

Molluscicides

U.S. ARMY CORPS OF ENGINEERS

Building Strong®

ANS Control: Molluscicides (Nonoxidizing molluscicides) – Quaternary and Polyquaternary Ammonium Compounds, Aromatic Hydrocarbons, Endothall as the mono (N,N-dimethylakylamine) salt, Metals and their salts, and Niclosamide

Targeted Species: Molluscicides are used to control mollusks. Specific ANS of Concern – CAWS¹ that may be controlled with molluscicides include the greater European pea clam (*Pisidium amnicum*), the European fingernail clam (*Sphaerium corneum*), and the European stream valvata (*Valvata piscinalis*).



Application of copper sulfate pentahydrate crystals to Lake Offutt, Offutt Air Force Base, NE, for control of invasive mussels

Selectivity: Molluscicides are non-selective against mollusk species; however,

activity is dependent upon proper concentration, method and timing of application, and contact time or length of exposure. Molluscicides may impact non-target aquatic organisms at use rates that control mollusks.

Developer/Manufacturer/Researcher: Molluscicides discussed in this fact sheet are proprietary formulations developed, registered, and sold by chemical manufacturers. Examples of available molluscicide products and their respective manufacturers include: Copper sulfate pentahydrate crystals and copper chelates, manufactured by Chem One LTD., Applied Biochemists, and SePRO Corporation (NatrixTM); TD2335 Industrial Biocide-Molluscicide, manufactured by United Phosphorus, Inc.; Barquat Molluscicide 80, manufactured by Lonza, Inc.; Clam-Trol® (numerous formulations are available), manufactured by Betz Laboratories, Inc.; Bulab®, manufactured by Buckman Laboratories; and Bayluscide, manufactured by Bayer and Pro-Serve, Inc.²

Pesticide Registration/Application: Pesticides, including molluscicides, 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.

Brief Description: Molluscicides are chemical substances or biocides developed specifically for destroying mollusks (Claudi & Mackie 1994). The mode of action of many of these compounds is stress to the water balance system of mollusk species. McCullough et al. (1980) determined that stress

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

² Manufacturers and products mentioned are examples only. Nothing contained herein constitutes an endorsement of a non-Federal entity, event, product, service, or enterprise by the U.S. Army Corps of Engineers or its employees.

on the water balance system alone can cause death of mollusks; additionally, the reduction of normal water flow in the mollusk body results in other disturbances in metabolism or physiological function, which will often lead to organism death. Other products cause toxic reactions to occur at gill membranes (Sprecher & Getsinger 2000).

Molluscicides are typically classified as either oxidizing or non-oxidizing compounds. Oxidizing chemicals include chlorine, chlorine dioxide, chloramines, ozone, bromine, hydrogen peroxide, and potassium permanganate (Claudi &Mackie 1994, Netherland & Getsinger 1998, Sprecher & Getsinger 2000). The information presented here focuses on those molluscicides described as non-oxidizing chemicals.³

Non-oxidizing chemicals (including organic film-forming antifouling compounds, gill membrane toxins, and nonorganics) can be classified into several distinct groups: quanternary and polyquaternary ammonium compounds (Clam-Trol®, some formulations of Bulab®, and Barquat Molluscicide 80); aromatic hydrocarbons (some formulations of Bulab®); endothall as the mono (N,N-dimethylalkylamine) salt (TD2335 Industrial Biocide-Molluscicide); metals and their salts (copper sulfate formulations and NatrixTM); and niclosamide (some formulations of Bayluscide). Bayluscide was initially developed as a sea lamprey larvicide, but has molluscicidal activity (Andrews et al. 1982; Sprecher & Getsinger 2000; Giovanelli et al. 2002).⁴ Non-oxidizing molluscicides have a higher pervolume cost than oxidizing chemicals, but remain cost-effective due to lower use rates, short exposure time requirements, and rapid toxicity. Sprecher and Getsinger (2000) reported that these products often provide better control of adult mussels, due to the inability of mussels to detect them; as such, mollusk shells remain open and shorter exposures to the toxicant are required. While some of these products are biodegradable, many require detoxification or deactivation to meet state and Federal discharge requirements (McMahon et al. 1993).

Prior Applications: Most of the non-oxidizing molluscicides were originally developed for bacterial disinfection and algae control in water treatment systems (Claudi & Mackie 1994). The use of molluscicides is a recognized procedure by the World Health Organization for the treatment of waters infested with snails carrying parasites that cause schistosomiasis⁵ (McCullough et al. 1980; McCullough 1992).

