July 2023

Chemical Additive Review Guidance







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This report is available in alternative formats upon request, and online at <u>www.pca.state.mn.us</u>.

Document number: wq-wwprm2-12

Acronyms

ACR	Acute-Chronic Ratio
ADWDF	Average Dry Weather Design Flow
CFS	Cubic Feet Per Second
EC50	Half Maximal Effective Concentration
EPA	Environmental Protection Agency
FAV	Final Acute Value
HBV	Health Based Value
HRL	Health Risk Limit
LC50	Lethal Concentration 50
MCL	Maximum Contaminant Level
MDF	Maximum Design Flow
MGD	Million Gallons Per Day
MPCA	Minnesota Pollution Control Agency
MSD	Material Safety Data
NPDES	National Pollutant Discharge Elimination System
SDS	State Discharge System
WET	Whole Effluent Toxicity
WWTPS	Waste Water Treatment Plants

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Introduction

Environmental Protection Agency (EPA), National Pollutant Discharge Elimination System (NPDES), and Minnesota State Discharge System (SDS) Permits require that you receive The Minnesota Pollution Control Agency's (MPCA) approval prior to use of any chemical additives to treat your discharges which are received by surface waters or groundwater. Many of these additives, and their residues, can find their way into the environment, especially in your facility wastewater discharge. An important part of effective water management is ensuring that chemical additives do not harm Minnesota's water resources. This is why the MPCA oversees chemical additive use.

This document explains the MPCA additive review process and guides you through the spreadsheet calculator that can be used to determine if an additive can be approved with respect to aquatic toxicity. The spreadsheet calculator contains the logic and equations outlined in this document. This document contains a flow chart of the additive review process that is necessary to understand the logic of the additive review process. The numbers in the flow chart correspond to the header numbers in this document. Sub header numbers of present definitions or explanations relevant to the spreadsheet calculator.

This is the general review process for chemical additives being discharged to the land:

- 1. The MPCA staff will complete the review of additives for land application
- 2. There will be information the permittee and the additive company will have to provide the MPCA. See the quick review checklist, sections 5.0 and 6.0 for more information.

This is the general review process for chemical additives discharged to surface water:

- 1. Calculate the projected effluent concentration of the additive.
- 2. Calculate the applicable aquatic toxicity-based limit(s) for the additive.
- 3. Determine if a chronic limit or acute limit is required.
- 4. Determine if the projected effluent concentration is below the applicable aquatic toxicity-based limit.
- 5. If the additive can be approved at the requested dose, email relevant information regarding the additive to the MPCA for approval.
- 6. MPCA reviews the additive submitted for aquatic toxicity and if need be, other potential considerations.
- 7. Receive approval for the additive from the MPCA.
- 8. Start using the additive at the approved dosage.

The Excel spreadsheet calculator associated with this document requires you to enter information into three 'forms' using either Button A, Button B or Button C and will perform steps one through four for you. By entering all of the required information into buttons A, B or C you should be able to know whether your additive will be approved for use with respect to aquatic toxicity before receiving full approval from the MPCA.

Spreadsheet Buttons:

- Button A Permit Information
- Button B Calculate Projected Effluent Concentration
- Button C Calculate Aquatic Toxicity Concentration

This guidance is created only for additives discharged in wastewater. It is not intended for sediments or sludge toxicity evaluation.

Quick additive review checklist

Required information

Permit related

- Permit Number
- Discharge Station
- Discharge Class (Municipal or Industrial)

Water flows

- Outfall Effluent Design Flows (MGD)
- Effluent Flow Type (Continuous vs Intermittent)
- Receiving Water 7Q10 Flow Rate (CFS)
- Receiving Water Classification (1, 2 or 7)

Additive dosing

- Additive Name
- Additive Dosing (Continuous vs Intermittent)
- Dosing Units (lb/day or gal/day)
- Max Dose Added over 24 hours
- Additive Density (if dosed in lb/day)
- Additive Removal Percentage

Additive toxicity

- Additive MSDS
- A Daphniidae Tox 48 hr LC/EC50 Concentration
- A Freshwater Fish Tox 96 hr LC/EC50 Concentration
- Additional Applicable Reference Toxicity
 Species
- Additional Reference Toxicity Species LC/EC50 Concentrations

Attachments

- MSDS
- Relevant Dosing Calculations (If needed)
- Relevant Degradation Rate Information (If needed)

MPCA contacts

General email Additives.pca@state.mn.us

Things to know

- 1. If you have questions/concerns please contact us. We are here to help.
- All of the information in the Checklist to the left is required to calculate the toxicity for your additive and complete the form.
- An in-depth explanation of the approval logic and definitions of terms in the checklist is available in the 'Additive Review Process Reference' document available on the MPCA website.
- Call us if you have proprietary or confidential information about your additive that you would like kept that way. We have ways to ensure that confidential information is kept confidential.
- 5. A separate excel spreadsheet is required for each additive discharged from each surface water discharge station for your facility. We acknowledge this is cumbersome if you use many additives, but because of programming limitations this is the best we can do at this time.
- The excel form is only intended to calculate the aquatic toxicity for your whole additive. It does not preclude the MPCA acknowledging nutrient loading, carcinogenicity, bioaccumulation or other considerations when approving your additive use.
- The excel spreadsheet is also not meant for land application uses. See the land application section below for submittal requirements.
- We are willing to work with chemical vendors directly if the permittee acknowledges the vendor as their designated additive representative. Email us if you would like your vendor to work directly with the MPCA.

- If you are using your additive for a trial period, please email us and we can accommodate your trial additive use for up to <u>seven days</u> without using this formal approval process.
- 10. If you do not know your 7Q₁₀ flow rate, give us a call. If you are a larger facility, and have a fact sheet in your NPDES

permit documents, the $7Q_{10}$ should be available there.

Submit to the MPCA

Email your completed spreadsheet along with the appropriate electronic attachments including: supplemental information or material safety data (MSDS) to the MPCA contacts listed.



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Whole Effluent Toxicity testing

Whole Effluent Toxicity (WET) testing measures the effects of exposure of reference organisms to wastewater. WET testing measures the toxicity of a wastewater without needing to identify any specific pollutant.

A permittee always has the option to request WET testing in lieu of calculating the estimated toxicity limits for that additive.

