A REVIEW OF FRESHWATER MACROBIOLOGICAL CONTROL METHODS FOR THE POWER INDUSTRY

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BACKGROUND

Prior industry surveys have estimated that condenser biofouling, on average, accounts for a 3% loss in generating unit availability, of which 40% can be attributed to macrobiological fouling (Chow, 1985). These proportions have certainly risen with the spread of freshwater zebra and quagga mussels (Dreissena polymorpha and D. bugensis), and the introduction of the large green mussel, Perna viridis, to US coastal waters in 1999. United States waters play host to a wide range of indigenous saltwater macrofouling species. Approximately 12% of US generating stations use saltwater cooling circuits, and a considerable body of power plant experience has been developed in coping with saltwater macrofouling, much of which is directly transferable to freshwater power plants. Unfortunately, many of the methods are an integral part of the facility design and may only be applicable to new plant construction. Europe has had greater experience in coping with freshwater macrofouling species, much of which can be applied to US facilities despite differing environmental regulations. Facilities in the southern areas of the country have had much greater experience with Asiatic clam (Corbicula fluminea) macrofouling than those in the Midwest. Research into more selective and environmentally benign control methods has been ongoing for several years in the public and private sectors, notably by EPRI (Electric Power Research Institute). The purpose of this paper is to provide a brief review of the many successful control methods, with a strong emphasis on the practical, the available and the economical methods for electric utilities today. The most appropriate control strategy for a particular installation is dependent on several factors which are often specific to facility design and operation. Consequently, no single macrofouling management option will be optimal for all power plants. In deference to the location of this conference, and the predominance of freshwater cooling circuits for US power plants, only freshwater macrofouling species will be considered. Although freshwater bryozoans ("Moss Animacules") are an occasional problem for power plants on captive northern lakes, and gastropods (snails) are occasionally a problem in cooling towers, the dominant freshwater macrofouling species in the northern half of the United States are the zebra mussel (Dreissena polymorpha) and the Asiatic clam (Corbicula fluminea). This paper will focus on control measures for those two species, although many of the techniques can be adapted to other macrobiological species as well.

Know Thine Enemy

The Asiatic clam and zebra mussel are familiar to most of us as small, hard-shelled mollusks. A very brief overview of their biology is essential to develop successful facility-wide management and control strategy. Mollusks are "bivalve" filter feeders, which feed by siphoning and exhausting water through a pair of small siphons, straining plankton and absorbing oxygen as the water passes over their gills. Both freshwater mollusks share a number of traits which enable them to out-compete and dominate other organisms in the environment and in power cooling circuits. These include:

- Lengthy spawning season, early spring to late fall
- Prolific reproductive capacity, 10,000 to 40,000 veligers per year per spawning adult
- Lengthy planktonic stage facilitates dispersal
- Colonization in dense populations, up to 10,000 organisms per square foot
- Broad temperature tolerance band, 32-95°F
- Tolerance for inimical environmental conditions (close shell, avoid contact)
- Exotic (introduced) species, few natural predators
- Relatively short life cycle
- High growth rates
- No parasitic larval stage

The last point merits further elaboration. Most native mollusks have a parasitic larval stage, generally attachment to the gills of a host fish. Consequently, the success of the mollusk is inexorably linked to the success and availability of a host population. This parasitic stage greatly limits the effective fecundity of native bivalve mollusk species to the relative few larvae that successfully locate and parasitize an appropriate fish host (McMahon, 1983). The Asiatic clam and zebra mussel are unique in that their larval development has no requirement for a host species. Consequently, their proliferation within the screened confines of a power plant cooling system is unrestrained by the relative absence of fish. In fact, the lack of fish and other predators within the screened intake structure contributes greatly to their success in colonizing those areas.

Asiatic Clams

The Asiatic clam (Corbicula fluminea) is thought to have been introduced to the Pacific Northwest as a food source by immigrant Asian workers in the 1930's. It has spread throughout the Southeast, and is now found in 40 of the 48 contiguous United States. Asiatic clams are hermaphroditic (capable of self-fertilization). There are generally two spawning peaks; a major peak in the spring and a smaller one in the fall, although some spawning is likely to occur throughout the warmer months in favorable environments. Veligers 100-200 microns in size are released from the spawning adult already equipped with a thin, transparent protective shell. Under favorable conditions, the veligers reach sexual maturity in six months, releasing a second generation of offspring in a single season. The larvae and juvenile clams are small enough to pass through the bar racks and traveling screens designed to guard the cooling system from debris. Once within the protective screening elements, they are capable of anchoring themselves to hard substrates with a mucosal byssus thread under gently flowing conditions up to a water velocity of approximately 1.5 feet per second (fps). As they grow to maturity within the protective confines of the intake structure, they lose their ability to attach and are strictly creatures of water velocity, being swept away by water velocities in excess of 1.5 fps. Relic shells are transported by water currents in excess of ½ -1 fps. A good rule of thumb is that Asiatic clams are found wherever one would expect to find silt and fine sand in infested waters. The adult uses its fleshy "foot" to burrow into substrates, leaving only its siphon tubes exposed (Figure 2). In Illinois, Asiatic clams will reach a size of approximately ½ inch at the end of the first season, ¾ inch by the end of the second season, and 1 inch after the third season.

