

DBNPA: MODELING EFFECTIVE AND ENVIRONMENTALLY ACCEPTABLE APPLICATION

Kent K. Herbst, CWT
U.S. Water Services
330 South Cleveland Street
Cambridge, MN 55008

The use of DBNPA is common in cooling tower systems that discharge to surface waters via NPDES permits. The paper derives useful formulas incorporating many systems variables for predicting active DBNPA concentrations in the tower and blowdown. This is not only useful in ensuring sufficient application dose but to also help ensure compliance with NPDES discharge limits.

INTRODUCTION

The use of 2,2-Dibromo-3-Nitrilopropionamine (DBNPA) is a common non-oxidizing biocide utilized in an overall biomanagement program in cooling water systems. This is particularly true if the cooling water system is discharged to a surface water discharge regulated by a National Pollutant Discharge Elimination System (NPDES) Permit. The reason for the common DBNPA use is that it readily hydrolyses depending on the pH and temperature into relative inert compounds that are safe to aquatic species.

The first step in a proper biomanagement program is to understand the dose required to achieve the desired bacterial kill rate to maintain the system from an operations standpoint as well as safety aspect. There are different methods to accomplish this but one of the easier methods is expanded upon.

The next step is to take this "pilot" study information and to model the system variables on applied DBNPA concentrations as well as discharge concentrations. Proper modeling will not only ensure compliance with a NPDES limit but will also minimize operating costs associated with biocide applications.

EFFECTIVE DOSE DETERMINATION

Every cooling system is unique from a biological standpoint. There are many variables that influence the bacterial populations in a system such as pH, temperature, flow rate, organic concentrations, etc. The goal of a proper water treatment program is to maintain these bacterial populations at an acceptable level as to prevent any operational impacts or human

health risks. In order to control bacteria populations, many times water treatment consultants rely on recommending a DBNPA dose somewhere in the range depicted on the product label depending on their impression of current system bacterial populations. Their analysis of current status may be based on dipslides, ATP, microbiological analyses, or others.

The applied acceptable product dose range can vary significantly depending on the system the biocide is being applied to. The chosen dose can significantly impact the operating economics of a water treatment program. Therefore, determining the minimum effective dose is important to the end user from an economic standpoint as well as discharge compliance. A relatively simple but powerful method can be utilized to determine what the proper site specific dose of DBNPA should be to achieve the desired kill rate. The only equipment needed in the field are samples of the product to be applied, pipettes, beakers, graduated cylinders, sealable bag and dip slides (Figure 1).

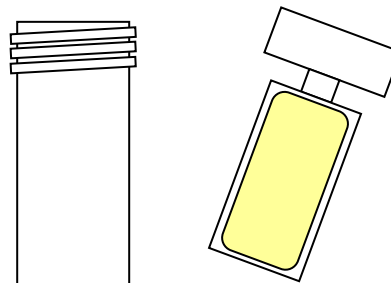


FIGURE 1
COMMON DIPSLIDE

The procedure outlined below can be used to model the resultant planktonic bacteria concentrations after various biocide doses.

1. Dilute concentrated product to a 0.1% solution by pipetting 0.5 mL of product with 99.5 mL of DI water.
2. Obtain a large representative sample of cooling water to be analyzed
3. Set one bulk tower water sample aside to be used as a blank
4. Record the temperature and pH of the bulk condenser water
5. For the second sample measure 99.5 mL of tower water and to it add 0.5 mL of the diluted product sample created in Step 1. This dilution represents an applied product dose of 25 ppm.
6. For the third sample measure 99.0 mL of tower water and to it add 1.0 mL of the diluted product sample created in Step 1. This dilution represents an applied product dose of 50 ppm.
7. For the fourth sample measure 98.0 mL of tower water and to it add 2.0 mL of the diluted product sample created in Step 1. This dilution represents an applied product dose of 100 ppm.
8. For the fifth sample measure 96.0 mL of tower water and to it add 4.0 mL of the diluted product sample created in Step 1. This dilution represents an applied product dose of 200 ppm.
9. Let these samples sit for a determined amount of time (i.e. 1-6 hours) to model various holding times after biocide additions. Ideally these samples would be in a sealable bottle and placed in the sump of the cooling water system to model the system at actual operating temperatures.
10. After the allotted time, conduct dipslide testing per the manufacturer's recommended protocol.
11. Incubate the dipslides per manufacturer's recommendation and record the results.

Steps 5-8 can be conducted at different concentrations by following the equation below:

$$M_2 = \frac{1,000,000 * V_1}{100} \quad (1)$$

Where,
 M_2 = Applied Concentration (ppm)
 V_1 = Volume of DBNPA Soln. (mL)

In addition, Step 9 can be conducted at different times to help determine the role contact time plays in biocidal kill rates.