If the permittee makes the choice to perform WET testing in lieu of calculating a toxicity limit they should be aware of the things below:

Chronic WET testing will be required and chronic toxic limits will need to be calculated.

Failing a WET test will force the following to occur:

- 1. Two repeat WET tests will be required within 45 days.
- 2. If repeat WET test fails, then the permittee will perform a Toxicity Reduction Evaluation. Toxicity Reduction Evaluations are notorious for producing delay and permitting headache.

WET testing is not cheap.

Assurance of appropriate water sampling for WET testing will be required.

Trial use for an additive

If you are intending to use an additive for a trial period of less than seven days, the additive does not need to be approved by the MPCA with respect to aquatic toxicity.

You still need to inform the MPCA that you will be using an additive for a trial period to test its effective in your treatment process. Email the MPCA with additive information including name and wastewater process to be tested in at <u>Additives.pca@state.mn.us</u>.

If you wish to use the additives outside the seven-day trial period, then you must receive formal approval for your additive from the MPCA.

Banned additives

Below are some additives that MPCA will not allow.

Nonylphenol ethoxylates:

CAS no. 9016-45-9 Poly (oxy-1,2-ethanediyl, alpha-(nonylphenyl)-omega-hydroxy-CAS no. 26027-38-3 Poly (oxy-1,2-ethanediyl, alpha-(4-nonylphenyl)-omega-hydroxy-CAS no.37205-87-1 Poly (oxy-1,2-ethanediyl, alpha-(isononylphenyl)-omega-hydroxy-CAS no. 68412-54-4 Poly (oxy-1,2-ethanediyl, alpha-(nonylphenyl)-omega-hydroxy-, branched CAS no. 127087-87-0 Poly (oxy-1,2-ethanediyl, alpha-(4-nonylphenyl)-omega-hydroxy-, branched Nonylphenol:

CAS no. 25154-52-3 Phenol, nonyl- (assumes linear alkyl, not viewed as descriptive of commercial NP) CAS no. 104-40-5 Phenol, 4-nonyl- (assumes linear alkyl, not viewed as descriptive of commercial NP) CAS no. 84852-15-3 Phenol, 4-nonyl-, branched.

The MPCA reserves the ability to ban additives containing certain ingredients in the future.

1.0 Is the additive a chemical that does not require review?

The additives listed below do not require you to do an additive review. If you think your additive should not require a review and should be added to this list, please contact the MPCA staff and we will discuss it with you.

NOTE: You are still required to notify the MPCA that you are using the chemicals below and their dosing rate; these chemicals just do not need to be officially approved using the spreadsheet calculator. A certificate of analysis for some chemicals that likely have a high mercury concentration will be required. You will need to contact the MPCA and provide your contact information, your permit number, the outfall number, a pdf of the MSDS sheets and the max rate of use per day (gal/day or lbs/day).

When using the chemicals listed below, be aware that they can be produced using the mercury amalgam cell process that can add substantial amounts of mercury to the final product. Check your certificate of analysis for the chemical to ensure minimal mercury loading from the chemicals you use. Reducing mercury loading from your chemical use can reduce your likelihood of having a mercury exceedance in your effluent.

- Sodium hydroxide (CAS 1310-73-2)
- Sulfuric acid (CAS 7664-93-9)
- Potassium hydroxide (CAS 130-58-3)
- Hydrochloric acid (CAS 7647-01-0)
- Ferric chloride (CAS 7705-08-0 or 10025-77-1)
- Sodium hypochlorite (CAS 7681-52-9)

Common acids

These acids can be added in any concentration as long as the pH requirements, salty discharge and CBOD₅ permit limits are met. Mixtures of these chemicals with each other are pre-approved but mixtures with any other chemical are not.

- Sodium hydroxide (CAS 1310-73-2)
- Calcium hydroxide (CAS 1305-62-0)
- Calcium oxide (CAS 1305-78-8)
- Sodium carbonate (CAS 497-19-8 or 5968-11-6 or 6132-02-1)
- Sodium bicarbonate (CAS 144-55-8)
- Potassium hydroxide (CAS 130-58-3)

Common disinfectants and de-chlorinators

These disinfectants can be added in any concentration as long as the pH requirements, salty discharge, dissolved oxygen and residual chlorine permit limits are met. If a facility does not have a residual oxidant limit, then these chemicals must be formally approved.

- Chlorine gas (CAS 7782-50-5)
- Sodium hypochlorite (CAS 7681-52-9)
- Calcium hypochlorite (CAS 7778-54-3)

- Sodium sulfite (CAS 7757-83-7)
- Sodium bisulfite (CAS 7757-83-7)
- Sodium metbisulfate (7681-57-4)
- Sodium thiosulfate (CAS 772-98-7 or 10102-17-7)

Common coagulants, flocculants, and filter aids

These coagulants and flocculants are pre-approved. Polymer based coagulants are approved using the traditional additive review process.

- Aluminum sulfate (CAS 10043-01-3 or 7784-31-8)
- Sodium aluminate(CAS 1302-42-7)
- Aluminum chloride (CAS 7446-70-0 or 10124-27-3 or 7784-13-6)
- Polyalumnium chloride
- Polyaluminum sulfate
- Ferric chloride (CAS 7705-08-0 or 10025-77-1)
- Ferric sulfate (CAS 10028-22-5 or 15244-10-7)
- Ferrous chloride (CAS 7758-94-3 or 16399-77-2 or 13478-10-9)
- Clay compounds (Bentonite, Kaolinite, and Diatomaceous Earth, etc.)

Herbicides for stabilization ponds

The specific additives below are approved for use as herbicides in stabilization ponds as a way to control vegetation growth. Any herbicide used to control aquatic vegetation must be labeled for aquatic use, and registered for use in Minnesota by the Minnesota Department of Agriculture and used according to the suppliers' instructions. Copper compounds can be used but monitoring for copper is required in the discharge.

- Potassium Permanganate (CAS 7722-64-7)
- Sodium Percarbonate (CAS 15630-89-4)
- Aqua Shade
- Alum
- Hydrothol 191

Approved ballast water management system (BWMS)

BWMS that are type-approved by the US Coast Guard (USCG) under 46 CFR subpart 162.060 and covered under the federal Vessel General Permit (VGP) are considered approved per the requirements of Minnesota's Ballast Water General Permit (MNG300000). This means that chemical additives used as a part of an approved BWMS do not require further approval by MPCA.

