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Zebra Mussel Research Technical Notes

Section 3 — Control Strategies

Technical Note ZMR-3-18

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Chemical Control Research Strategy for Zebra Mussels

Background and purpose

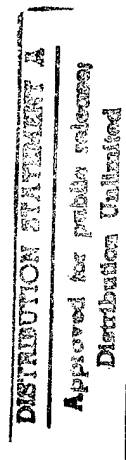
Chemical control is a versatile and proven cost-effective method that can be used in a reactive manner to rapidly reduce the impacts of an established zebra mussel infestation. In addition, chemicals can be used proactively to prevent zebra mussel establishment at susceptible public facilities. Facilities identified as susceptible to zebra mussel infestation include those associated with raw water systems used in potable water treatment, agricultural irrigation, industry, and power generation (for example, intake structures and cooling water, irrigation, house service water and fire protection lines) and those associated with management and control of inland waterways (including navigation structures, water level control structures, vessel locks, stream level gauging stations, pumping stations, and drainage structures) (McMahon, Ussery, and Clarke 1994).

Zebra mussel infestations in facilities associated with raw water intakes are readily amenable to chemical treatment due to the closed nature of the piping systems; however, treatment of structures associated with inland waterways presents greater technical difficulties as well as increased environmental concerns due to the requirement for direct application to source waters.

The Non-indigenous Aquatic Nuisance Prevention and Control Act of 1990 (Public Law 101-646) required the Secretary of the Army to develop a program of research and technology development for the environmentally sound control of zebra mussels at public facilities. The Zebra Mussel Research Program at the U.S. Army Engineer Waterways Experiment Station (WES) was initiated to develop environmentally compatible control strategies. Although several nonchemical alternatives are presently under consideration or development, it is likely that chemicals will remain an important part of an integrated approach to zebra mussel control. Therefore, research and guidance on the safe and effective use of chemicals should be continued.

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Since the majority of zebra mussel chemical control in the United States is conducted with chlorine, state or Federal restrictions on the use or discharge of chlorine could have significant impacts on current chemical control strategies in raw water systems. Concerns about the continued and increasing use of chlorine have prompted research into alternative chemicals (Waller and others 1993). The purpose of this technical note is to summarize available chemical options and to establish a framework for identifying new, environmentally compatible compounds for future evaluation as zebra mussel control agents.

Additional information

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Chemical control

If a zebra mussel-fouled facility is forced into an operational shutdown, chemicals can be applied to rapidly reduce or eliminate the infestation. While this once-through off-line method may actually reduce chemical requirements and environmental impacts, economic losses associated with downtime, mussel removal and disposal, and loss of system performance have been identified as disadvantages (McMahon, Ussery, and Clarke 1994). In contrast, on-line technologies that do not result in facility downtime include a reactive approach, for mitigating existing zebra mussel infestations before they have a detrimental impact on facility operation, or a proactive approach, in which continuous or semicontinuous low rates of chemical are applied to deter veliger settlement.

Oxidizing compounds

Chemical agents for zebra mussel control are classified as either oxidizing or nonoxidizing compounds. Available oxidizing chemicals presently used or proposed for zebra mussel control include compounds such as chlorine, chlorine dioxide, ozone, and potassium permanganate. Oxidizers are quite effective at preventing zebra mussel establishment; however, their high level of toxicity to nontarget species requires that discharge limits be strictly regulated. Problems associated with the use of oxidizers include enhanced corrosion of facility components and requirements for special handling and storage (McMahon, Shipman, and Long 1993). While treatments with oxidizers can be very effective for controlling zebra mussels, costs for onsite generation of certain compounds (for example, ozone or chlorine dioxide, ClO_2) can be quite high. In addition, adult zebra mussels can often detect oxidizers (chlorine), flush mantle water, and seal their valves for up to 2 weeks, requiring longer exposure periods and therefore increased amounts of chemical to control established populations (Claudi and Evans 1993).

Because of its low cost, excellent history of efficacy, and current acceptance for use by regulatory agencies, chlorine is the most heavily used chemical (oxidizing or nonoxidizing) for zebra mussel

control. Research that has been conducted to improve the performance of chlorine serves as a good model for future work with zebra mussel chemical control agents. Chlorine research has played a significant role in reducing use rates and promoting more effective treatment strategies. Treatment options now include periodic (regular elimination of adults from system), intermittent (high rates at intervals to eliminate newly settled post-veligers), continuous pulse (takes advantage of mussel shell opening and closure response to chlorine), and continuous (low rates to eliminate incoming veligers) applications (Claudi and Evans 1993, Jenner and Janssen-Mommen 1993, Claudy and Mackie 1994).

