

Biocide/Chemical Pretreatment Worksheet - Form PT101 (PT101.word) *Revised October 1997*

INTRODUCTION

Many users of biocides discharge their wastewater to a municipal wastewater treatment plant or Publicly Owned Treatment Works (POTW). The POTW treats the wastewater, then discharges it to a stream. A biocide is a substance which inhibits the growth of nuisance organisms (algae, bacteria, fungi, etc.). These chemical substances may be found in diverse applications ranging from active ingredients in deodorant soaps, to mouth wash, to antifouling additives in boat bottom paints. Biocides are frequently used in industrial cooling systems and air conditioning units to control biological growth (e.g. algae, fungi) which might impair cooling efficiency. They are also used in many manufacturing processes for purposes specific to the product end use.

The North Carolina Division of Water Quality Pretreatment Group oversees the POTW's Pretreatment Programs under which the POTW's regulate Users of their wastewater treatment plant. DWQ has developed this Biocide/Chemical Pretreatment Worksheet-Form PT101 to help POTW's evaluate biocide discharges. The purpose of the biocide review is to determine:

- the aquatic toxicity of a proposed biocide,
- its intended use,
- the allowable concentration of biocide in the POTW's receiving water body (regulated limitation) necessary to protect aquatic life in the receiving stream, and
- the predicted concentration of the biocide in the water body (discharge concentration).

This form is modeled after the Biocide/Chemical Treatment Worksheet-Form 101, completed by biocide users discharging directly into the surface waters of North Carolina.

The form is provided in two formats. PT101.word which follows the same format as Form 101 and is completed by hand. PT101.excel is a spreadsheet based form and can be completed either by hand or on a computer with Microsoft Excel 5.0. **The POTW name, average flow, receiving stream, and 7Q10 are supplied by the POTW (see Part I), with the remainder completed by the biocide user or their consultant.** This worksheet must be completed separately for each biocidal product in use. This worksheet is to be returned with all appropriate data entered into the designated areas with calculations performed as indicated.

PART I and II-BIOCIDES DATA AND CALCULATIONS

PART III. INHIBITION CRITERIA

PART IV and V. BIOCIDES TOXICITY DATA

PART VI. METALS

This PT101.word Form is distributed by Triangle Wastewater Treatment Plant and should be returned to the following address:

Name: Stephanie Brixey

Title: Compliance Manager

POTW: Triangle Wastewater Treatment Plant

Address: 5926 NC Hwy 55

City, State, Zip: Durham, NC 27713

Phone Number: 919-560-9034

Final Review by Industry:

Printed Name of Industry Authorized Representative _____

Signature of Industry Authorized Representative _____ Date _____

Person Completing Form (if different from above): Printed Name _____

Date _____ Signature _____

Confirm Inhibition Criteria evaluation Passes (see Part III.c.): YES NO

Confirm Biocide Toxicity evaluation Passes (see Part V.c.): YES NO

Confirm Metals section complete (see Part VI): YES NO

Confirm Special Discharges section complete (see Part VIII): YES NO

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Part I

I.a. Industry Name _____
 Industrial User Permit Number _____
 *Municipality/POTW Name Triangle Wastewater Treatment Plant
 *Municipality/POTW NPDES # NC0026051 *Outfall #001
 *Municipality/POTW County Durham
 *Municipality/POTW Average Flow (MGD) 5.0
 *Municipality/POTW Receiving Stream 7Q10 (cfs) 0
 *Municipality/POTW Biological Treatment Units Present in POTW Activated Sludge
 (* information supplied by the POTW)

I.b. What is the Average Daily Discharge (ADD) volume from the water handling systems to the POTW?

ADD = _____ (in MGD)

I.c. Calculate the Percent of Industry Flow at POTW Influent (Ind IWC @ POTW influent, in percent) of this discharge at the POTW influent. This value represents the waste concentration to the POTW during average flow conditions.

$$\text{Ind IWC @ POTW influent} = \frac{(\text{ADD}) \times 100}{(\text{POTW Ave. Flow}) + (\text{ADD})} =$$

$$\frac{(\quad) \times 100}{(\quad) + (\quad)} = \text{_____}\%$$

PART II

II.a. What is the name of the whole product chemical treatment proposed for use in the discharge identified in Part I? _____

Please list the active ingredients and percent composition:

_____ %
 _____ %
 _____ %

II.b. What feed or dosage rate (DR) is used in this application? The units must be converted to maximum grams of whole product used in a 24hr period.