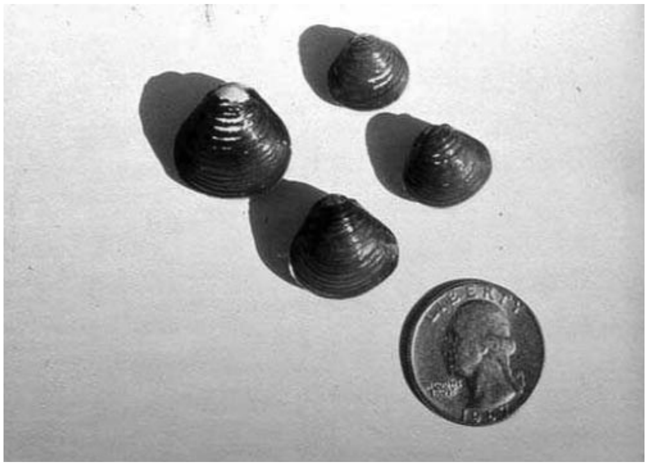


Figure 1: Asiatic clams shown next to quarter for size comparison.

Figure 2: Asiatic clams in natural sandy substrate, siphon tubes extended.

Growth rates in consistently warm, favorable areas can be significantly faster, with a peak size of 1.25-1.75 inches after 4 to 5 years. Asiatic clams are very tolerant of low dissolved oxygen conditions (1-2 ppm) for extended periods, and can even thrive in fire protection systems which are anoxic for short periods. The Asiatic clam forms a comparatively thick shell, and has little trouble forming a shell even in waters that are significantly undersaturated with respect to calcite (negative LSI). They tolerate high temperatures up to 95°F and low temperatures down to 32°F for short exposures. The adults and relic shells have been observed to pile up as high as 10-14 feet in low flow areas in the corners of intake structures. The clams and relic shells reach an angle of repose and are eventually swept into the cooling system, where they become lodged on tube sheets or within tubes.

Zebra Mussels

The first successful zebra mussel (Dreissena polymorpha) colonization in US waters is believed to have occurred in 1986 in Lake St. Clair, which lies between Lake Huron and Lake Erie at Detroit. It is generally accepted that the mode of introduction was ballast water discharge from a commercial ship traveling from a European port. One tantalizing speculation is that the US - Russian grain embargo resulted in grain ships travelling to freshwater Canadian ports instead of to saltwater US ports. There is widespread belief that tighter environmental controls improved water quality in the lower Great Lakes to the point where it presented a suitable habitat for the first time in decades. Whatever the means of introduction, the zebra mussel has become rapidly and firmly entrenched on the

Figure 3:* *Cluster of zebra mussels showing characteristic striped shell.

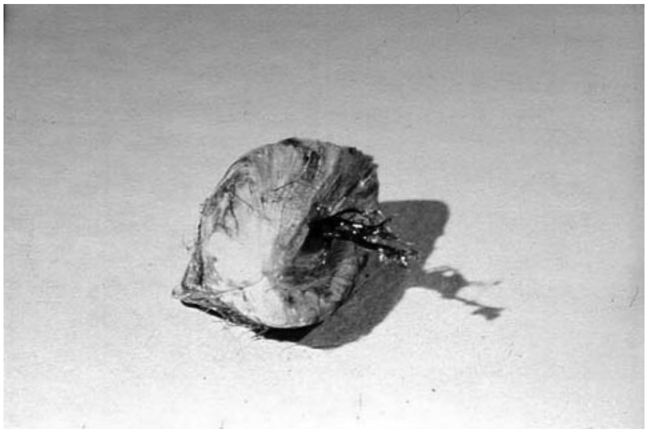


Figure 4:* *Zebra mussel removed from substrate, showing byssus threads.

North American continent. Its range now includes all five Great Lakes, Lake Champlain, the Ohio and Mississippi drainage areas through New Orleans, and many freshwater lakes from Wisconsin to New England. Zebra mussels are thought to have evolved from saltwater mollusks in the Caspian Sea as the sea was transformed from a saltwater sea to a fresh water lake eons ago. They retained one adaptive trait of the saltwater mollusks - the ability to attach firmly to hard substrates through a mass of tough byssus threads secreted one at a time from a gland in the foot.

The zebra mussel and its close relative, the quagga mussel (Dreissena bugensis), are the only fresh water mollusks that have the ability to attach firmly to hard substrates. However, their attachment capabilities are more limited than those of common salt water mollusks. Zebra mussel colonization is sparse or nonexistent under continuously flowing water velocities above 3.0-4.0 fps, whereas the common salt water blue mussel (Mytilus edulis) is known to colonize substrates up to 6-7 fps. However, zebra mussels will attach at localized low flow areas, such as expansion joint crevices, the depressions in corrugated pipe, and water box manway edges even when the superficial water velocity is above 4 fps.