It must be noted that although the federal VGP allows for a discharge of 100 ug/L for Total Residual Oxidants (TROs), the MPCA permit requires the system meet the final acute value (FAV) of Total Residual Chlorine (TRC). This equates to a level of 38 ug/L per Minn. R. 7050.0220 Subp. 3a(6). The applicable TRC limits are based on the duration of the discharge. Below are the applicable limits/duration:

- 0.2 mg/L TRC limit for discharge duration of 2 hours or less
- 0.1 mg/L TRC limit for discharge duration between 2 and 6 hours
- 0.038 mg/L TRC limit for discharge duration greater than 6 hours

This is guidance and not a binding rule. The MPCA may require further evaluation on a case-by-case basis.

2.0 Use the calculator tool.

Enter permit information

Begin by clicking on Button A and enter the permit information for your NPDES permit and outfall location. Press the save button to ensure your information is saved. You can click on any button with a '?' to get a more detailed explanation of a field.

Notes:

- 1. You must have macros enabled for the form to work.
- 2. Button A will save all the required information upon clicking on the 'Save' button. The data you entered will be visible in the Button A summary section of the 'Additive Info' tab.

This screenshot shows the form associated with Button A. Enter the required information in Button A in the text boxes. Once you click save, the data will be stored and will be visible in the Button A summary section in the 'Additive Info' tab.



3.0 Calculate the projected effluent concentration (End of pipe concentration).

The calculated projected effluent concentration is calculated using Button B. Enter the information in

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the form that appears after clicking on Button B and click Calculate/Save. You can click on any of the "?" buttons and get an explanation of what that field means.

3.1 Definitions

Projected effluent concentration – The maximum likely concentration of your additive in the effluent of the facility. This is the end of pipe concentration.

Average Dry Weather Design Flow (ADWDF) – This design flow applies only to municipal facilities. If your facility does not have a ADWDF then the Wet Weather Design Flow should be used.

Maximum Design Flow (MDF) - This design flow applies only to industrial facilities.

Continuous flow – A year-round discharge (municipal wastewater treatment plants (WWTPs)); flows that occur without interruption throughout operating hours of the facility (industrial WWTPs).

Intermittent addition – Any flow rate that is not continuous.

Dosing units – The units used to define the amount of additive added to the treatment system. If the dose is defined in other than gal/day or lbs/day, the dose must be converted to either of those units.

Max dose added per day – The maximum amount of additive dosed over any 24-hour period.

Density – The ratio between the mass of additive and the volume that that mass occupies. Density is expressed in the spreadsheet calculator in grams per cubic centimeter.

Specific gravity – The ratio of the density of the additive to the density of water.

Cooling tower cycles – The number of times the water in the cooling tower is recirculated before discharge.

Removal Rate: What percentage of the additive is removed from the effluent or destroyed in the WWTP? This information may require assistance form the Additive representative or the additive company.

3.2 Explanation/additional information

This section shows how to use the spreadsheet calculator to calculate the projected effluent concentration and outlines the equations involved.

Click on Button B to enter the required information.

You are not required to use the spreadsheet calculator to calculate a projected effluent concentration; but if you do not use the calculator, you must provide the MPCA with your calculations for review.

3.2.1 Self-calculation of projected effluent concentration

If you have calculated the projected effluent concentration, enter that concentration into the form by clicking the uppermost button in Button B. You need to provide the MPCA with details of the calculation as an email attachment. We will review your calculations once you have submitted them to the MPCA.

If you have not calculated the projected effluent concentration, the calculator will do it for you, provided you enter the correct information into Button B.

32.2 Calculation of projected effluent concentration

Step 1. Determine if the additive is removed/consumed before discharge by any method, e.g. hydrolysis, adsorption, biodegradation, etc. If the additive is removed, check the 'Is the additive removed before discharge' checkbox. Consult with the additive company about removal rates.

Step 2. Enter the flow rate for the facility. If it is a municipal facility, enter the ADWDF in million gallons per day (MGD). If it is an industrial facility, enter the MDF in MGD.

Step 3. Select the dosing units of either gal/day or lbs/day.

Step 4. Enter the dosage rate of the additive.

Step 5. Enter the density of the additive.

Step 6. If the additive is removed before discharge, then enter the additive overall removal percentage.

Step 7. Press the save/calculate button to see the projected effluent concentration of the additive.

Equations used to calculate the projected effluent concentration. In the first equation, the dosage is in gal/day in the second equation the dosage is in lbs/day:

$$Projected \ Effluent \ Concentration \ (\frac{mg}{L}) = \frac{(1 - \% Removal) * Dosage \ \left(\frac{gal}{day}\right) * Density \ (\frac{g}{cc})}{ADWDF \ or \ MDF \ (MGD)}$$

Projected Effluent Concentration
$$(\frac{mg}{L})$$

= $\frac{(1 - \% Removal) * Dosage(\frac{lb}{day}) * 453592(\frac{mg}{lb})}{ADWDF \text{ or } MDF(MGD) * 3.78(\frac{l}{gal})}$

4.0 Is the discharge to Class 1 water?

4.1 Definitions

Class 1 Water – A drinking water source classification. A surface water that has water quality standards to protect the water for human domestic consumption.

4.2 Explanation/additional information

If your downstream receiving water is a Class 1 classification then your receiving water must comply with protections for drinking water with respect to additives. If your receiving water is a drinking water source water then chronic criteria with respect to additives apply.

The classification of your receiving water can be found in your permitting documents.

A useful, searchable GIS based map of the receiving waters in Minnesota can be found at the link below. Be sure to double check Minn. 7050.0470 because this map/visualizer is not the official classifier of Minnesota water bodies. <u>http://pca-gis02.pca.state.mn.us/eda_surfacewater/</u>.

5.0 How is the additive dosed?

5.1 Definitions

Continuous addition – An additive that is dosed without ceasing during the periods when the facility is treating water

Intermittent addition – An additive that is not dosed without ceasing during the periods when the facility is treating water

5.2 Explanation

You must determine how your additive is dosed and classify the dosing method as either 'continuous' or 'intermittent'. If your additive is dosed continuously then chronic criteria for your additive apply.

Use the drop-down box in Button C to classify the dosing method of your additive. Fill in the text box with text explaining how your additive is dosed (duration and frequency of dosing) if you dose intermittently.