DR = _____ grams/24hr period

Please note, fluid ounces (a volume) must be converted to grams (a mass). The formula for this conversion is:

Grams of product =

$$\text{fluid oz. of product} \times \frac{1 \text{ gal. water}}{128 \text{ fl. oz.}} \times \frac{8.34 \text{ lbs.}}{1 \text{ gal. water}} \times \text{specific gravity of product} \times \frac{453.59 \text{ g.}}{1 \text{ lb.}}$$

II.c. Estimate total volume of the water handling system between entry of biocidal product and discharge point into POTW. On an attached sheet, please provide justification for this estimate (system volume, average cycles per blowdown, holding lagoon size, etc.).

Volume= _____ million gallons

II.d. What is the pH of the handling system prior to biocide addition? If unknown, enter N/A.

pH = _____

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II.e. What is the decay rate (DK) of the product? If unknown, assume no decay (DK=0) and proceed to the next step. The degradation must be stated at pH level within 1/2 pH standard unit within handling system. Enter the half life (HL). (Half Life is the time required for the initial product to degrade to half of its original concentration.) **Please provide copies of the sources of this data.**

HL = _____ Days

$$DK = \frac{1}{HL} \times 0.69 = \underline{\hspace{2cm}}$$

II.f. Calculate degradation factor (DF). This is the first order loss coefficient.

$$DF = \frac{(\text{ADD from Part I.b.})}{(\text{Volume from II.c.})} + (DK) = \frac{(\hspace{1cm})}{(\hspace{1cm})} + (\hspace{1cm}) = \underline{\hspace{2cm}}$$

II.g. Calculate Steady State Discharge Concentration (Dischg. Conc.) in the discharge to the POTW:

$$\text{Dischg Conc.} = \frac{(\text{DR from II.b.})}{(DF)(\text{Volume from II.c.})(3785)} = \frac{(\hspace{1cm})}{(\hspace{1cm})(\hspace{1cm})(3785)} = \underline{\hspace{2cm}} \text{ mg/l}$$

II.h. Calculate concentration of biocide in the POTW influent during average POTW influent flow conditions.

$$\text{POTW Influent Biocide Concentration} = \frac{(\text{Dischg. Conc.}) \times (\text{IWC @ POTW influent})}{100} =$$

$$\frac{(\hspace{1cm}) \times (\hspace{1cm})}{100} = \underline{\hspace{2cm}} \text{ mg/l}$$

PART III

III.a. List all inhibition criteria available for the whole product according to the following columns. List criteria only for those biological processes (activated sludge, trickling filter, digester, etc.) actually present at the POTW (listed in Part I.a. of this form). Note that units should be in mg/l. **Please provide copies of the sources of this data.**

| Process Unit | Inhibition Criteria (mg/l) |
|--------------|----------------------------|
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |

III.b. Choose the lowest Inhibition Criteria = _____ mg/l and compare to POTW influent biocide concentration from Part II.h. above: _____ mg/l.

III.c. Check the correct statement.
 _____ POTW influent biocide concentration is less than all above inhibition criteria.
 or
 _____ POTW influent biocide concentration is greater than at least one of the above inhibition criteria. (PLEASE NOTE BIOCIDES IS UNACCEPTABLE FOR USE AT CURRENT CONDITIONS).

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PART IV

IV.a. List all LC50 data available for the whole product according to the following columns. Note that units should be in mg/l. **Please provide copies of the sources of this data.**

| Organism | Test Duration | LC50 (mg/l) |
|----------|---------------|-------------|
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |

IV.b. Choose the lowest LC50 listed above: _____

Enter the half life (HL) from II.e. above: _____

i) If the half life (HL) is less than 4 days, perform the following calculation.

$$\text{Regulated Limitation} = 0.05 \times \text{LC50} = \text{_____ mg/l}$$

ii) If the half life (HL) is greater than or equal to 4 days or unknown, perform the following calculation.

$$\text{Regulated Limitation} = 0.01 \times \text{LC50} = \text{_____ mg/l}$$

IV.c. Choose the appropriate regulated limitation from i) or ii) immediately above. Biocide concentrations in the POTW's receiving stream must not exceed this amount.