Unlike the Asiatic clam, zebra mussels have separate sexes and fertilization is external. According to the literature, an adult female releases from 30,000 to 1 million eggs per spawning event and may lose nearly half its soft tissue weight during spawning. The fertilized eggs develop into a planktonic veliger stage approximately 70-100 microns in size. The planktonic stage lasts for 1-2 weeks or longer, allowing thorough dispersal throughout lakes, rivers and cooling systems. Veliger densities as high as 500,000 /m^3 have been reported in Lake Erie in late summer. Settlement densities can reach 10,000 /ft^2, as the organisms literally cover every square inch of hard surface, including the shells of other zebra mussels and mollusks. Once thought to colonize only hard surfaces, they have been observed to colonize sandy and even silty substrates under favorable water conditions. Zebra mussels are less tolerant of poor water quality than are Asiatic clams. The Zebra Mussel Risk Assessment Calculator offered by the Zebra Mussel Information System (ZMIS) offers a "slim to none" risk assessment for dissolved oxygen (DO) less than 4.6 ppm. Zebra mussel shells are thick enough to block cooling circuits, but thinner than Asiatic clam shells. The zebra mussels apparently find it energetically unfavorable to form shells in waters that are significantly undersaturated with respect to calcite. Their lack of success in the southeastern states is frequently attributed to low pH and calcium. By contrast, waters flowing over the predominantly limestone substrata in the US Midwest (and in most of Europe) are often supersaturated with respect to calcite and support some of the highest recorded zebra mussel population densities.

Zebra mussels are less tolerant of high water temperatures than Asiatic clams and will not withstand temperatures greater than 90°F for more than a few days. They are more tolerant of colder water than Asiatic clams, and will resist extended periods at 32°F. Table 1 below compiled by the US Army Corps of Engineers in 1993 using data from the New York State Sea Grant Zebra Mussel Clearinghouse provides a reasonable assessment of zebra mussel colonization potential as a function of water quality (Tippit and Miller, 1993).

As with the Asiatic clams, the zebra mussel larvae readily pass through traveling screens and colonize within the cooling system. Zebra mussels preferentially colonize vertical surfaces, whereas adult Asiatic clams are found exclusively in low velocity areas on the horizontal surfaces. Their ability to attach poses additional threats to power plant operation. The zebra mussels can colonize on top of each other, bridging

Variable	***High***	***Moderate***	***Low***	***V. Low***
Salinity, ppt	0 - 1	1 - 4	4 - 10	10 - 35
Ca (as $CaCO_3$), ppm	62 - 312	50 - 62	30 - 50	<30
pH	7.4 - 8.5	7.0 - 7.4 8.5 - 9.0	6.5 - 7.0	<6.5 >9.0
Water Temp. (°F)	63 - 77	77 - 81	59 - 63	<59, >81
Turbidity, cm (Secchi Disk)	40 - 200	20 - 30	10 - 20 200 - 250	<10, >250
Dissolved Oxygen, ppm	8 - 10	6 - 8	4 - 6	<4
Water Velocity (ft/sec)	1.6 - 2.3	0.3 - 1.6 2.3 - 3.3	3.3 - 6.6	>6.6

Table 1: Effects of water quality on zebra mussel colonization

openings much larger than the diameter of an individual shell. This frequently results in an excessive pressure drop across bar screens ("trash racks"), which are generally not equipped to remove them. Zebra mussels can also break loose in clusters, enabling them to block small diameter pipes larger than a single shell diameter. They can also colonize inside pipes several inches in diameter, severely restricting flow. The 6-in. pipe section below was removed from a BetzDearborn biomonitoring trailer after a three-month evaluation at a power plant in heavily infested waters.

The average growth rate of zebra mussels is similar to that of Asiatic clams, the rule of thumb being approximately 1 mm growth per month. Zebra mussels in the Illinois area can be expected to attain a shell size of $^{5}/_{8}$ inch in their first season of growth, 1 inch at the end of the second, and 1¼ inch after the third season of growth. The average life span for adult zebra mussels in the natural environment is probably 3½ years, but individuals often live to 5 years. Growth rates in favorable areas such as the western basin of Lake Erie, have been reported to be nearly double the averages listed above during the first year of growth.

Figure 5: Zebra mussels colonizing a ladder in an intake structure.

Available Control Methods

Fresh water macrobiological control methods applicable to power plants can be broadly classified into 5 categories.

- Mechanical
- Physical
- Thermal
- Paints and Coatings
- Chemical

All of the above control strategies have achieved a reasonable measure of success at some stations, and will be considered in greater detail in the succeeding sections.

Figure 6: Zebra mussels clog 6-in. biomonitoring trailer discharge pipe after only three months.