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24 Scott.Kyser@state.mn. 25	<u>us</u> 651.757.2665								
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6.0 What is the stream dilution ratio?

6.1 Definitions

Stream Dilution Ratios – The ratio between the receiving water $7Q_{10}$ flow rate and the WWTP effluent flow rate.

7Q₁₀ – The annual lowest 7-day average flow rate in a stream that occurs on average once every 10 years. The $7Q_{10}$ flow rate for your facility is located on the fact sheet in your NPDES permitting documents. If you do not have a fact sheet call us, and we can quickly provide you with the annual $7Q_{10}$ flow rate for your facility.

WWTP Effluent Flow Rate – For the purposes of calculating stream dilution ratios, the effluent flow rate is defined as the ADWDF for municipal WWTPs and the MDF for industrial WWTP.

6.2 Explanation/additional information

The stream dilution ratio is used to determine if chronic limits are applicable. If the stream dilution ratio is less than 20:1 then a chronic limit is necessary. If the stream dilution ratio is greater than 20:1 then a chronic limit is not necessary.

The 20:1 dilution ratio is used when setting ammonia limits as a threshold below which effluent from a WWTP can have disproportionate effects on the receiving waterbody. We believe that the 20:1 ratio is an effective threshold for setting chronic limits and is protective of receiving waterbody designated uses.

Enter the stream dilution ratio in Button C by clicking on the 'Calculate Effluent Flow Rate to Receiving Water Flow Rate Dilution Ratio' button. Enter the information and it will automatically calculate the stream dilution ratio.

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17 explained in the referen	ce document.		lf it	says 'NO' then g	o back to Button B and	re-		
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36 Permit Number	123	Discharge Type	Continuous	Dosage Type		ontinuous		
37 Facility Type	Municipal	Dosing Units	gal/day	Stream Dilution Ratio	,	32.3206206		
38 Discharge Station	5/2/1900	Dose Per Day	1	Number of Reference	Species	2		
39 Contact First Name	123	Specific Gravity	1	Minimum LC/EC50 of	Reference Species	2	Close Save/Calculate Toxic	ty Standard
40 Contact Last name	123	Overall Removal Rate (%)	99.0	Final Acute Value (m	<u>e/L)</u>	0.154		
41 Contact Email	123	Projected Effluent Concentration (mg/L)	0.01	Chronic Standard (m	g/L ; Dilution Adjusted)	0.285		
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7.0 Calculated Chronic Limit is applicable

7.1 Definitions

Half Maximal Effective Concentration (EC50) – The toxicant concentration of the whole additive that causes equilibrium loss, immobilization, mortality or other debilitating effects in 50% of the exposed organisms during a specific time of observation. Interchangeably used with LC50.

Final Acute Value (FAV) – A toxic concentration that can never be exceeded in the effluent discharge. The FAV is independent of available stream dilution and is applicable regardless of whether a chronic water quality standard is also applicable.

Lethal Concentration 50 (LC50) – The concentration of the additive killing 50% of the exposed organisms in a specific time of observation. Interchangeably used with EC50. This concentration must be for the whole additive, not a specific individual ingredient.

Daphniidae – Species in the 'water flea' family. Species in this family are required reference species in aquatic toxicology testing when calculating the FAV. A minimum of a 48-hour long test must be used to determine a LC50 or EC50. Operationally, we define 'Daphniidae' as the species below. If you would like to use a species other than the ones in the list, please contact us for approval.

- Daphnia Pulex
- Daphnia magna
- Ceriodaphnia dubia
- Simocephalus

Freshwater Fish – Any animal that looks like a fish, has been widely used in aquatic toxicity literature, and does not just live in seawater. A minimum of a 96-hour long test must be used to determine a LC50 or EC50 concentration. Operationally, we define 'freshwater fish' as the species below. If you would like to use a species other than one of these, please contact us for approval.

- Fathead minnow (Pimephales promelas)
- Bluegill (Lepomis macrochirus)
- Zebra fish (Danio rerio)
- Rainbow trout (Oncorynchus mykiss)
- Mosquito fish (Gambusia affinis)
- Channel catfish (Ictalurus punctatus)
- Atlantic salmon (Salmo salar)
- Smallmouth bass (Micropterus dolomieui)
- Brook trout (Salvelinus fontinalis)
- Chinook salmon (Oncorhynchus tshawytscha)
- Rio Grande minnow (Hybognathus amarus)
- Green sunfish (Lepomis cyanellus)
- Orfe (Leuciscus idus)

Freshwater aquatic insects – Any animal that looks like an insect and does not just live in seawater. We do not have a defined list of 'freshwater aquatic insects' reference species, it is best to use your judgment and call us if you have any questions as to what species are applicable.

Freshwater crustaceans – Any animal that looks like a crustacean and does not just live in seawater. We do not have a defined list of 'freshwater crustacean' reference species, it is best to use your judgment and call us if you have any questions as to what species are applicable.

Algae – Any 'Algae' species can be used for aquatic toxicity, call us if you have any questions as to what species are applicable.

Chronic criterion – The highest concentration of a toxicant to which the test organisms can be exposed indefinitely without causing chronic toxicity.

Acute-Chronic Ratio (ACR) – The ratio of the additive acute toxicity expressed as LC50 or EC50 to the additive chronic toxicity. The ACR is used as a factor for estimating chronic toxicity on the basis of acute toxicity.

7Q₁₀ – The lowest seven-day average flow rate in a stream that occurs on average once every ten years

WWTP Effluent Flow Rate – For the purposes of calculating stream dilution ratios, the effluent flow rate is defined as the ADWDF for municipal WWTPs and the ADF for industrial WWTPs.

7.2 Explanation/additional information

Chronic limits for your additive are applicable if you meet the criteria below:

- 1. You discharge to or above a class 1 stream.
- 2. You dose your additive continuously.
- 3. The stream to effluent dilution ratio is less than 20:1.

Button C in your calculator will calculate the chronic limit for your additive. Button C will also determine whether a chronic limit for your additive is necessary.

Begin by entering the required information in the form for Button C. All of the labels are clickable; if you click one, it should either provide you with more information or perform a calculation for you.

