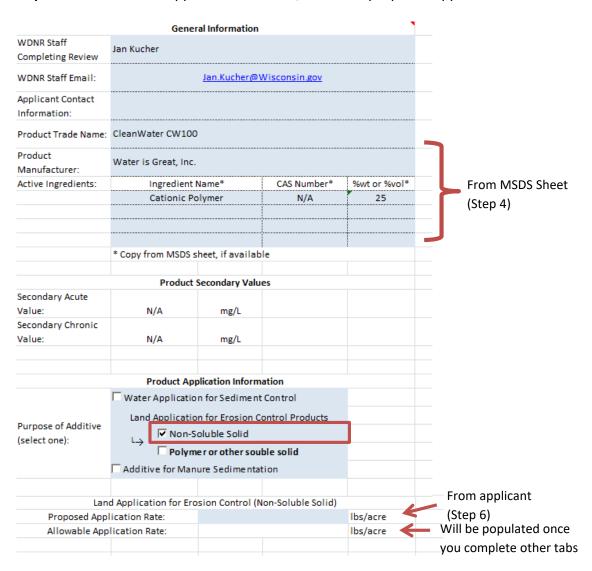
Note: Folder naming convention is "company name_product name" and spreadsheet naming convention is : "Year_Product Name_Initials".



Step 4: In the "General Information" section, fill in all highlighted cells for which you have data. You will likely need to refer to SDS sheets and product technical documents to complete this tab.

Step 5: For "Purpose of Additive", select the "Non-Soluble" box.

Step 6: In the "Product Application" section, enter the proposed application rate.



Appendix D: Additive Review for Non-Soluble Additives

NON-SOLUBLE ADDITIVES

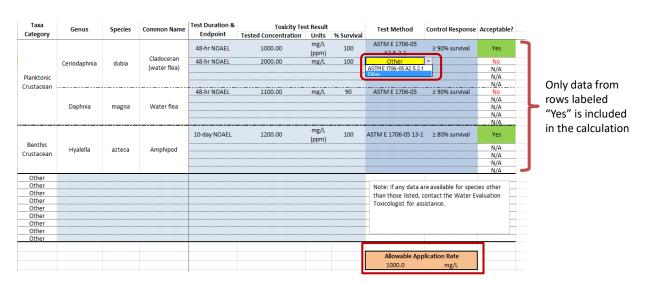
Step 7: Use the dropdown menus to fill in the toxicity information provided from the SDS sheet(s) and/or lab sheet(s). This should also include test method data provided by the lab.

Tip: Test method data may be available via lab reports or through lab correspondence. Work with the applicant to ascertain these data.

Note: Only the species and toxicity endpoints listed in this tab may be used to review non-soluble solid additives.

Step 8: Review the spreadsheet, in particular the "Acceptable?" column (Column L), to determine if data can be used to calculate secondary values. Column L will automatically be labeled "Yes" if data are acceptable. In some cases, data is not flagged as acceptable because "Other" was selected as the "Test Method" (Column I). If this is the case, contact the Water Evaluation Toxicologist for assistance.

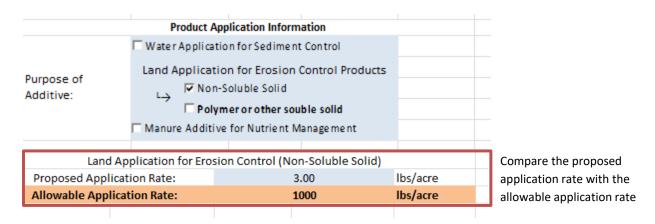
Step 9: Once the acceptable information has been entered, the spreadsheet will automatically calculate the allowable application rate.



If Test Method is "Other", contact the Water Evaluation Toxicologist for assistance.

SECONDARY VALUES REPORT

Step 10: Compare the allowable application rate to the proposed application rate to determine if the product can be used as proposed.



