# Biocides for Industrial Use

**U.S. ARMY CORPS OF ENGINEERS** **Building Strong®**

**ANS Controls:** See Table 1 of this fact sheet for a list of biocides.

**Targeted Species:** Biocides may control many types of species. See Table 2 of this fact sheet for the types of Organisms of Concern – CAWS that may be controlled by biocides.[1]

**Selectivity:** Biocides are non-selective. See Table 2 for more details.

**Developer/ Manufacturer/ Researcher:** There are many manufactures of biocides.

**Pesticide Registration/Application:** Pesticides, including biocides, must be applied in accordance with the full product label as registered by the U.S. Environmental Protection Agency (USEPA). Users must read and follow the pesticide product label prior to each application. The registration status, trade name, and availability of pesticides are subject to change. The listing of a pesticide in this fact sheet or Appendix B does not represent an endorsement by the U.S. Army Corps of Engineers or the USEPA regarding its use for a particular purpose.


**Biocides are chemicals designed to kill all sizes and life stages of organisms, especially microorganisms.**

**Brief Description:** Biocides are chemicals designed to kill all sizes and life stages of organisms, especially microorganisms, and the effectiveness of biocides varies with the concentration of a biocide and duration of the exposure. Species that are exposed to sub-lethal concentrations, or for too short of time, may be injured but may survive.

Biocides are used for drinking water treatment, wastewater treatment, ship ballast water treatment, disinfectants and as antifouling agents that prevent mollusks from accumulating in industrial pipes. Biocides are produced in liquid and powder forms, in ready-to-use formulations or as concentrates, and are applied using a variety of techniques. Table 1 provides a list of biocides that have been evaluated to potentially control or inactivate ANS in ballast water. Though examined for use in ballast water treatment, these biocides may be effective at controlling select Organisms of Concern – CAWS[2] (Bowman et al. 1998, Chattopadhyay et al. 2004, TenEyek 2009). See Table 2 and the *General Effectiveness* and *Operating Constraints* sections of this fact sheet for more information on biocide effectiveness.

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[1] For a list of the 39 specific ANS of Concern – CAWS, please see Table 1 of the main report.

[2] Algaecides, herbicides, molluscicides and piscicides are also considered biocides. They are each covered in more detail in separate fact sheets (titled "Algaecides," "Aquatic Herbicides," "Molluscicides," and "Piscicides").

Depending on the type of biocide, ship ballast water treated with biocides must be detoxified using methods that avoid discharging unwanted concentrations of residual biocide and toxic byproducts into the environment (Chattopadhyay et al. 2004). Many biocide applications for ballast water treatment require chemical neutralization prior to discharge. Most ships neutralize treated ballast water before discharge, but some rely on minimum hold times to provide an opportunity for sufficient degradation of residuals (Lloyd's Register 2010). Water temperature and salinity affect the rate at which chemical biocides function and break down (Albert et. al. 2010).

**Prior Applications:** Biocides are widely used in the health, food, and water treatment industries. Biocides have been studied as a means to prevent ANS introductions in ballast water via international shipping (Chattopadhyay et al. 2004).

**General Effectiveness:** Biocides used in industry can be effective at controlling ANS when used properly. Factors that influence the efficacy of biocides on microorganisms and other aquatic species include the biocide's chemical properties, the size and characteristics of the organism, biocide concentration, treatment/application process, contact time, and water quality (e.g., salinity, pH, temperature, oxygen content) (Chattopadhyay et al. 2004).

The U.S. Coast Guard (USGS) Research and Development Center conducted a qualitative assessment of potential ballast water biocides and their effect on different organisms (Table 2). For this qualitative assessment, this evaluation of biocide effectiveness does not consider conditions under which the biocide was tested; rather the evaluation considers only whether the outcome of the study resulted in the desired effect. Except for otherwise noted, the information on biocide effectiveness referenced in this fact sheet was obtained from literature search conducted to complete USGS's assessment and was not the result of scientific research targeted specifically for ballast water treatment or use in an open flowing system, and must be used cautiously (Chattopadhyay et al. 2004).

**Operating Constraints:** Biocides have specific use restrictions and requirements, which are found on the product label. The following are only a few of the numerous operating constraints that would require consideration. To be effective, target concentrations and specific contact times must be obtained throughout the water column. Additionally, depending on the selected biocide, it may be necessary to deactivate or neutralize the biocide to avoid killing non-target organisms upon release of treated water, or downstream of a treatment area. Certain biocides may create toxic by-products, persist in the environment and accumulate in sediment, making sediment reuse or disposal problematic.

A compilation of the physiochemical properties, treatment efficacy against target organisms, environmental acceptability, and other vendor information for many biocides can be found in Chattopadhyay et al. (2004).