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1 Bogin By Bogding This	Importanti	
Begin by Reduing This:	<u>important:</u>	Number of Species
In order to have your additive approved you must do the following, inorder: Button A. Click the 'Enter General Permit Info [®] button and fill in the general permit information.	Make sure that the 'Potentially Approvable' cell below says 'YES' before submission to the MPCA.	Species Used for LCS9/EC50 Reference Toxioty Test Concentration mg/L
Button B. Click the 'Calculate Projected Effluent Concentration' button and generate a projected effluent concentration.	If it says 'YES' then the additive does not pose	Daphnidae Tequired Species 2
11 Button C. Click the 'Calculate Aquatic Toxicity Concentration' button and generate an aquatic 13 toxicity reference concentration.	toxic threats to the environment at its current dose. You can now send a copy of this	Predwater Figh Zebra Figh (Danio renio)
A checklist of required information to fill out this form can be found left of this window.	calculator to the MPCA for final approval.	
A process from chart is available below this window; All of the boxes in the flow chart are explained in the reference document. Macros MUST be enabled for this worksheet to function!!!! MrCA Contact	If it says 'NO' then go back to Button B and re- calculate a dosage for your additive that would be less than the toxic dosage calculated in Button C. Do not formally send anything to the	
22 Scott Kyser 24 Scott Kyser@state.mn.us 651.757.2665	approved.	
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37 Facility Type Municipal Dosing Units gal/	day Stream Dilution Ratio 32.3206206	
38 Discharge Station 5/2/1900 Dose Per Day 1	Number of Reference Species 2	Close Save/Calculate Toxicity Standard
23 Specific Gravity 1 Contact First Name 123 Overall Removal Rate (%) 99	Minimum LL/ELSU of Reference Species 2	
41 Contact Email 123 Projected Effluent Concentration (mg/L) 0.0	01 Chronic Standard (mg/L; Dilution Adjusted) 0.285	
42 Contact Phone Number 123	Chronic Standard Applicable (Yes/No) Yes	
43 Date of Submittal 8/1/2014	Potentially Approvable at Current Dose (Yes/No) Yes	
Additive Review Pro Additive Info Additive Info	cess Chart	
		S 🗞 N S 🕫 🖶 0 1045 AM

Click the 'Save/Calculate' button to see if Chronic Limits are applicable to your additive and what the concentration limit you must comply with is.

7.3 Chronic limit calculation

This section explains the logic behind how the chronic limit is calculated. Button C performs all of these calculations for you using the logic described below.

7.3.1 Calculate the FAV

Step 1. Obtain the additive 48-hour LC50 or 48- hour EC50 concentration for the Daphniidae species. This information is usually in the MSD sheet that the additive manufacturer provides. You must have the additive LC50 or EC50 for a 'Daphniidae' species because it is required to calculate the additive FAV.

Step 2. Obtain the additive LC50 or EC50 concentration for the Freshwater fish species. This information is usually in the MSD sheet that the additive manufacturer provides. You must have the additive LC50 or EC50 for a Freshwater fish species because it is also required to calculate the additive FAV. All tests have to be either 48-hour duration or 96-hour duration.

Step 3. Determine the number of other reference species for which a 48-hour or a 96-hour LC50 or a 48-hour or a 96-hour EC50 concentration is available. You can use up to seven total species. The species types listed below can be used:

- Freshwater aquatic insects
- Freshwater crustaceans
- Freshwater fish (That hasn't already been used)
- Daphniidae (That hasn't already been used)

Step 4. Determine the lowest LC50 (EC50) out of all the acceptable reference species.

Step 5. Divide the lowest LC50 by the safety factor in the table below. The safety factor is a function of the number of the available LC50 (EC50) for the reference species. If you have more than seven reference species please contact us; it is extremely uncommon to have more than seven reference species that have available LC50s for an additive. (Consult Minn. R. 7050.0218 and contact the MPCA for additional information if you have more than seven reference species).

Number of Species	Safety Factor
2	13
3	8
4	7
5	6.1
6	5.2
7	4.3

$$FAV\left(\frac{mg}{L}\right)$$

Lowest LC50 From All Available, Acceptable Reference Species for your additive $\left(\frac{mg}{L}\right)$

Safety Factor

7.3.2 Calculate the chronic criterion

A default ACR value of 18 is used based on Minn. R. 7050.0218 Subp. 5 G.(10). If you have data that suggests that the ACR is different than 18, please read the statutes that specify how to calculate a ACR (Minn. R. 7050.0218 Subp. 5 A,F1) and contact MPCA staff.

Chronic Criterion
$$\left(\frac{mg}{L}\right) = \frac{FAV(\frac{mg}{L})}{ACR}$$

7.3.3 Adjust chronic criterion for stream dilution ratios to calculate final limit

We use a mass balance equation to determine the allowable concentration on of the additive in the effluent based on available stream dilution. The limit calculated in this section is the limit that your facility must comply with if chronic standards are applicable.

We make the following assumptions:

- 1. The receiving water concentration of the additive is 0 mg/L.
- 2. There is instantaneous and complete mixing of the effluent with the receiving water at the point of discharge.
- 3. The receiving water flow rate is at the $7Q_{10}$ flow rate.

$$C_{Limit} = \frac{(Q_{WWTP} + Q_{7Q10}) * C_{CC}}{Q_{WWTP}}$$

C_{limit} = The maximum allowable concentration in the WWTP discharge in mg/L that cannot be exceeded on a chronic basis. If a chronic limit is necessary for the additive

 Q_{wwtp} = The effluent flow rate for the WWTP in MGD.

 Q_{7Q10} = The 7 Q_{10} flow rate of the receiving water in MGD.

 C_{cc} = The chronic criterion calculated in 10.2

The chronic limit is the value calculated in the formula above. This is the concentration you must dose your additive to meet in the effluent of wastewater.

8.0 Only calculated Final Acute Value is applicable

8.1 Definitions

Effective Concentration (EC50) – The toxicant concentration of the whole additive that causes equilibrium loss, immobilization, mortality or other debilitating effects in 50% of the exposed organisms during a specific time of observation. Interchangeably used with LC50.

Final Acute Value (FAV) – A toxic concentration that can never be exceeded in the effluent discharge. The FAV is independent of available stream dilution and is applicable regardless of whether a chronic water quality standard is also applicable.

Lethal Concentration 50 (LC50) - The concentration of the additive killing 50% of the exposed organisms in a specific time of observation. Interchangeably used with EC50.