5. References

ASTM E 1706-, "Standard Test Method for Measuring the Toxicity of Sediment-Associated Contaminants with Freshwater Invertebrates", in Annual Book of ASTM Standards, Section 11 Water and Environmental Technology, vol. 11.06, Environmental; Biological Effects and Environmental Fate; Industrial Biotechnology. ASTM International, West Conshohocken, PA.



1. Introduction

The main body of this guidance document contains information for calculating secondary values for products that are added to waste streams for the treatment of wastewater, stormwater runoff, and manure (Fig. E1). These products come in a variety of chemical formulations including, but not limited to, chemical salts, polymers, acids and bases, and organic chemicals.

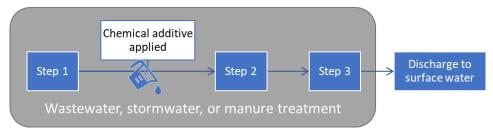


Figure E1. General schematic showing how chemical additives are employed. Examples of these "typical" additives include: biocides, boiler water treatments, clarifying agents, corrosion inhibitors, industrial process polymers, pH or scale control, settling flocculent logs, soil stabilizers, erosion control products, and stormwater and frac sand process water clarification products.

In recent years, however, there have been an increasing number of requests for review and approval of a different type of additive that is implemented using different methods than those discussed above and shown in Figure E1. These "filter" or "pass-through" additives are used primarily for nutrient removal, and typically contain a filter material enclosed in a sock, porous bag, barrel, etc. through which water is passed before ultimately reaching a surface water (Fig. E2).

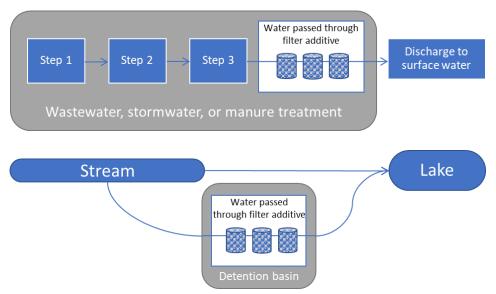


Figure E2. General schematics showing the two most common ways that filter or pass-through additives are employed for nutrient reduction purposes.

Filter or pass-through additives are marketed as inert and insoluble. Because they are typically contained, they are different from the "typical" wastewater or water treatment additives shown in Fig. E1 in that they are expected to remain in the enclosed sock, bag, or barrel and not reach a surface water. Nonetheless, it is possible that some of the product or its constituents may leach out during the filtering process and may cause harm to aquatic life.

Thus, Department staff need to formulate a consistent evaluation process for these additives and methods for assessing potential risks to aquatic life. This appendix will lay out the process for reviewing filter or pass-through additive products or systems.

2. Department Authority

This guidance supports the authority of s. 283.31(3)(d)1. and ss. 102.04(1)(d), Wis. Stats., and s. NR 102.04(d), 105.02(3), 105.05, 106.05(1)(b), 106.07(7), 106.08, and 106.10, Wis. Adm. Code, to protect Wisconsin's surface water resources from pollutants.

3. Review Process

Review of a filter or pass-through additive typically begins with a request for its use from an outside applicant to Department staff. From there, staff will consult the Previously Reviewed Additives spreadsheet to determine whether that product has already been reviewed and whether secondary values have been calculated.

If secondary values have not been calculated, staff will reach out to the applicant to obtain toxicity information for the product and/or its leachate. Typically, if toxicity data is not initially provided, that means the product has not been tested. If the applicant would like to pursue use of the filter or pass-through additive they should work with staff and a Department toxicologist to set up a toxicity test in-house, or contract with an outside laboratory to conduct a test. Requirements for the set-up of these tests can be found in Section 4 of this appendix. Upon receipt of the toxicity data, a toxicologist will review the data and calculate secondary values for the product and/or its leachate.

Once secondary values have been calculated, staff will use those secondary values to determine potential risks to aquatic life at the applicant's proposed dosage rate and/or use configuration and a permitting decision will be made. Staff may consult with a toxicologist and other water resources personnel to make this decision. Based on outcome of the evaluation, the Department may allow use of the product as requested without restrictions, or staff may request that the applicant conduct additional water chemistry monitoring, or use of the product may be restricted to a particular waterbody or configuration as in the case of a pilot test.