The widespread and expanding use of chlorine for zebra mussel control has increased concerns regarding the effects of its cumulative discharge on the environment. The high level of nontarget toxicity and possible formation of potentially hazardous by-products (trihalomethanes) are under scrutiny. Although it is likely that chlorination will remain the standard treatment for raw water systems due to its cost-effectiveness and predictable zebra mussel control, an integrated approach involving chemical and nonchemical technologies needs to be developed to reduce reliance on chlorine and provide practical alternatives in case its use is restricted.

The use of the oxidant ClO_2 as an alternative to chlorination for the control of zebra mussels has shown promise and is currently being investigated by several groups (Garrett and Laylor 1995; Rusznak and others 1995; Rybarik, Byron, and Germer 1995; Tsou and others 1995). Results indicate that excellent veliger and adult mussel control can be achieved using ClO_2 at rates of 0.25 to 5.0 mg/L for 3 to 9 days. Potential benefits of ClO_2 over chlorination include the following: efficacy at lower concentrations, and no production of trihalomethanes; not affected by pH or ammonia; and shorter treatment duration, which has less effect on station operation (Tsou and others 1995). Potential disadvantages of ClO_2 use include the requirement for onsite generating equipment; storage of HCl, NaOCl, and HOCl as precursors; high oxidant demand in the system, which requires higher treatment rates and can reduce efficacy on zebra mussels; and conversion of ClO_2 to chlorite, which limits the amount of ClO_2 that can be applied without excessive chlorite discharge.

Nonoxidizing compounds

One potential alternative to chlorine or other oxidizing biocides is the use of nonoxidizing molluscicides. McMahon, Shipman, and Long (1993) and Green (1995) have listed several potential advantages of nonoxidizing chemicals versus oxidizers including: a) cost-effectiveness (due to lower use rates and rapid toxicity); b) better control of adult mussels versus chlorine; c) inability of mussels to detect treatment resulting in shorter exposure requirements; d) ease of application and minimal maintenance and cost of application equipment; e) noncorrosive properties; and f) readily inactivated and no formation of toxic by-products. Nonoxidizers are generally proprietary chemicals and therefore are often more costly on a per-volume (for example, gallon) basis than oxidizing chemicals. Nonetheless, the increased per-volume cost

must be balanced against lower use rates, shorter exposure requirements, and different application strategies.

Treatment with nonoxidizing compounds is usually conducted on a periodic basis during the warm-water season to remove newly settled mussels or adults. Due to the reactive nature of these treatments, it is important that nonoxidizers are used in coordination with veliger and mussel settlement data to minimize the frequency of applications (Green 1995). In addition, water temperature should be closely monitored to determine the treatment concentration and length of exposure required. While it is unlikely that nonoxidizers would be cost-effective using a continuous application technique, they can be less expensive and more efficacious than oxidizers if applied as intermittent, periodic, or semicontinuous applications for adult mussel control.

The list of nonoxidizing compounds that have received Federal and state approval for once-through control of zebra mussels is fairly limited. The majority of approved nonoxidizing compounds are polyquaternary ammoniums such as Bulab 6002, Calgon H-130, MacTrol 7326, and Clamtrol Ct-1. In addition, the aromatic hydrocarbon Bulab 6009 is also currently registered. Potential disadvantages of the Bulab products include their long-term exposure requirements (200 to 800 hr) (McMahon, Shipman, and Long 1993, Martin and others 1993b) and comparatively high toxicity to fish (Waller and others 1993). Calgon H-130 and Clamtrol Ct-1 both showed rapid zebra mussel toxicity at relatively low use rates (1.0 to 2.0 mg/L for 6 to 24 hr) (McMahon, Ussery, and Clarke 1994). Although both of these compounds are biodegradable, they often require detoxification by complexing with negatively charged particles such as bentonite clay. Following adsorption onto clays and naturally occurring anionic substrates, polyquaternary ammonium compounds are strongly bound and are not harmful to aquatic, benthic, or microorganisms (Dobbs and others 1995). A review of the comparative target and nontarget toxicity of registered molluscicides as well as several other compounds showing potential for zebra mussel control is provided by Waller and others (1993).