Daphniidae - Species in the 'water flea' family. Species in this family are required reference species in aquatic toxicology testing when calculating the FAV. A minimum of a 48-hour long test must be used to determine a LC50 or EC50. Operationally, we define 'Daphniidae' as the species below. If you would like to use a species other than the ones in the list, please contact us for approval.

- Daphnia Pulex
- Daphnia magna
- Ceriodaphnia dubia
- Simocephalus

Freshwater Fish- It is any animal that looks like a fish, has been widely used in aquatic toxicity literature and does not just live in seawater. A minimum of a 96-hour long test must be used to determine a LC50 or EC50 concentration. Operationally, we define 'freshwater fish' as the species below. If you would like to use a species other than one of these, please contact us for approval.

- Fathead minnow (Pimephales promelas)
- Bluegill (Lepomis macrochirus)
- Zebra fish (Danio rerio)
- Rainbow trout (Oncorynchus mykiss)
- Mosquito fish (Gambusia affinis)
- Channel catfish (Ictalurus punctatus)
- Atlantic salmon (Salmo salar)
- Smallmouth bass (Micropterus dolomieui)
- Brooktrout (Salvelinus fontinalis)
- Chinook salmon (Oncorhynchus tshawytscha)
- Rio Grande minnow (Hybognathus amarus)
- Green sunfish (Lepomis cyanellus)
- Orfe (Leuciscus idus)

Freshwater aquatic insects – Any animal that looks like an insect and does not just live in seawater. We do not have a defined list of 'freshwater aquatic insects' reference species, it's best to use your judgment and call us if you have any questions as to what species are applicable.

Freshwater crustaceans – Any animal that looks like a crustacean and does not just live in seawater. We do not have a defined list of 'freshwater crustacean' reference species, it is best to use your judgment and call us if you have any questions as to what species are applicable.

Algae – Any 'Algae' species can be used for aquatic toxicity, call us if you have any questions as to what species are applicable.

Chronic criterion – The highest concentration of a toxicant to which the test organisms can be exposed indefinitely without causing chronic toxicity.

Acute-Chronic Ratio (ACR) – The ratio of the additive acute toxicity expressed as LC50 or EC50 to the additive chronic toxicity. The ACR is used as a factor for estimating chronic toxicity on the basis of acute toxicity.

7Q10 – The lowest 7-day average flow rate in a stream that occurs on average once every 10 years

WWTP Effluent Flow Rate – For the purposes of calculating stream dilution ratios, the effluent flow rate is defined as the ADWDF for municipal WWTPs and the ADF for industrial WWTPs.

8.2 Explanation/additional information

Chronic limits for your additive are applicable if you meet the criteria below:

1. You discharge to or above a class 1 stream.

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1 A B C D		Receiving Water Flow Rate Dilution Ratio
Begin By Reading This:	Important!	Number of Species 2
In order to have your additive approved you must do the following, in order:	Make sure that the 'Potentially Approvable' cell	Control land for
6 Button A. Click the 'Enter General Permit Info' button and fill in the general permit	below says 'YES' before submission to the	Reference Toxidity Test Concentration mg/L
8 Information.	MPCA.	
Button B. Click the 'CalculateProjected Effluent Concentration' button and generate a projected effluent concentration.	If it says 'YES' then the additive does not pose	Daphnidae Daphna magna 🗸 2
12 Button C. Click the 'Calculate Aquatic Toxicity Concentration' button and generate an aquatic	toxic threats to the environment at its current	Frachwater Fieh Zebra Fish (Danio rerio)2
13 toxicity reference concentration.	dose. You can now send a copy of this	*Required Species
A checklist of required information to fill out this form can be found left of this window.		
A process flow chart is available below this window; All of the boxes in the flow chart are explained in the reference document.	If it says 'NO' then go back to Button B and re-	
18	calculate a dosage for your additive that would	
20 Macros MUST be enabled for this worksheet to function	be less than the toxic dosage calculated in Button C. Do not formally send anything to the	
21 MPCA Contact 22	MPCA for approval that you know will not be	
23 Scott Kyser	approved.	
25		
26		
28 Button A Button B	Button C	
30 Permit Info Effluent Concentration	ToxicityConcentraiton	
31		Notes for
33		MPCA Staff
34 Button A summary Button B summary 35 Permit Name 123 Flow (MGD)	1 Additive Brand Name 1234	FAV (mg/L) 0.15384615384 True Applicable Chronic 0.28479162868
36 Permit Number 123 Discharge Type Conti 27 Earlithe Tune Municipal Device Unit	nuous Dosage Type Continuous	Standard (mg/L)
37 Facility type Municipal Dosing Units gal 38 Discharge Station 5/2/1900 Dose Per Day	1 Number of Reference Species 2	
39 Contact First Name 123 Specific Gravity	1 Minimum LC/EC50 of Reference Species 2	Close Save/Calculate Toxicity Standard
40 Contact Last name 123 Overall Removal Rate (%) 99 41 Contact Empile 132 Projected Effluent Concentration (mg/l) 0	9.0 Final Acute Value (mg/L) 0.154 01 Observe Standard (mg/L) Dilution Adjusted) 0.255	
41 Contact Phone Number 123 Projected criticent concentration (mg/c) 0.	Chronic Standard (mg/L; Dilution Adjusted) 0.285 Chronic Standard Applicable (Yes/No) Yes	
43 Date of Submittal 8/1/2014	Potentially Approvable at Current Dose (Yes/No) Yes	
44 Notes sdfg		1
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2. You dose your additive continuously.

3. The stream to effluent dilution ratio is less than 20:1.

Button C in your calculator will calculate the chronic limit for your additive. Button C will also determine whether a chronic limit for your additive is necessary.

Begin by entering the required information in the form for Button C. All of the labels are clickable; if you click one, it should either provide you with more information or perform a calculation for you.

8.3 Final acute value calculation

Step 1. Obtain the additive LC50 or EC50 concentration for the Daphniidae species. This information is usually in the MSD sheet that the additive manufacturer provides. You must have the additive LC50 or EC50 for a 'Daphniidae' species because it is required to calculate the additive FAV.

Step 2. Obtain the additive LC50 or EC50 concentration for the Freshwater fish species. This information is usually in the MSD sheet that the additive manufacturer provides. You must have the additive LC50 or EC50 for a Freshwater fish species because it is also required to calculate the additive FAV.