Receiving Stream Regulated Limitation = _____ mg/liter

PART V

V.a. Calculate the Instream Waste Concentration (POTW's IWC @ POTW receiving stream, in percent) of the POTW's discharge to the receiving stream. This value represents the waste concentration of the POTW's effluent to the POTW's receiving stream during average POTW flow conditions and 7Q10 receiving stream conditions.

Average POTW flow (from Part 1.a.) = _____

POTW's receiving stream 7Q10 (from Part 1.a.) = _____

POTW's IWC @ POTW receiving stream =

$$\frac{(\text{average POTW flow}) \times 100}{(\text{POTW's receiving stream 7Q10})(0.646) + (\text{average POTW flow})} =$$

$$\frac{(\text{_____}) \times 100}{(\text{_____})(0.646) + (\text{_____})} = \text{_____}\%$$

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V.b. Calculate concentration of biocide in the POTW's receiving stream during average POTW flow conditions and 7Q10 receiving stream conditions. (NOTE: Assumes POTW influent biocide concentration = POTW effluent biocide concentration.)

$$\text{POTW Receiving Stream Biocide Concentration} = \frac{(\text{POTW influent biocide conc. from Part II.h.}) \times (\text{POTW's IWC@POTW receiving stream})}{100} =$$

$$\left(\frac{\quad}{100} \right) \times \left(\frac{\quad}{\quad} \right) = \quad \text{mg/l}$$

From Part IV.c., enter the POTW Receiving Stream Regulated Limit: _____ mg/liter

V.c. Check the correct statement:

____ POTW receiving stream concentration is less than POTW receiving stream regulated limit.

or

____ POTW receiving stream concentration is greater than POTW receiving stream regulated limit.

(PLEASE NOTE BIOCIDES ARE UNACCEPTABLE FOR USE AT CURRENT CONDITIONS).

PART VI. METALS

If metals are present in the proposed biocidal compound, but no current operation exists, please perform all data entry and calculations below. Complete a separate form for each metal present in the biocide.

If any metals are present in the proposed biocidal compound and if the system is already in operation with that biocide, please complete only the first row (metal name through concentration in biocide). Additionally, provide sampling data showing the concentrations in the discharge to the POTW. Samples must be flow proportional 24 hour composites unless otherwise approved by the POTW, shall be collected and analyzed in compliance with 40 CFR 136, and must be analyzed by a North Carolina Division of Water Quality Certified Laboratory that is certified in the analysis of the pollutant in wastewater. Complete a separate form for each metal present in the biocide.

| <u>Metal</u> | <u>Chemical Formula</u> | <u>Molecular Weight of Metal</u> (MW) | <u>Formula Weight</u> (FW) | <u>Metal Concentration in Biocide</u> (MCC) |
|--------------|-------------------------|--|-------------------------------|--|
| | | | | |

EXAMPLE

Copper *CuSO4·5H2O* *63.546 g/mole* *249.680 g/mole* *0.2 %*

VII.a. Dosage rate of Biocide (DR) and Average Daily Discharge (ADD) (from II.b.):

DR = _____ grams/day

ADD = _____ million gallons/day

VII.b. Discharge Concentration (DC) of Biocide:

$$\text{DC} = \frac{\text{DR}}{\text{ADD}} = \frac{\left(\frac{\quad \text{grams/day}}{\quad \text{million gallons/day}} \right)}{\quad} = \quad \text{grams/million gallons}$$

VII.c. Convert DC to milligrams/liter (ppm):

DC (mg/l) =

$$\quad \text{DC (grams/million gal)} \times \frac{(1,000 \text{ mg/g})}{(3,785,000 \text{ liters/million gal.})} = \quad \text{mg/l}$$