**Table 1. Biocides Considered for Potential Treatment of Ballast Water**
(adapted from Table 3-1 and Table 3-3, Chattopadhyay 2004[3] unless otherwise noted in footnote)

| Biocide | Common Application | General Characteristics |
|---|---|---|
| **Metal** | | |
| Silver (ionic or salts) | Disinfection of industrial water systems | • Limited applications of metal ions or salts<br>• Not generally used due to human side effect risk |
| **Oxidizing – *Halogen containing compounds*** | | |
| Bromine<br>Chlorine (free chlorine, hypochlorous acid, hypochlorite salts)<br>Chlorine dioxide<br>Iodine<br>Sodium chlorite | Disinfection of drinking water, cooling systems, and surfaces | • Corrosive<br>• Presence of organic matter limits the effectiveness and may require higher dosage<br>• Residuals remain in water after treatment<br>• Possibly create harmful byproducts<br>• Requires frequent applications<br>• Presence of organic matter limits the effectiveness and may require higher dosage |
| **Oxidizing – *Non-halogen containing compounds*** | | |
| Hydrogen peroxide<br>Potassium permanganate | Disinfection of drinking water, cooling systems, and surfaces | • Presence of organic matter limits the effectiveness and may require higher dosage<br>• Moderately corrosive<br>• Some residuals remain in water after treatment |
| **Oxidizing – *Acids*** | | |
| Peracetic acid (Peraclean®) | Wastewater treatment | • Effective disinfectant with no known toxic residual<br>• More potent than hydrogen peroxide<br>• Rapidly active at low concentrations against a wide range of microorganisms<br>• Corrosive<br>• Highly efficient in presence of organic matter |
| **Non-oxidizing Biocides – *Aldehydes*** | | |
| Glutaraldehyde | Disinfectant in hospitals, laboratories, and biological fixatives | • Slight to moderate efficiency in presence of organic matter<br>• Some residuals remain in water after treatment |

[3] Of the biocides that are identified in the *Chattopadhyay,2004* paper, only ones that are not identified in a different fact sheet or that have been found to be effective on the ANS of Concern – CAWS are included. Biocides identified in *Chattopadhyay,2004* but are found in other fact sheets are copper compounds found in the "Algaecides" and "Molluscicides" fact sheets, and ozone found in the "Alteration of Water Quality" fact sheets. Biocides listed in the *Chattopadhyay,2004* report that were not included because they were not effective on the ANS of Concern – CAWS are the following: cationic surfactants, Grotan, and zinc pyrithione. Formaldehyde was not included as it was classified as a carcinogen in the 2011 National Toxicology Program in it Twelfth Report on Carcinogens.

**Table 1 (cont.). Biocides Considered for Potential Treatment of Ballast Water**
(adapted from Table 3-1 and Table 3-3, Chattopadhyay 2004[4] unless otherwise noted by footnote)

| Biocide | Common Application | General Characteristics |
|---|---|---|
| **Non-oxidizing Biocides - *Amines and halogenated amides*** | | |
| Dibromonitrilopropionamide (DBNPA) | Pulp and paper water treatment systems; disinfection of industrial water systems | |
| Fatty amines (Mexel® 432) | Corrosion inhibitor; scale dispersant | • Rapid degradation in the environment |
| **Non-oxidizing Biocides - *Heterocyclic ketones*** | | |
| Polyhexamethylene biguanide (PHMB) | Disinfection of industrial water systems | |
| Isothiazolone (Sea-Nine®) | Antifouling agent | • Proposed as alternative to organotin compounds (chemical compounds that contain at least one bond between tin and carbon) |
| **Other Biocides** | | |
| 2-Thiocyanomethylthio benzothiazole (TCMTB) | Disinfection of industrial water systems; antifouling agent | • Proposed as alternative to organotin compounds (chemical compounds that contain at least one bond between tin and carbon) |
| Benzalkonium chloride | Disinfection of industrial water systems | • Corrosive |
| Chlorothalonil | Fungicide | • Proposed as alternative to organotin compounds (chemical compounds that contain at least one bond between tin and carbon) |
| Dichlofluanid | Antifouling agent | • Proposed as alternative to organotin compounds (chemical compounds that contain at least one bond between tin and carbon) |
| 1-(3-Chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride | Metalworking fluids, preservative for paints | • Not persistent and degrades rapidly under acidic conditions |
| 2-Methylthio-4-tertbutylamino-6-cyclo-propylamino-striazine (Irgarol® 1051) | Antifouling agent | • Proposed as alternative to organotin compounds (chemical compounds that contain at least one bond between tin and carbon) |
| Phenol | Disinfectant | • Low corrosivity<br>• Little or no residuals remain in water after treatment |
| Vitamin K (SeaKleen®) | Ballast water treatment | • Toxic to a broad spectrum of marine and freshwater organisms (fish larvae and eggs, planktonic crustaceans, bivalve larvae, *Vibrio* bacteria, and dinoflagellates) |
| Sodium hydroxide [5] | Saponification; food preparation, cleaning agent, industrial drilling, paper making | • Also known as lye, caustic soda, and sodium hydrate<br>• Caustic washing |
| Triclosan | Wastewater treatment | • Stable and incompatible with strong oxidizing agents |
| Zineb (thiocarbamate) | Disinfection of industrial water systems; antifouling agent | |

[4] Of the biocides that are identified in the *Chattopadhyay,2004* paper, only ones that are not identified in a different fact sheet or that have been found to be effective on the ANS of Concern – CAWS are included. Biocides identified in *Chattopadhyay,2004* but are found in other fact sheets are copper compounds found in the "Algaecides" and "Molluscicides" fact sheets, and ozone found in the "Alteration of Water Quality" fact sheets. Biocides listed in the *Chattopadhyay,2004* report that were not included because they were not effective on the ANS of Concern – CAWS are the following: cationic surfactants, Grotan, and zinc pyrithione.