Step 3. Determine the number of other reference species for which a 48 hour or 96-hour LC50 or EC50 concentration is available. You can use up to seven total species. The species types listed below can be used:

- Freshwater aquatic insects
- Freshwater crustaceans
- Freshwater fish (That hasn't already been used)
- Daphniidae (That hasn't already been used)

Step 4. Determine the lowest LC50 (EC50) out of all the acceptable reference species.

Step 5. Divide the lowest LC50 by the safety factor in the table below. The safety factor is a function of the number of the available LC50 (EC50) for the reference species. If you have more than seven reference species please contact us; it is extremely uncommon to have more than seven reference species that have available LC50s for an additive. (Consult Minn. R. 7050.0218 and contact the MPCA for additional information if you have more than seven reference species).

Number of species	Safety factor
2	13
3	8
4	7
5	6.1
6	5.2
7	4.3

 $FAV\left(\frac{mg}{L}\right)$

Lowest LC50 From All Available, Acceptable Reference Species for your additive $\left(\frac{mg}{L}\right)$

Safety Factor

9.0 Self-approval

You must self-approve your additive dosage rate before sending it to the MPCA. In order to self-approve your additive you must step through the flow chart steps and reach either of the self-approval boxes using the Excel spreadsheet calculator.

We want you to perform the required calculations and send the results of your calculations to us. Please do not send us a request for additive approval that you know we will disapprove.

Self-Approval is not final approval. You must email your completed spreadsheet along with the appropriate attachments to the MPCA for final approval. Only after final approval can you use your additive and only at the intended dose.

The cells highlighted in yellow and pointed to with the arrow below must say "YES" indicating that they are potentially approvable before you send your document to the MPCA. If the Value says "NO" then you must recalculate your dosing to comply with the limits generated in Button C.

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10 11	Button B. Click the 'Ca projected effluent con	culate Projected Eff centration.	luent Concentration' button and ge	enerate a	If it says	YES' then t	he additive	e does not p	oose	Water Flor o Outfall Ef	WS fluent Design Flows (N	AGD)		definitio the 'Ado available	ns of terms in ti litive Review Pro on the MPCA v	ne checklist i ocess Referen vebsite.	is available in nce' document		
12 13 14	Button C. Click the 'Cai toxicity reference cond	culate Aquatic Toxic entration.	city Concentration' button and gen	erate an aquatic	dose. Yo	u can now s	end a copy	y of this		o Effluent F o Receiving o Receiving	low Type (Continuous Water 7Q ₁₀ Flow Rate Water Classification (vs intermittent) e (CFS) 1, 2 or 7)	4	. Call us if informal like kept	you have propr tion about your that way. We h	ietary or cor additive that ave ways to	nfidential t you would ensure that		=
15 16 17 18	A checklist of required A process flow chart is explained in the refere	information to fill o available below thi nce document.	out this form can be found left of t s window; All of the boxes in the f	his window. Iow chart are	If it says	NO' then g	o back to B	Button B an	d re- would	Additive D o Additive N o Additive D o Dosing Ur	losing lame Dosing (Continuous vs hits (Ib/day or gal/day)	5	confidential information is kept confidential. 5. A separate excel spreadsheet is required for each additive discharged from each discharge station for your facility. We acknowledge this is						
19 20 21	Macros MUST k	e enabled for	r this worksheet to func	tion!!!!	be less th Button C	an the tox	ic dosage ca rmally send	alculated in d anything	to the	o Max Dox o Additive D o Additive F	Added per Day Density (if dosed in Ib/ Iemoval Percentage	6	because best we The exce						
22 23 24	Scott Kyser Scott.Kyser@state.mn	<u>us</u> 651.757.2665			MPCA for approval that you know will not be approved.					Additive T o Additive N o A Daphnia	<mark>oxicity</mark> ASDS dae Tox 48 hr LC/ECSC	Concentration		aquatic toxicity for your whole add&ive. It does not preclude the MPCA acknowledging nutrient loading, carcinogenicity, bio-accumulation or other corridering when accounting and the second					
25 26 27 28 29 30 31 32	Scott Liver Batter muss 651.757.2665 Betton A Entre General Permit Info Efficient Concentration Efficient Concentration					Button C Calculate Aquatic Toxicity Concentration					ater Fish Tox 96 hr LQ I Applicable Reference I Reference Toxicity Sj ations Its Dosing Calculations Degradation Rate Info	EC50 Concentration Toxicity Species pecies LC/EC50 rmation	7	We are directly as their us if you the MPC if you ar please ed trial add	willing to work v if the permittee designated addi 'd like your ven 'A. e using your add -mail us and we it ive use for up	vith chemica acknowledg tive represen dor to work o ditive for a tr can accomm to seven day	al vendors tes the vendor tes the vendor ntative. E-mail directly with rial period modate your ys without		
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37	Facility Type	Municipal	Dosing Units	gal	/day Stree	m Dilution Ratio			32.32062)6			E-mai	il your com	pleted form alo	ng with the a	appropriate		
38	Discharge Station	5/2/1900	Dose Per Day		1 Num	ber of Reference	Species		2	Scott Kyser@	state.mn.us 651.757.	2665	electr	onic attach	ments (MSDS,	alculations,	etc) to the		
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10.0 Send to MPCA for final approval

When you have determined that the additive concentration is below applicable toxicity reference values then send the form to the MPCA.

Be sure to double check the Button C summary and make sure that the 'Potentially Approvable at Current Dose' says Yes. Do not email a request for final approval until the 'Potentially Approvable at Current Dose' says Yes.

You cannot use your additive until the MPCA has officially approved your additive for use at your intended dose.

The MPCA is committed to giving 90% of permittees notification of approval or disapproval within 5 days, assuming all of the submitted information was correct and complete at time of submission to the MPCA.

You MUST email these materials along with your completed spreadsheet calculator:

Additives.PCA@state.mn.us

- 1. MSDS for your additive that includes the appropriate toxicity information outlined in this document. The checklist is a useful document to see what needs to be included with your email review.
- 2. Dosing Calculations (If needed).
- 3. Additive Degradation Rate/Percentage (If needed).
- 4. Dosing Frequency
- 5. Where is additive used in the process?