There is limited information published in scientific literature concerning prior application and effectiveness of molluscicides on mollusk species of the ANS of Concern – CAWS (particularly the European fingernail and pea clams and the European stream valvata); however, some information exists on other invasive mollusk species and may be applicable. Molluscicides have been utilized extensively against the invasive zebra mussel (*Dreissena polymorpha*) (McMahon et al. 1993; Waller et al. 1993; Claudi & Macki 1994; Piccirillo et al. 1997; Netherland & Getsinger 1998; Sprecher & Getsinger 2000). Most molluscicides have very restricted uses due to their toxic effects on non-target aquatic organisms, and are primarily used in closed-end industrial systems or recirculating and once-through cooling water systems (Claudi & Mackie 1994; Sprecher & Getsinger 2000). Niclosamide (as

³ For further information on the oxidizing chemicals listed, please see the fact sheet titled "Biocides for Industrial Use."

 $[\]frac{4}{5}$ For further information on Bayluscide use to control fish, please see the fact sheet titled "Piscicides."

⁵ Schistosomiasis is a parasitic disease caused by worms of the genus *Schistosoma*. It is a chronic illness that can damage internal organs in humans and impair growth and cognitive development in children. Freshwater snails serve as a host in the *Schistosoma* life cycle.

the formulation Bayluscide 70% Wettable Powder) is currently labeled by the USEPA as a molluscicide for control of snail populations in aquaculture ponds (USEPA, 2004). Niclosamide has been used to control ram's horn snail (*Helisoma* sp.) infestations in commercial channel catfish ponds (Terhune et al. 2003). The ram's horn snail was identified as the intermediate host in the life cycle of a trematode (*Bolbophorus* sp.) which caused high mortality rates and decreased production in channel catfish (Terhune et al. 2003). Niclosamide is designated as a restricted use pesticide by the USEPA; therefore it can be purchased and used only by trained and certified applicators to avoid possible adverse human health and environmental effects (USEPA 2004).

Copper and potassium salts have lethal activity against mussels and have been used primarily to control zebra mussels and snails that are hosts to parasites that cause schistosomiasis. In addition, Hosea and Finlayson (2005) reported that copper sulfate solutions containing 252 mg/L copper, were effective for controlling New Zealand mudsnails (*Potamopyrgus antipodarum*) from infested wading and angling gear. Copper products (copper sulfate and copper carbonates or chelates) can be used to control mollusks in open water systems, but require a Special Local Need Label (also known as a Section 24-c) issued by the USEPA. A lake-wide application of copper sulfate (as pentahydrate crystals) was applied to Lake Offutt, Offutt Air Force Base, Nebraska, in 2008, under a Special Local Need Label, in an attempt to eradicate zebra mussels (URS Group, Inc. 2009). Copper sulfate applied at a rate of 1 part per million (ppm) was effective for controlling zebra mussels in Lake Offutt; however, some non-target fish mortality was observed following treatment. Similarly, a Special Local Need Label is available for the use of the copper carbonate formulation, Natrix[™], for control of invasive and exotic aquatic mussels, snails, oysters and clams in Idaho (SePRO Corporation 2011a), Georgia (SePRO Corporation 2011b), Missouri (SePRO Corporation 2010a), South Carolina (SePRO Corporation 2010b), and Texas (SePRO Corporation 2010c).

Laboratory and field trials conducted by Piccirillo et al. (1997) to evaluate the mollusicidal effects of TD2335 showed that an 8-hour exposure to concentrations of 2 mg/L and higher controlled zebra mussels. A 1-hour exposure to 80 mg/L endothall (as the dimethylalkylamine salt; active ingredient in TD2335 Industrial Biocide-Molluscicide) killed 100% of red-trimmed milania snails (*Melanoides tuberculata*) in studies by Mitchell et al. (2007).

General Effectiveness: When properly applied and in accordance with product label directions, molluscicides can be effective for controlling targeted mollusks. Currently, only copper sulfate and copper chelate formulations have been utilized as a viable molluscicide treatment in open water systems with proper permitting. Niclosamide may be used for controlling snail (mollusks) populations in aquaculture ponds.

Operating Constraints: Constraints for using molluscicides in aquatic environments will be defined on the manufacturer product label and may include: restrictions on water use after application; when, where, and how the product can be applied; frequency and maximum rate of application; conditions that can reduce product efficacy; and potential impacts to sensitive, non-target species. Continuous use of copper-based molluscicides may result in an accumulation of copper in sediments and, consequently, may restrict sediment reuse and disposal (Cooke et al. 1993).

Cost Considerations: The cost of this technology would depend on product choice and method and rate of application.

Implementation: Implementation costs would involve planning, purchase and application of the molluscicide. Most products are labeled for treatment of mollusk-infested waters in closed systems, and application of chemicals to treat mollusks in open water may require special labeling from the USEPA.

Planning and design activities in the implementation 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:* Operation and maintenance costs would include monitoring effectiveness of treatment and reapplication for long-term control, and may include a water quality monitoring program. Other possible costs include "detoxification", as some molluscicides require detoxification prior to discharge of treated water, since they are harmful to fish and other aquatic organisms.
- *Mitigation:* Design and cost for mitigation measures required to 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.

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