Mechanical Control Methods

Mechanical controls involve screens, strainers and filters, all of which can play a role in the success or failure of the macrofouling control program. Generally speaking, mechanical control methods are favored because of their minimal environmental impact, but limited in their effectiveness by the practical aspects of removing microscopic larvae from the large water flows typical of power generating facilities. High capital costs and physical plant constraints also limit the ability to retrofit existing facilities.

Screens

All power plants have an intake screen system of one form or another to prevent the water circuit from entraining macrofouling fish and debris. In US power plants, water intakes take the form of either a shoreline intake equipped with a coarse bar screen followed by a $^3/_8$-inch mesh traveling screen, or an offshore intake. The onshore intake is used where there is consistent and reliable deep water close to the shore. Offshore intakes involve an offshore intake structure connected to an onshore pumping facility with an inlet tunnel or pipe. Screening systems for offshore intakes may consist of either an offshore coarse bar screen, followed by a $^3/_8$-inch mesh traveling screen onshore in front of the pumps, or an offshore wedge-wire strainer assembly equipped with an air-pulse backwash system. The latter system is not practical for large once-through cooling systems, but can easily be applied to even the largest cooling tower intakes. Paradoxically, these intake screening systems, which were designed prior to the introduction of the Asiatic clam and zebra mussel to protect the plant from macrofouling, are generally the largest cause of macrofouling problems in infested waters. The coarse screens do nothing to restrict the entry of microscopic mollusk veligers, as illustrated in the photo below of the clean side of an intake screen. Yet, the conservative water velocities (¾ fps) in the screen pit designed to reduce fish entrainment are ideal to support the settlement and growth of clams and mussels. Moreover, they effectively strain out possible predator species while the circulating pumps maintain a steady stream of fresh plankton and oxygenated water. The screen pits or pump cribs serve as nearly perfect breeding grounds, maintaining a healthy population of adults releasing their spawn directly into the plant water systems. Intake tunnels are also generally designed with conservative water velocities in the range of 3 fps to limit pressure drop in essentially gravity or suction piping. These tunnels are often 500-1500 feet long, very often of a corrugated metal construction, and provide an enormous and productive breeding surface. Zebra mussels have a particular knack for colonizing the intake bar screens and even bridging the gap between the bars, which increases the pressure drop across the bars and eventually starves the pumps. Mussels can also colonize and restrict the flow through traveling screens, as shown below, if the operation of the screens and the knock-off water sprays is not properly attended to.

Figure 7: Asiatic clam and native unionid larvae pass through intake screen and grow to maturity on "clean" side of screen.

Figure 8: Mussels attach tightly to traveling screen.

Despite the general ineffectiveness of these screening systems, there are several steps that can reduce the extent to which they contribute to the problem. Offshore stainless steel wedge-wire straining devices can be refitted with biofouling resistant copper alloy wedge-wire. The air backwashing system can be beefed up and operated more frequently to dislodge mussel veligers before they become firmly attached. Knock-off sprays on traveling screens should be similarly inspected and repaired, and their flow capacity and spray power increased. The screens should be cycled completely at least once per shift, not just on high pressure differential, to dislodge veligers before they attach solidly. More modern "dual-flow" traveling screen designs maintain the "dirty" side of the screen on the outside and reduce the tendency to transport live mollusks and shells to the pump side of the screen. In areas where Asiatic clams are the primary macrofouling species, particular attention should be paid to the water velocities in the corners of the intake structure. Boosting the water velocity sweeping along the floor from ¾ fps to 1½ fps or above will control Asiatic clam settlement in the bay. Contouring the floor of the bay can remove low velocity breeding areas in the corners as well as reducing cavitation potential. Zebra mussel growth on the bar screens can be retarded by employing construction materials that resist attachment, such as galvanized steel, or outfitting the screens with mechanical rakes that are easily and frequently operated, scraping or hydrojetting the bar surfaces with sufficient force to dislodge juvenile zebra mussels.

Cleanliness of the intake structure and inlet tunnel is absolutely the most critical aspect of the macrofouling control program, especially in a freshwater environment. Once the circulating water pumps pick up the water, the 7 fps water velocity typical of pressurized water flow prevents Asiatic clam settlement and restricts zebra mussel attachment and growth to minor accumulations in occasional crevices. Care must be exercised for peaking facilities or facilities subject to long outages when larvae are present in the water column. During the downtime, larvae may attach and grow to maturity within the pressure piping downstream of the pump and come loose once the unit resumes operation.

Another type of screening device is aimed at reducing the tendency for shells to become lodged in the tubes. These screening devices are placed directly at the inlet tube sheet. In the simplest form, this can be a ¼-inch mesh galvanized screen laid across the face of the tube sheet, or mounted on a simple frame to stand approximately 6 inches off the tube sheet. A commercial variation is a plastic mesh device, inserted and glued into each tube inlet, which protrudes or stands off 1-2 inches from the tube inlet. Shells impinging on the mesh are directed to the tube sheet webbing between the tubes, where they have negligible impact on flow. An incidental benefit of tube sheet screening is to keep chip scale "arrowheads" out of tubes. Disadvantages are that the screens are not compatible with on-line mechanical tube cleaning systems and complicate certain maintenance activities, such as shooting scrapers through the tubes and leak detection.