MODELING SYSTEM & DISCHARGE CONCENTRATIONS

Based on the information obtained during this modeling, the water treatment consultant will have a better understanding of the impacts of applied concentration and time on the resultant planktonic bacteria populations. The next step is taking this theoretical data, which could be viewed as pilot study data, and scale it up to large scale application. To do this, a modeling equation needs to be derived to predict the net system effect. Applied DBNPA concentrations in a cooling system can be impacted by pH, temperature, reducing agents, neat product concentrations, introduction rate, blowdown rate, light, and consumption due to various reactions. This paper will not focus on reducing agents, light, and consumption due to other reactions. These are very difficult to derive equations for and would need to be taken into consideration on a case-by-case basis.

For the sake of this paper we will look at evaluating the active DBNPA concentrations in a cooling system based on the following generalized equation:

$$m_{DBNPA, Final} = m_{DBNPA, Initial} + m_{DBNPA, In} + m_{DBNPA, Out} + m_{DBNPA, Re act} \quad (2)$$

Where,

$m_{DBNPA, Final}$ = Final DBNPA Mass
 $m_{DBNPA, Initial}$ = Initial DBNPA Mass
 $m_{DBNPA, In}$ = DBNPA Mass In
 $m_{DBNPA, Out}$ = DBNPA Mass Out
 $m_{DBNPA, In}$ = DBNPA Mass In
 $m_{DBNPA, Re act}$ = DBNPA Lost Due to pH & Temperature Hydrolysis

To effectively determine the concentration of DBNPA for a given time period you must use rate calculations that take the various variables into account. We will first focus on the DBNPA concentration as a function of product concentration, pumping capacity, and time to determine the effect of metering chemicals into the system. The following equation can be derived for these variables:

$$[DBNPA]_{s, t_f} = [DBNPA]_{s, t_i} + \frac{1,000,000 \cdot q_p \cdot C_c \cdot \rho_c \cdot \frac{P_s \cdot P_v}{100} (t_f - t_i)}{(V_s \cdot 1440 \cdot 8.34)} \quad (3)$$

Where,

- q_p = Chemical Pump Capacity (gpd)
 C_c = Chemical DBNPA Conc. (%)
 ρ_c = Chemical Density (lb/gal)
 P_s = Pump Stroke (%)
 P_v = Pump Speed (%)
 V_s = System Volume (gal)

Next, the effect of DBNPA concentration decline due to blowdown of the system needs to be figured. The following equation depicts the rate loss:

$$d[DBNPA]_s = -[DBNPA]_s \frac{q_o}{V_s} dt \quad (4)$$

Where,

- q_o = Blowdown Rate (gpm)
 V_s = System Volume (gal)

Solving for the equation as a function of time yields:

$$[DBNPA]_{s,t_f} = [DBNPA]_{s,t_i} e^{-\frac{q_o}{V_s}(t_f - t_i)} \quad (5)$$

Finally, the consumption of DBNPA via hydrolysis due to pH and temperature needs to be accounted for. The following equation outlines this effect [1]:

$$\ln \frac{[DBNPA]_{s,t_f}}{[DBNPA]_{s,t_i}} = k(OH)^x (t_f - t_i) \quad (6)$$

Where,
 $x = 0.91$

Given the rate constant [1],

$$k = 2.5 \cdot 10^{11} e^{-\left(\frac{6029}{T}\right)} \quad (7)$$

Where,
 k = Rate Constant in $\frac{1}{mol * min}$

T = Temperature in K

Given,

$$(OH)^- = \frac{10^{-pK_w}}{10^{-pH}} \quad (8)$$

Given the value of pK_w as a function of temperature [2],

$$pK_w = \frac{142613.6}{T} + 4229.195 \log T - 9.7384T + 0.0129638T^2 - 1.15068 \cdot 10^{-5} T^3 + 4.602 \cdot 10^{-9} T^4 - 8909.483 \quad (9)$$

Substituting Eqs. (7), (8), and (9) into Eq. (6) and rearranging yields,

$$[DBNPA]_{s,t_f} = [DBNPA]_{s,t_i} e^{-2.5 \cdot 10^{11} e^{-\left(\frac{6029}{T}\right)} \left(10^{\frac{-\left(\frac{142613.6}{T} + 4229.195 \log T - 9.73847 + 0.0129638 T^2 - 1.15068 \cdot 10^{-5} T^3 + 4.602 \cdot 10^{-9} T^4 - 8909.483\right)}{10^{-pH}}} \right)^{0.91} (t_f - t_i)} \quad (10)$$

Depending on the time relative to biocide addition and bleed, Eqs. (3), (5), and (10) can be used to easily model the final DBNPA concentration in the system. This modeling is a powerful tool in ensuring the proper DBNPA concentration is reached in the system to achieve the desired bacteria control obtained in the pilot study work.