[5] (Bowman et. al. 1998), (TenEyek 2009)

**Table 2. Summary of Biocides Considered for Ballast Water Treatment Adapted From Chattopadhyay 2004[6] Unless Otherwise Noted by Footnote**

| | May Be Effective on ANS of Concern – CAWS | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Biocide** | **Algae** | **Annelid** | **Bryozoan** | **Crustacean** | **Fish** | **Mollusk** | **Plant** | **Protozoan** |
| **Metal** | | | | | | | | |
| ***Silver*** | x | | | | | | | |
| **Oxidizing** | | | | | | | | |
| ***Halogen containing compounds*** | | | | | | | | |
| Bromine | | x | | x | x | x | | |
| Chlorine (free chlorine, hypochlorous acid, hypochlorite salts) | x | x | | x | x | x | | |
| Chlorine Dioxide | | x | | | x | x | | |
| Iodine | | | | x | | x | | |
| Sodium Chlorite | x | x | | x | x | x | | |
| ***Non-halogen containing compounds*** | | | | | | | | |
| Hydrogen Peroxide | x | x | | x | | x | | |
| Potassium Permanganate | x | x | | x | | x | | |
| **Non-oxidizing** | | | | | | | | |
| ***Acids*** | | | | | | | | |
| Peraclean (peracetic acid) | | | | | x | | | |
| ***Aldehydes*** | | | | | | | | |
| Formaldehyde | x | x | | x | x | x | | |
| Glutaraldehyde | x | x | | | | x | | |
| ***Amines and halogenated amides*** | | | | | | | | |
| Dibromonitrilopropionamide (DBNPA) | x | | | x | | | | |
| Mexel® 432 (fatty amines) | | x | | | | x | | |
| ***Heterocyclic ketones*** | | | | | | | | |
| Polyhexamethylene biguanide (PHMB) | | x | | | | x | | |
| Sea-Nine (isothiazolone) | x | x | | x | | x | | |
| ***Others*** | | | | | | | | |
| 2-thiocyanomethylthio benzothiazole (TCMTB) | | x | | x | x | x | | |
| Benalkonium chloride | | x | | x | x | x | | |
| Chlorothalonil | | | | x | | | | |
| Diclofluanid | | x | | | x | x | | |
| Dowicil® 75 (N-(3-chloroallyl)hexaminium chloride) | | | | x | | | | |
| Irgarol® 1051 (2-methylthio-4-tert-butylamino-6-cyclo-propylamino-s-triazine) | | | | | x | | | |
| Phenol | | x | | | | | | |
| SeaKleen® (Vitamin K) | x | x | | x | x | x | | |
| Sodium Hydroxide[7] | x | x | | x | x | x | | |
| Triclosan | | | | | x | | | |
| Zineb (thiocarbamate) | | | | | x | | | |

[6] Except for sodium hydroxide, a biocide was considered effective and designated with a "X" if the LC50 (i.e., the biocide concentration that is lethal to 50 percent of the tested organisms) was determined to be 1,000 micrograms per liter (µg/L) or less, if the EC50 (i.e., the effective biocide concentration at which 50% of the tested organisms are impacted) included mortality of the organism as an impact, or if the reviewed literature designated the biocide as "effective." "May Be Effective on ANS of Concern – CAWS" was designated with an "X" in this Table and Appendix A if the above criteria were met.

[7] (Bowman 1998), (TenEyek 2009)

## Cost Considerations:

***Implementation:*** Implementation costs of biocide applications would include the cost of the biocide, the detoxicant (if required to neutralize the biocide), and the application method. Planning and design activities in this phase may include research and development of this Control, modeling, site selection, site-specific regulatory approval, plans and specifications, and real estate acquisition. Design will also include analysis of this Control's impact to existing waterway uses including, but not limited to, flood risk management, natural resources, navigation, recreation, water users and dischargers, and required mitigation measures.

***Operations and Maintenance:*** Operations and maintenance costs would include application of the biocide and detoxicant, and effectiveness and water quality monitoring programs.

***Mitigation:*** Design and cost for mitigation measures required address impacts as a result of implementation of this Control cannot be determined at this time. Mitigation factors will be based on site-specific and project-specific requirements that will be addressed in subsequent, more detailed, evaluations.

## Citations:

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Greenman, D., K. Mullen, & S. Parmar. 1997. Ballast water treatment systems: a feasibility study. United States Coast Guard Office of Response, Worcester Polytechnic Institute

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