Strainers

In the US power industry, strainers have traditionally been associated with relatively coarse mesh ($^1/_8$ inch) devices that protect smaller service water or auxiliary water heat exchangers from debris that might clog their generally smaller tubes. More often, these are of a self-cleaning design, capable of cleaning themselves with little operator attention. When the strainers are properly specified and designed, the velocity is sufficient to dislodge attached zebra mussels, at least in the backwash mode. Although they are uncommon in fresh water installations, in-line strainers are available in all sizes including ones capable of serving the once-through cooling needs of a nuclear power station, although they can be quite costly. Such traditional coarse strainers are useful in protecting downstream equipment from shells which break loose from the intake structure or piping. However, they are not capable of preventing the ingress of larvae, and are of limited value when downstream piping or equipment presents a suitable habitat. More recently, manufacturers have begun offering micro-fine straining elements that remove particles as fine as 60 microns, small enough to halt the passage of larvae. Although the micro-fine elements severely restrict strainer throughput and impose heavy backwash requirements, they may represent an attractive alternative for service water systems in small fossil-fueled plants or hydroelectric facilities.

Filters

Standard sand filters routinely remove particles much smaller than macrofouling larvae and are effective in protecting downstream equipment, provided the filters are properly maintained. An additional benefit is that they remove fine silt particles that might settle out in shell-side heat exchangers and other areas of low water velocity. Although pressure sand filters are usually reserved for small systems serving critical needs, a few fossil-fueled plants are equipped with sand filters for their entire auxiliary cooling system. In-ground upflow sand filters are routinely used for flows well in excess of 10,000 gpm in paper mills and other industrial installations requiring substantially silt free water. Although, to the best of the authors' knowledge, none are in operation in power plants today, upflow filters might be a reasonable alternative for some facilities depending on local environmental constraints and other options. Disadvantages of fine filtration include high capital and operating costs and high pumping costs for pressure filters.

Physical Control Methods

Physical control methods, consisting of vacuuming Asiatic clams from the floors of intake bays and scraping mussels off the walls of intake bays and tunnels, are perhaps the oldest known macrofouling mitigation measures used at power plants. Physical control methods are environmentally benign and require no significant capital expenditure. The major drawbacks to these methods are:

- The equipment generally must be capable of being taken out of service on an annual basis to provide adequate control. The cleaning can be laborious and expensive, particularly for long intake tunnels
- Visibility limitations and other difficulties of working underwater may reduce cleaning thoroughness
- The mass of decaying mollusks must be properly disposed of at additional cost
- Small diameter piping fouled with mollusk shells is often inaccessible.

With respect to Asiatic clams, which do not attach, vacuuming of horizontal surfaces is readily accomplished using divers with suction hoses. The strategy consists of vacuuming out the affected areas, principally the intake bays, before the clam shells grow to a size which threatens plant operation. The tolerated size is governed by the size of the smallest heat exchanger tube in the circuit. For typical US condensers with 1-inch tubes, a single cleaning at the annual outage affords sufficient protection. Under no circumstances should the frequency exceed 2 years, since a large portion of the population will begin to die off in 2-3 years and the relic shells are more buoyant and likely to be transported further into the system. Units with smaller tubes have been observed to experience less macrofouling problems, a factor which should be taken into consideration when designing a new facility or contemplating a new heat exchanger or condenser bundle. Power plants with salt water intakes are typically designed with 1 to 1¼ inch tubes to cope with the relatively severe macrofouling in that environment.

As with saltwater mollusks, physically removing zebra mussels is more problematic owing to the fact that they must be scraped, jetted or blasted free from the surface before they can be vacuumed out. Additionally, vertical surfaces have greater area than horizontal surfaces in a typical intake system, particularly for offshore intakes with long inlet tunnels. Various adaptations of this technology have been reported in the literature. The removal process can be accomplished underwater, using divers equipped with a tool consisting of a vacuum hose with a scraper attached to the end, or with high pressure water jets. Alternatively, the affected areas can be dewatered and blasted with water, CO_2 pellets or more conventional media. High pressure water cleaning at 4,000 - 10,000 psi works well, with little damage to most hard substrates. Carbon dioxide pellets leave no residue, are potentially less damaging to the substrate than sand, and embrittle soft tissues, rendering them easier to remove.