6. For discharges to surface water, the cells highlighted in yellow and pointed to with the arrow below must say "YES" indicating that they are potentially approvable before you send your document to the

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5 In order to have	e your addi	tive approved yo	ou must do the follow	ving, in order:		1	Make sure	that the 'P	otentially	Approval	ole' cell	Donmit	Delated		1	 If you have questions/concerns please contact us!!! We are here to he b!!! 					
6 Button A. Click	the 'Enter G	General Permit I	nfo' button and fill in	thegeneral p	ermit	- t	below says	'YES' befo	re submis	sion to th	e	o Permit	Number			 All of the required 	e information in t I to calculate the	toxicity for your a	additive		
/ information.						- 1	MPCA.					o Discha	rge Station			and com	plete the form.				
9 Button B. Click 10 projected efflu	the 'Calcula Jent concent	ate Projected Eff tration.	luent Concentration'	button and g	enerate a		lfit says 'Y	ES' then th	e additive	e does not	pose	o Discha Water F	rge Class (Municipal or lows I Effluent Design Flows	(MGD)	3	 An in-de definitio the 'Ado 	pth explanation of ns of terms in the litive Review Proc	of the approval lo e checklist is avail cess Reference' d	ogic and ilable in document		
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16 A process flow 17 explained in the	chart is ava	ilable below thi document.	s window; All of the	boxes in the	flow chart a	ire	If it says 'NO' then go back to Button B and re-						ve Name ve Dosing (Continuous	vs intermittent)	-	 A separate excel spreadsheet is required for each additive discharged from each discharge station for your facility. We acknowledge this is 					
18 19 Manaras M		underland for	ahia waskaha				calculate a dosage for your additive that would						; Units (lb/day or gal/di ox Added per Day	ay)		cumbers	some if you use m	it			
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24 Scott.Kyser@st	tate.mn.us	651.757.2665				- 6	approved.						/e MSDS poidee Tox 48 br I C/FC	50 Concentration		loading, carcinogenicity, bio-accumulation or other considerations when approving your additive use.					
25													hwater Fish Tox 96 hr L	C/EC50 Concentration							
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38 Discharge Sta	ation	5/2/1900	Dose	Per Day		1	Number	of Reference S	pecies		2	Scott Kyse	r@state.mn.us 651.75	7.2665	elect	ronic attach	ments (MSDS, ca	alculations, etc)	to the		
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MPCA. If the Value says "NO" then you must recalculate your dosing to comply with the limits generated in Button C.

11.0 MPCA final approval process

In order to 'Finally Approve' your additive, the MPCA will follow these procedures:

- 1. Double check info in the user-submitted additive form. (Screen for typos, transmittal errors, omissions, etc.).
- 2. Verify that the projected effluent concentration is below the applicable toxicity-based standard to ensure no toxicity in the receiving water body would be present when using the additive.
- 3. Use best professional judgment and applicable scientific literature to see if the additive requires additional review for other non-lethal or chronic effects.
- 4. Use the **Phosphorus Evaluation Flowchart** below to determine if the additive needs to be evaluated for phosphorus before final approval.
- 5. Once the additive has been determined to be safe for use at its intended dose, then the MPCA will send notice to the affected parties that the additive is approved and can be used in your treatment system.





Chemical additives discharged via land application

12.0 Land application checklist

- 1. Total discharge flow from the permittee per day.
- 2. MSDS sheet for each additive.
- 3. A complete list of all the ingredients associated with each additive and the percentage associated with each ingredient. The parent additive company will need to contact the MPCA staff directly, i.e. proprietary information.
- 4. A percentage estimate of how much each additive used up or destroyed in what it is intended to be used.

You MUST email these materials to:

Additives.PCA@state.mn.us

MPCA staff will complete the additive review process noted below.

12.1 Definitions

Rapid infiltration basins – Permeable earthen basins, designed and operated to treat and disperse municipal wastewater.

On-Site infiltration – A facility that infiltrates wastewater on-site and operates under the MNG49 permit.

Spray irrigation – A method of disposal of wastewater where the wastewater is applied to farm fields directly.

Land application of industrial by-products – Similar to spreading biosolids on a field; but instead of bioolids, industrial by-products are applied.

12.2 Explanation/additional information

If the effluent goes to a rapid infiltration basin, or is used to irrigate or is otherwise land applied or infiltrates using the MNG49 permit, then the facility is considered to be a 'land applier' and then drinking water standards apply (proceed to 6.0).

If the effluent is not land applied then you must determine if the effluent is discharged to Class 1 water (proceed to 7.0).

13.0 Does a drinking water standard exist?

13.1 Definitions

EPA – Environmental Protection Agency.

Maximum Contaminant Level (MCL) – Enforceable drinking water standard.

Health Based Value (HBV) – It is the concentration of a chemical (or a mixture of chemicals) that is likely to pose little or no risk to human health.

Health Risk Limits (HRL) – It is the concentration of a substance or chemical adopted by rule by The Commissioner of the Department of Health (MDH) that is a potential drinking water contaminant

because of a systemic or carcinogenic toxicological result from consumption (based on 2013 MDH statutes, 103H.005 subdivision 3).

Final Acute Value (FAV) – A toxic concentration that must never be exceeded in the effluent discharge. The FAV is independent of available stream dilution and is applicable regardless of whether a chronic water quality standard is also applicable.

13.2 Review Process when drinking water standards are applicable to additives

The MPCA staff will determine there are State or Federal drinking water standards associated to be an additive being land applied (see 5.0 above) or to an additive being discharged to a class 1 surface water (see 7.0 below). Section 6.3 is a brief explanation of the drinking water standard review process and is meant as a guide for MPCA staff.

13.3 Explanation/additional information

The list of EPA drinking water MCLs can be found in <u>http://water.epa.gov/drink/contaminants/#one</u>.

The list of the MDH, HRL, and HBV can be found in http://www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html.

Check the additive or additive active ingredients against the two lists above. If the projected effluent concentration of the additive is below the MCL, HRL, or HBV, the additive is approved at the proposed dose.

If you are at step 6.0 then you must use the lowest applicable MCL, HBV or HRL as the FAV. The projected effluent concentration calculated must be less than the FAV in order to preliminarily approve the additive.

14.0 MPCA final approval process (land applied chemical additives)

14.1. The MPCA will review the chemical additive and send the approval to the submitter via email.