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VII.d. Calculate the fraction of metal in the metal-containing compound (MF):

$$MF = \frac{MW}{FW} = \frac{(\text{grams/mole})}{(\text{grams/mole})} = \underline{\hspace{2cm}}$$

VII.e. Calculate the fraction of metal in the biocidal compound (BF):

$$BF = MF \times \frac{MCC (\%)}{100} = \underline{\hspace{2cm}} \times \frac{\%}{(100)} = \underline{\hspace{2cm}}$$

VII.f. Calculate the concentration of metal in the discharge (M, mg/l):

$$M = DC \times BF = \underline{\hspace{2cm}} \text{ mg/l} \times \underline{\hspace{2cm}} = \underline{\hspace{2cm}} \text{ mg/l}$$

VII.g. Calculate metal in discharge in lbs/day (M, lbs/day):

$$M \text{ (lbs/day)} = M \text{ (mg/l)} \times \text{ADD (MGD)} \times 8.34 = \underline{\hspace{2cm}} \text{ mg/l} \times \underline{\hspace{2cm}} \text{ MGD} \times 8.34 = \underline{\hspace{2cm}} \text{ lbs/day}$$

NOTE: POTW must compare above concentration and lbs/day levels in the discharge to its current reserve of its Maximum Headworks Allowable Load (MAHL) (see "Total Loading Still Available" on Allocation Table) and make a case-by-case evaluation of the acceptability of the above metals levels.

Concentrations and lbs/day acceptable to POTW: YES NO
POTW Representative Date

PART VIII - Special Discharges, including maintenance procedures

VIII. Provide a summary of scheduled maintenance or other procedures that would result in a discharge different from the typical daily discharge. This should include but is not limited to, any seasonal shutdown procedures or procedures where the water handling system is totally emptied. For each procedures, please briefly describe the procedures and include the names of any contractors that may provide this scheduled service for the cooling towers, and any chemicals that are introduced to enhance the cleaning process. Attach additional pages as necessary.

NOTE: The POTW, at their discretion, may establish requirements for prior notification for these types of procedures, as well as any other requirements necessary to protect their wastewater treatment plant from adverse effects.

Final Review by POTW Staff:

Printed Name of POTW Representative
Signature of POTW Representative Date
Confirm Inhibition Criteria evaluation Passes (see Part III.c.): YES NO
Confirm Biocide Toxicity evaluation Passes (see Part V.c.): YES NO
Confirm Metals evaluation Passes (see Part VI): YES NO
Confirm Special Discharges addressed adequately: YES NO

Frequently Encountered Biocide Terms:

Active ingredient - (a.i.) the chemical in a biocide formulation that is primarily responsible for its biocidal activity and that is identified as the active ingredient on the product label. See "formulation."

Acute toxicity - lethality or other harmful effects sustained by either resident aquatic populations or indicator species used as test organisms in a controlled toxicity test due to a short-term exposure (relative to the life cycle of the organism) to a specific chemical or mixture of chemicals (as in an effluent). Short term exposure for acute tests is generally 96 hours or less.

A.D.D. - Average Daily Discharge, usually expressed in millions of gallons.

Air washer - a mechanical device that removes dust, particulates, or odor from the incoming plant or process air. It is also used for humidity adjustment.

Biocide - a chemical used to control nuisance organisms. Generally classified into oxidizing or non-oxidizing biocides.

Chemical name - the name applied to a biocide active ingredient that describes its chemical structure according to rules prescribed by the American Chemical Society. It is always listed in the ingredient statement on the label, example: the chemical name for the active ingredient of *Bio Control 368* would be "5-chloro-2-methyl-4-isothiazolin-3-one." See also, "Common name."

Chlorine demand - difference between the amount of chlorine applied and amount of free, combined or total available chlorine remaining after a specific contact time.

Chronic toxicity - any harmful effect sustained by either resident aquatic populations or indicator species used as test organisms in a controlled toxicity test due to long-term exposure (relative to the life cycle of the organism) or exposure during a substantial portion of the duration of a sensitive period of the life cycle to a specific chemical substance or mixture of chemicals (as in an effluent). In absence of extended periods of exposure, early life stage or reproductive toxicity tests may be used to define chronic impacts.