Another more recent addition to the physical control methods involves dewatering the structure and either freezing or desiccating the mussels. Time to mortality is reported at less than 2 hours for zebra mussel clusters exposed at 14°F and 39 hours at 29°F (Payne, 1992a). Air exposure was also reported to induce 100% mortality as a function of time, temperature, and humidity according to the following relationship (Payne, 1992b):

$$\ln(t) = 5.917 - 0.082\,(T) + 0.010\,(RH)$$

Where: t = time (hours)
T = temperature (°C)
RH = relative humidity (%)

Thermal Control Methods

Thermal control measures have been used in US saltwater installations for many years. Many of the once-through saltwater stations along the California coast were constructed with elaborate capabilities to reverse flow and send heated discharge water back through the long intake tunnels. The shock of hot water resulted in fairly rapid mortality to the macrofouling organisms adapted to the cold Pacific waters, and the reverse flow flushed the shells and other debris out of the tunnels. Although this equipment would be difficult to retrofit to existing installations, it is a reasonable and effective design feature which could be incorporated into new facilities. US freshwater facilities lack backwash capabilities. However, some stations with once-through cooling systems have been able to redirect heated effluent back to their intake area, reaching a temperature lethal to the zebra mussel in a few hours. The possibility of off-line thermal treatment of intake bays and tunnels is an attractive option that has not been fully explored. With an adequate steam supply, it is possible to rapidly elevate an off-line intake bay to temperatures that are lethal to mollusks in a matter of a few minutes. Power plants with cooling towers generally conduct an effective thermal treatment of their tower circuit for zebra mussels every summer, although Asiatic clams often survive in cooling tower basins in the northern half of the US

On-line thermal treatments must be conducted with considerable care for both the equipment and the environment. The required water temperature often sends turbine back pressures near or over the typical turbine manufacturer's limit of 5.0 in. Hg. Provided the elevated temperature can be tolerated without reducing unit load, thermal treatments can be very economical. Water temperatures that are lethal to zebra mussels and clams are also lethal to nontarget aquatic organisms. However, in today's chemo-phobic society, it is often easier to modify thermal limits than to wrestle with the intricacies of biocide regulations and environmental fate and effects issues.

Several researchers have published data on the time and temperature relationship required to control zebra mussels. As might be expected, there is considerable scatter due to the size, age, health and condition of the organisms, as well as the acclimation temperature. A more rapid temperature rise will produce equivalent mortality with shorter exposures, as will a lower acclimation temperature. A review of published data for 100% mortality at a 77°F acclimation temperature was fit to the following relationship (Jenner, et al., 1998).

$$\text{Log [exposure time (min.)]} = 11.38 - 0.251 \times T(°C)$$

Where: t = exposure time (min.)

$r^2 = 0.95$

Asiatic clams can also be treated thermally. However, their tolerance for slightly higher (~5°F) temperatures than zebra mussels makes this more difficult to accomplish on-line. Additionally, the clams will be found along the bottom of gently flowing areas, and the less dense hot water will tend to stratify along the top unless adequate mixing is provided.

Due to the speed with which thermal treatments can be accomplished (hours vs. days for many other methods), thermal treatments are amenable to periodic off-line applications at regularly scheduled outages, or whenever a single intake bay or section of pipe can be taken out of service for a few hours. Power plants which have the ability to heat the water, but not to a critical lethal temperature, may find it advantageous to apply chemical treatments in conjuction with the thermal treatment to shorten the required duration of the chemical treatment (Petrille and Werner, 1993; Harrington, 1993)

Paints and Coatings

Paints and coatings have been the method of choice for controlling salt water macrofouling on boat hulls for more than a century. Copper sheeting was once widely used on boat hulls and has seen some use on stationary marine structures. The most effective coatings have been ones containing tin compounds, especially tributyl tin oxide (TBTO) or tributyl tin fluoride (TBTF). In some respects, these compounds have become victims of their own success. Tin compounds have been shown to produce deformities in oyster shells at part per trillion concentrations. Although the release rate of tin from the coating can be controlled to a considerable extent by the paint formulator, adverse affects on the biota were observed in harbors near boat anchorages and near dry dock facilities where tin-based coatings were applied. In recent years, the use of tin-based coatings has been severely restricted. Copper has supplanted tin as the heavy metal of choice in antifouling coatings.

The effectiveness of the coating varies depending on the release rate and bioavailability of the metal at the surface. This, in turn, is a function of the pH, corrosivity and hardness of the water, as well as the ablation rate of the coating at the prevailing water velocity and grit content. Over time, the formation of corrosion-resistant oxide films or biofilms diminishes the effectiveness of the coating. In most cases, the coating requires initial "activation" and semiannual "reactivation" by hand scrubbing or light abrasive blasting to provide the desired effectiveness. There is at least one manufacturer of a copper-epoxy coating. The coating is hard enough and sufficiently abrasion resistant to be utilized on bar screens, and the overall release of copper to the environment from the coating is a trace.