Recent research thrusts in the zebra mussel chemical control area include life-stage efficacy testing (Fisher and others 1994), nontarget toxicity of various chemicals (Waller and others 1993), potential synergistic reactions between oxidizing and nonoxidizing chemicals, application techniques to take advantage of zebra mussel response (Martin and others 1993b), and temperature effects on chemical efficacy (Martin and others 1993a). Research on the chemical control of zebra mussels has provided guidance for minimizing use rates, identifying new products, and applying unique treatment strategies to reduce the environmental impact of a chemical application.

New products

Length of time (5 to 10 years) and high costs (\$10 to \$20 million) associated with registering a new pesticide with the U.S. Environmental Protection Agency (EPA) (Burns 1994) severely limit the development by industry of new compounds for zebra mussel control. Any new zebra mussel control products will likely be

identified from currently registered products considered by industry for expanded uses. Selection of new chemicals for zebra mussel control research should emphasize those that have the greatest potential to improve on current options and have a good chance to receive EPA approval for use. The following criteria will be followed for selecting new chemicals for evaluation under the Zebra Mussel Research Program:

- Efficacious with potential for cost-effective control of zebra mussels.
- Nonpersistent with no detoxification required.
- Low to intermediate nontarget toxicity.
- Likely to be submitted to EPA and approved for use.
- No bioaccumulation or formation of toxic metabolites.

Using these criteria, it is not likely that new oxidizing chemicals will be identified; however, some nonoxidizing products being investigated by industry show potential. It is interesting to note that none of the currently registered chemicals used for zebra mussel control (for example, chlorine, polyquats) would strictly adhere to the above guidelines. Therefore, use of these criteria may aid in the identification of more environmentally compatible chemicals.

Research thrusts

The compound TD 2335 (Elf Atochem North America) has been identified as a new candidate molluscicide that meets the criteria established above and deserves further research attention. TD 2335 contains the active ingredient endothall, a highly water-soluble dicarboxylic acid, currently EPA-registered for use in aquatic systems as an algicide/herbicide. This compound has a long history (over 30 years) of direct aqueous application, and its effects on aquatic ecosystems have been extensively studied (Elf Atochem 1992). Endothall is nonpersistent and is rapidly degraded by microbes to carbon, hydrogen, and oxygen (Simsiman 1976). Its short persistence and rapid mineralization (to C, H, and O) indicate that endothall does not bioaccumulate, form toxic metabolites, or require detoxification. Preliminary laboratory and field studies have shown that TD 2335 is efficacious on zebra mussels at rates of 0.5 to 1.5 mg/L for a 3- to 12-hr exposure time. These rates and exposure times would be expected to produce low to intermediate nontarget toxicity. Preliminary evidence also suggests that TD 2335 application at the lower rate of 0.5 mg/L results in byssal thread detachment (personal communication, Vincent Picirillo, NPC, Inc., Sterling, VA).

Determination of the efficacy, concentration/exposure requirements, optimal application strategies, and nontarget toxicity of TD 2335 for zebra mussel control requires further evaluation. The recommended use rates and treatment strategies will ultimately determine if TD 2335 use is cost-effective and environmentally sound. Its history of application to open-water aquatic sites suggests the potential to expand this chemical control option to facilities or components of facilities not currently considered for treatment due to environmental or label restrictions on other efficacious compounds. While these types of

treatments would not be recommended on a routine basis, they could be used to respond to an emergency situation.

Research with TD 2335 in the near future will include efficacy evaluation of various endothall concentrations and treatment strategies at the Cleveland Eastlake hydroelectric power plant on Lake Erie. Although initial demonstrations will not be conducted at Corps facilities, the Corps of Engineers operates 75 hydroelectric power plants, all of which have been identified as being susceptible to zebra mussel fouling. In addition to power plants, navigation lock and dam facility components such as transducers, gauging stations, raw water cooling systems, and project irrigation and fire prevention lines have been identified as critical components that cannot tolerate zebra mussel infestations. Information gained from these operational pilot studies can be used to provide guidance for controlling zebra mussels at Corps or other public facilities.

Research and development benefits

Determining optimal treatment rates and regimes for these highly susceptible facilities or components of facilities will be incorporated into research and development plans. Furthermore, the ability to reduce the environmental impact following a chemical treatment for zebra mussel control will be emphasized. Zebra mussel chemical control research will focus on employing the minimum effective chemical use rates and most effective application strategies. This approach will provide operational guidance on environmentally compatible and cost-effective chemical strategies for controlling zebra mussels.