A diagram of the review process can be found on the next page in Figure E3.

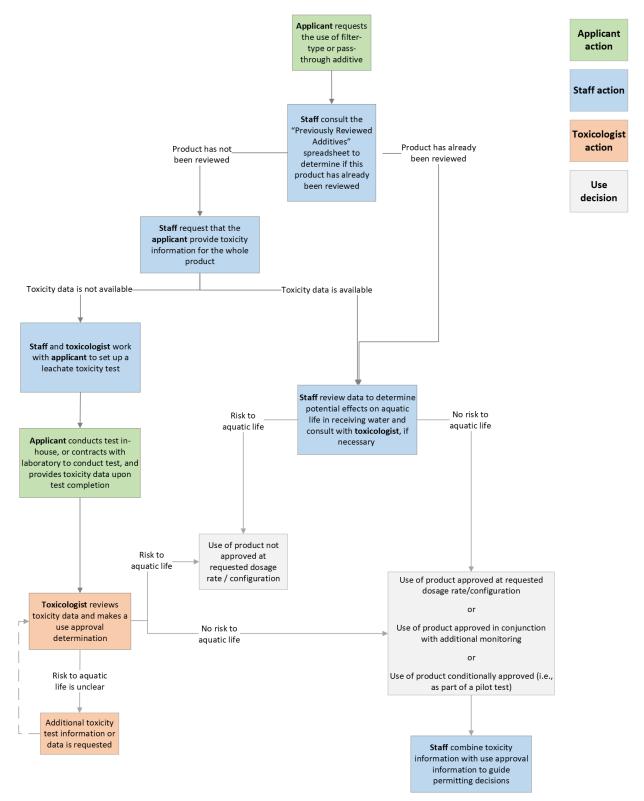


Figure E3. Flow chart illustrating the steps in the review process for filter or pass-through additive products/systems. Colors indicate who is primarily responsible for each step.

4. Conducting toxicity tests with leachate

- "Leachate" refers to water that was passed or filtered through the additive product.
- It is recommended, but not required, that toxicity tests are conducted using leachate from water passed through a higher concentration of filter material than what is expected to be in the sock/bag/barrel during use in the field.
 - For example, if the planned concentration of the filter material within the sock/bag/ barrel is 500g/m³, the Department recommends creating leachate by passing water through a higher concentration, such as 750g/m³
 - Testing leachate from water that was passed through a higher concentration of filter material ensures a margin of safety in case the project ultimately uses a higher concentration.
- Tests conducted on leachate from water that has passed through the <u>whole system</u> (product plus containment vessel) is needed in order to evaluate the potential for toxicity. Tests conducted with active ingredients only are not sufficient.
- At a minimum, the Department must receive data from an acute test conducted with a water flea (i.e., *Ceriodaphnia* or *Daphnia*) species, as per s. NR 105.05(4), Wis. Adm. Code. The <u>Additive</u> Review Worksheet lists additional species that may be tested in addition to water flea species.
- The test should be done using the standard protocols of a Whole Effluent Toxicity (WET) test with the following recommended test setup:
 - o Dilution series: 100%, 50%, 25%, 12.5%, 6.25%, 0% (control)
 - o Endpoints: LC₅₀ or EC₅₀ (acute), NOAEL and LOAEL (chronic)
 - o Number of replicates per dose: ≥ 4
 - Number of individuals per replicate: ≥ 5
 - o Temperature: 20 or 25°C
 - Control types: receiving water and laboratory water
 - Control survival: ≥ 90% (acute tests) or ≥ 80% (chronic tests)
 - More details regarding test conditions, results acceptability, and data analysis can be found in:
 - State of Wisconsin Aquatic Life Toxicity Testing Methods Manual
 - <u>EPA-821-R-02-012</u> (acute tests)
 - EPA-821-R-02-013 (chronic tests)