Zinc based coatings, in the form of galvanizing, have been used for many years to protect steel structures from corrosion. Although less toxic to most aquatic life than copper by an order of magnitude, the corrosion rate of zinc, and consequently its release rate and availability to the organism, is also much higher. One evaluation of zebra mussel substrate preferences indicated that settling was totally absent on zinc, poor on copper and brass, moderate on tin, concrete and Plexiglas, and intense on PVC and iron. A US Army Corps of Engineers technical note reviewing thermal sprayed coatings cites anecdotal evidence from the US Coast Guard suggesting that galvanized steel is resistant to zebra mussel fouling (Race, 1992). A zinc-rich surface, whether applied by galvanizing or thermal spraying, appears to be a reasonable material selection not only for corrosion resistance and appearance but for controlling zebra mussel attachment as well. Zinc-rich coatings would be best suited for hard steel surfaces, such as bar screens, and would be very economical in new construction.

Very effective non-toxic coatings have also been developed in recent years. In several studies, the most effective types are rubbery silicone-oil based compounds, which are offered by a few manufacturers. These coatings can be applied to a variety of substrates, but require careful surface preparation involving several precoats. They are reported to provide excellent biofouling resistance in freshwater and saltwater applications for at least four years before their performance begins to fall off. The silicone-based coatings are a reasonable choice for coating concrete intake bay walls and intake tunnels. The primary limitation on these coatings is the need to completely dewater, clean and dry the surface prior to application (and reapplication). Other limitations include poor resistance of the soft material to mechanical damage, concerns relating to debonding of coating sheets, the need to recoat after several years and the high installed coat of the coating, reported to be in the \$10-\$20 /ft^2 range.

Chemical Control Methods

Compared to other methods, the use of chemicals is the most widespread approach for controlling macrofouling for several reasons. Capital costs are generally much lower, and chemicals are more versatile, can be easily adapted to existing facilities, and may serve a dual role in limiting microbiological fouling as well as macrofouling. All chemicals sold in the US which are used for biological control, or for which biological control claims are made, are required to be registered with the pesticide branch of the US (Federal) EPA according to the provisions of FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act). This requirement includes commodity materials such as sodium hypochlorite bleach, as well as biocide precursors, such as sodium bromide. Properly registered materials will be labeled with the EPA registration number and explicit instructions for use. The label also states that the product can only be discharged in accordance with a site NPDES permit and only after the permitting authority has been notified in writing of its use. A few states also require that the addition of any biocidal chemical, including chlorine, be administered by a state-certified pesticide applicator.

Chemical control compounds may be broadly classified as metals, oxidizing and nonoxidizing materials.

Metals

As mentioned earlier, the two most effective metals in use for macrofouling control, apart from the banned tributyl tin compounds, are copper and zinc. Although environmental agencies often restrict the use of metals due to their persistence, they are effective at low concentrations and are often used either purposely or incidentally for macrofouling control. The no-effect concentration (NOEC) for copper on zebra mussels as measured by 48-hour filtration rate was found to be 16 ppb, with 100 ppb producing an 85% reduction in filtration (Kraak, et al, 1993). The same researchers reported that exposure to 49 ppb of copper for 9 weeks produced 24% mortality. The NOEC for copper bioaccumulation was found to be 28 ppb. Asiatic clams are more sensitive to copper than are zebra mussels, with a chronic NOEL in the range of 6 ppb. The effective concentration for zebra mussels is only slightly higher than the EPA's national ambient water quality criterion applied to the boundary of the effluent mixing zone, and generally below the incidental copper concentration for power plant cooling towers with copper alloy condensers. The EPA 4-day average freshwater quality criterion (CCC) for copper is given by the following expression (Federal Register, 1999):

$$\text{Cu (ppb)} = 0.960 \times \exp[0.8545 \times \ln(\text{hardness}) - 1.465]$$

Where: Hardness = Total hardness expressed as ppm $CaCO_3$

For a total hardness of 100 ppm as $CaCO_3$, this equates to a calculated ambient copper concentration of 11 ppb at the boundary of the effluent mixing zone.

The authors are not aware of a single power industry cooling tower serving a copper condenser with copper concentrations low enough to support Asiatic clams, although clam growth is common in the sumps of cooling towers serving stainless steel condensers in the northern US Although the intentional addition of copper salts to control macrofouling would involve pesticide registration and NPDES permitting, copper ion generators that release copper ions in situ through the action of electric currents on copper anodes are apparently considered devices, and may not be subject to the same regulations.