References

- Burns, F. M. (1994). "Registration process required by the USEPA for a new pesticide," Technical Note ZMR-1-22, Zebra Mussel Research Program, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Claudi, R., and Evans, D. W. (1993). "Chemical addition strategies for zebra mussel (*Dreissena polymorpha*) control in once-through service water systems." *Zebra mussels: Biology, impact and control*. T. F. Nalepa and D. W. Schloesser, ed., Lewis Publishers, Boca Raton, FL, 563-74.
- Claudi, R., and Mackie, G. L. (1994). *Practical manual for zebra mussel monitoring and control*. Lewis Publishers, Boca Raton, FL.
- Dobbs, M. G., Cherry, D. S., Scott, J. C., and Petrille, J. C. (1995). "Environmental assessment of a alkyl dimethyl benzyl ammonium chloride (ADBAC) based molluscicide using laboratory tests." *Proceedings, 5th International Zebra Mussel and Other Aquatic Nuisance Organisms Conference*. 87-101.
- Elf Atochem. (1992). "Review of the effects of endothall products on aquatic ecosystems," Philadelphia, PA.
- Fisher, S. W., Dabrowska, H., Waller, D. L., Babcock-Jackson, L., and Zhang, X. (1994). "Sensitivity of zebra mussel (*Dreissena polymorpha*) life stages to candidate molluscicides," *Journal of Shellfish Research* 13, 373-77.
- Garrett, W. E., and Laylor, M. M. (1995). "The effects of low level chlorination and chlorine dioxide on biofouling in a once-through

service water system." *Proceedings, 5th International Zebra Mussel and Other Aquatic Nuisance Organisms Conference*. 133-51.

Green, R. F. (1995). "Strategies for application of non-oxidizing biocides." *Proceedings, 5th International Zebra Mussel and Other Aquatic Nuisance Organisms Conference*. 175-81.

Jenner, H. A., and Janssen-Mommen, J. P. M. (1993). "Monitoring and control of *Dreissena polymorpha* and other macrofouling bivalves in the Netherlands." *Zebra mussels: Biology, impact and control*. T. F. Nalepa and D. W. Schloesser, ed., Lewis Publishers, Boca Raton, FL, 537-54.

Martin, I. D., Mackie, G. L., and Baker, M. A. (1993a). "Acute toxicity tests and pulsed-dose delayed mortality at 12 and 22 °C in the zebra mussel (*Dreissena polymorpha*)," *Archives of Environmental Contamination and Toxicology* 24, 389-98.

Martin, I. D., Mackie, G. L., and Baker, M. A. (1993b). "Control of the biofouling mollusc *Dreissena polymorpha* (Bivalvia: Dreissenidae) with sodium hypochlorite and with polyquaternary ammonia and benzothiazole compounds," *Archives of Environmental Contamination and Toxicology* 24, 381-88.

McMahon, R. F., Shipman, B. N., and Long, D. P. (1993). "Laboratory efficacies of nonoxidizing molluscicides on the zebra mussel (*Dreissena polymorpha*) and Asian clam (*Corbicula fluminea*)." *Zebra Mussels: Biology, impact and control*. T. F. Nalepa and D. W. Schloesser, ed. Lewis Publishers, Boca Raton, FL, 575-98.

McMahon, R. F., Ussery, T. A., and Clarke, M. (1994). "Review of zebra mussel control methods," Technical Note ZMR-2-14, Zebra Mussel Research Program, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Rusznak, L., Smolik, N., Hale, L., and Freymark, S. (1995). "Evaluation of the potential of chlorine dioxide for use in zebra mussel veliger control." *Proceedings, 5th International Zebra Mussel and Other Aquatic Nuisance Organisms Conference*. 371-78.

Rybarik, D., Byron, J., and Germer, M. (1995). "Chlorine dioxide treatment for zebra mussel control." *Proceedings, 5th International Zebra Mussel and Other Aquatic Nuisance Organisms Conference*. 379-98.

Simsiman, G. V. (1976). "Diquat and endothall: Their fates in the environment," *Residue Reviews* 62, 131-74.

Tsou, J., Coyle, J., Pallo, S., Massalli, Y., and Martin, P. (1995). "Evaluation of the use of chlorine dioxide to control zebra mussels." *Proceedings, 5th International Zebra Mussel and Other Aquatic Nuisance Organisms Conference*. 461-74.

Waller, D. L., Rach, J. J., Cope, W. G., Marking, L. L., Fisher, S. W., and Dabrowska, H. (1993). "Toxicity of candidate molluscicides to zebra mussels (*Dreissena polymorpha*) and selected non-target organisms," *Journal of Great Lakes Research* 19(4), 695-702.