Combined residual chlorine - chlorine residuals reacted with ammonia or other organic nitrogen compounds.

Common name - an accepted, commonly used name for a chemical. Only common names which are officially accepted by the US Environmental Protection Agency may be used in the ingredient statement on the biocide label. The official common name may be followed by the chemical in the list of active ingredients. For example, a label with the trade/brand name *Bio Chem 223* would have as its common name *DBNPA*, followed by *2,2-dibromo-3-nitrilopropionamide* as its chemical name.

Concentration - the mass of a substance per volume of liquid.

Discharge - the addition of any man-induced waste effluent either directly or indirectly to state surface waters.

Dispersant - a surface active chemical that aids in keeping air washer surfaces clean and free of deposits.

D.F. - Degradation factor. It is the first-order loss coefficient.

D.K. - Decay rate. This integrated rate derives the biocide concentration with respect to time. The half-life for a first-order reaction such as this is independent of the biocide concentration, hence the equation $D.K. = 1/H.L. \times 0.69$.

D.R. - Dosage rate. The amount, in grams, of whole product used per 24 hour period.

Formulation - a biocide preparation supplied by the manufacturer for practical use. The formulation includes all contents in the container: active ingredient (actual toxicant) plus inert ingredients (everything else) such as solvents, diluents, and adjuvants.

Free residual chlorine - unreacted excess HOCl and OCl.

Freshwater - all waters that under natural conditions would have a chloride ion content of 500 mg/l or less.

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Half-life (H.L) - The time required for the initial product to degrade to half its original concentration or preferable in this context, to half its initial aquatic toxicity.

IWC - Instream waste concentration, expressed as a percent. The IWC represents the portion of the receiving stream volume comprised of effluent during a 7Q10 condition. Whole effluent toxicity limitations and monitoring requirements are based upon the IWC during conditions of maximum permitted effluent flow and 7Q10 stream flow.

LC50 - the concentration of chemical predicted to cause 50 percent lethality in test organisms within a specified time.

Lethal concentration - in an acute toxicity test of an effluent or substance, the concentration causing death in test organisms. LCs are reported as the concentration proving lethal to a percentage of the organisms (example: LC50).

Non-oxidizing biocide - does not have the ability to take electrons from other atoms, generally stable and longer lasting effects, slower killing (example: glutaraldehyde/quats).

Oxidizing biocide - has ability to take electrons from other atoms, inhibits growth, quick killing (example: brominated hydantoin, chlorinated isocyanurates).

Permitted flow - the greatest waste volume that is allowed to be discharged to the receiving water body (usually expressed as a daily average).

Quaternary Ammonia Compound ("Quats") - has cationic charge and ability to bond with negatively charged cell wall, affecting cell wall permeability and energy uptake.

7Q10 - defined as the minimum average flow for a period of seven consecutive days that has an average recurrence of once in ten years.

Synergism - the cooperative action of two materials so that the total effect is greater than the sum of the two effects taken separately.

Total residual chlorine - total amount of free (HOCl) and combined chlorines (chloramines) residuals remaining after the initial chlorine demand has been satisfied.

Toxic substance - any substance or combination of substances (including disease-causing agents), which after discharge and upon exposure, ingestion, inhalation, or assimilation into any organism, either directly from the environment or indirectly by ingestion through food chains, has the potential to cause death, disease, behavior abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunctions or suppression in reproduction or growth) or physical deformities in such organisms or their offspring or other adverse health effects.

Toxicant - see "toxic substance."

Trade name - or brand name. Each manufacturer has a trade name for its product. Different manufacturers/suppliers may use different trade names for the same biocide active ingredient. Most companies register each brand/trade name as a trademark, example: "*Bio Control 368*" would be the trade name for the chemical "5-chloro-2-methyl-4-isothiazolin-3-one." See also, "Common name."

Water quality standard - (WQS) a law or regulation that states the use of a body of water, the numeric and narrative water quality criteria necessary to protect this use, and an antidegradation statement.