In addition to ensuring a proper DBNPA concentration in the system, this model is also an important tool in ensuring compliance with permit limits. These limits are intended to protect the aquatic environment.

MODELING EXAMPLES

The graph below depicts the effect of pH on a system feeding DBNPA with all other variables held constant:

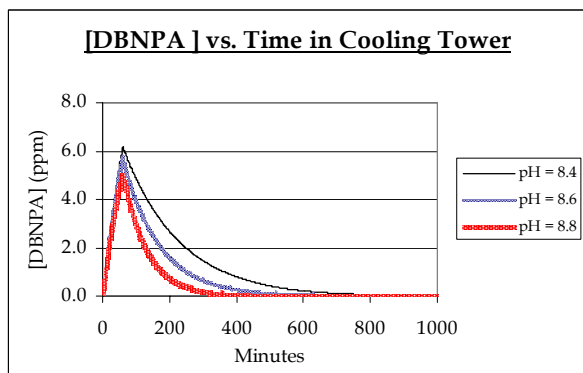


FIGURE 2
EFFECT OF PH ON [DBNPA]

In going from a pH of 8.4 to 8.8, the maximum concentration of DBNPA in the system was reduced from ~6.19 ppm to ~5.02 ppm, or an 18.9% reduction.

The graph below depicts the effect of temperature on a system feeding DBNPA with all other variables held constant:

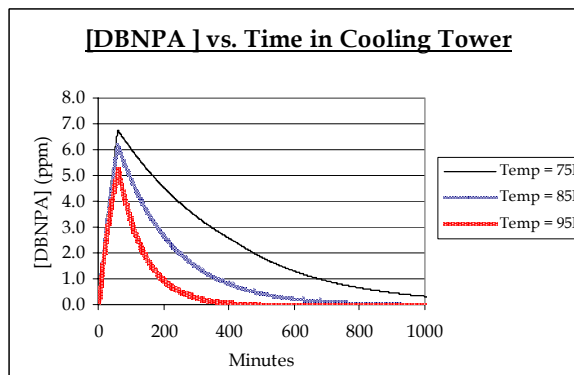


FIGURE 3
EFFECT OF TEMPERATURE ON [DBNPA]

In going from a temperature of 75°F to 95°F, the maximum concentration of DBNPA in the system was reduced from ~6.77 ppm to ~5.24 ppm, or a 23% reduction.

Finally, the graph below depicts the effect of chemical pump capacity on a system feeding DBNPA with all other variables held constant:

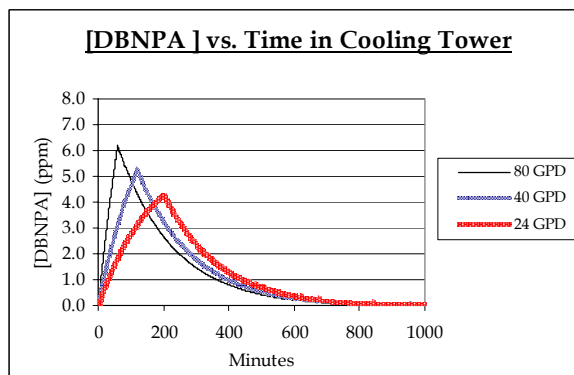


FIGURE 4
EFFECT OF CHEMICAL PUMP CAPACITY ON [DBNPA]

In going from a chemical pump capacity of 80 gpd to 24 gpd, the maximum concentration of DBNPA in the system was reduced from ~6.19 ppm to ~4.29 ppm, or a 31% reduction.

CONCLUSIONS

Effective cooling water bacteria programs utilizing DBNPA as a biocide require careful thought and consideration. This is particularly true if the system is being discharged to an outfall regulated with a NPDES discharge. Beginning with a pilot study of the product to be applied at various concentrations and durations will help simulate the system demand for the DBNPA. With this information, proper scale up needs to be modeled using the equations derived to take into effect the variable that can impact applied concentrations. These variables also significantly impact the concentration of DBNPA in the discharge with a lower pH, lower temperature, and lower pump capacity all increasing the discharge concentrations. Effective bacterial control and environmentally acceptable DBNPA application requires careful consideration and system modeling.

REFERENCES

- [1] A. Meitz and L. Magnusson, "Temperature and pH Hydrolysis of 2,2 Dibromo-3-Nitrilopropionamine," Cooling Tower Institute, 1983, pp. 4-6.
- [2] G. Olofsson and L.G. Hepler, "Thermodynamics of Ionization of Water of Wide Ranges of Temperature and Pressure," J. Solution Chemistry 4, 1974, pp. 127-143.