Zinc is less toxic to mollusks and other aquatic life than is copper, but can still provide effective mollusk control. The EPA 4-day average freshwater quality criterion (CCC) for zinc is given by the following expression (Federal Register, 1999):

$$\text{Zn (ppb)} = 0.986 \times \exp[0.8473 \times \ln(\text{hardness}) + 0.7614]$$

Where: Hardness = Total hardness expressed as ppm $CaCO_3$

For a total hardness of 100 ppm as $CaCO_3$, this equates to a calculated ambient zinc concentration of 100 ppb (rounded to two significant figures) at the boundary of the effluent mixing zone. Under BAT standards, most power plants are permitted to use up to 1,000 ppb (1 ppm) of zinc as a cooling system corrosion inhibitor. The no-effect level for zinc on zebra mussels, based on a 48-hour filtration rate study, was found to be 191 ppb, and a zinc concentration of 1,350 ppb (1.35 ppm) was found to reduce zebra mussel filtration rate by half (Kraak, 1993). Those studies were conducted at a high water hardness of 268 ppm as $CaCO_3$. The CCC for zinc at 268 ppm total hardness is 240 ppb according to the above equation. As with copper, Asiatic clams are more sensitive to zinc than are zebra mussels. The authors are aware of a service water application where 1 ppm of zinc applied as a corrosion inhibitor was completely effective in ridding the system of Asiatic clams. The application of zinc as a corrosion inhibitor can be expected to have an incidental benefit of reducing or controlling macrofouling in power plants and industrial facilities.

Zinc is NSF approved as a corrosion inhibitor for potable systems at concentrations up to 5 ppm, and its use as a corrosion inhibitor will provide effective incidental macrofouling control in those systems. The US limit for copper in potable systems is 1 ppm. Whereas zinc is a corrosion inhibitor, copper is known to accelerate carbon steel corrosion. Copper ions are alternate electron acceptors at the cathodic site of the corrosion cell and plate out on the steel surface, resulting in a 0.75 V galvanic corrosion cell.

Oxidizing Compounds

Several oxidixing compounds have been utilized for macrofouling control. These include:

- Chlorine (gas and sodium hypochlorite bleach)
- Chloramines
- Bromine
- Chlorine Dioxide
- Hydrogen Peroxide
- Ozone
- Potassium Permanganate

As a group, all of the oxidizers are readily detected by the mollusks' sensitive chemoreceptor system at effective concentrations. The mollusks respond by immediately withdrawing their siphon tubes and closing their shells to avoid contact. This avoidance response is rather effective in limiting exposure to the oxidizer. The mollusk in effect "holds its breath" until the oxidizer has passed, and then resumes siphoning within minutes. Asiatic clams and zebra mussels can remain dormant for several days up to a few weeks with little or no siphoning activity. Consequently, the oxidizers require lengthy exposure times to achieve effective treatments. The long duration generally precludes the use of these compounds for off-line static treatments. Moreover, the lengthy exposures require relatively large amounts of the chemical and can be costly. The required treatment duration is dependent upon a number of factors related to the health and condition of the organism, but most decidedly is a function of water temperature. Higher temperatures result in faster respiration rates and limit the ability of the organism to remain dormant. At temperatures near their upper survival limits, the mollusks are very stressed and must siphon continuously to survive. Consequently, all oxidizing treatment programs are effective with lower concentrations and exposure times in warmer water. Any action to elevate the water temperature, such as the use of deicing lines, will reduce chemical requirements.

Oxidizing chemistries tend to be nondiscriminatory in their action. They oxidize and destroy sensitive cell tissues, eventually resulting in the destruction of the organism. The nonspecific mode of action has been both a blessing and a curse for the oxidizers. They are effective in controlling a wide range of fouling organisms, including bacterial slimes, pathogens such as Legionella, algae and mollusks. Unfortunately, they are also lethal to desirable nontarget species such as plankton passing through the system, and fish. Moreover, their reactive nature gives rise to a host of undesirable byproducts including THM's, AOX's, aldehydes, secondary oxidants, chlorites and chlorates. The toxicity of the effluent can be mitigated to a considerable extent through the addition of sulfur (IV) compounds, such as sodium bisulfite, which react rapidly with the stronger oxidizing species but may require minutes to days to react with weakly oxidizing byproducts such as chlorite and some chloramines. The properties and effectiveness of each of the oxidizers varies sufficiently to warrant considering them individually.

Chlorine

Chlorine in either gas or liquid bleach (sodium hypochlorite) form is the most widely used of the oxidizing compounds. It has been used by electric utilities to control microbiological slime and salt water macrofouling since the 1930's. Personnel exposure concerns, insurance requirements, and community safety issues and regulations have caused the majority of utilities to switch from chlorine gas in ton cylinders to sodium hypochlorite bleach, at a 3-fold cost premium. Handling and feeding hypochlorite is surprisingly problematic for a liquid. The sodium hypochlorite bleach is generally sold as a comparatively dilute 12.5% (15% "by trade") solution, containing a little more than 1 lb. equivalent chlorine per gallon, which requires large volumes of the liquid to be handled. Polyethylene storage tanks are subject to stress cracking in the presence of bleach, and fiberglass tanks can delaminate. Hypochlorite's low surface tension and aggressiveness to sealing compounds enable it to "find" leaks in loose or threaded joints. The hypochlorite can undergo rapid degradation in storage depending on the initial concentration, the level of trace metal contaminants, UV light exposure and temperature. Degradation produces chlorates and oxygen gas, the latter of which can cause metering pumps to lose their prime. Metering pumps with heads that purge the gas are available. It is good practice to maintain flooded suc-

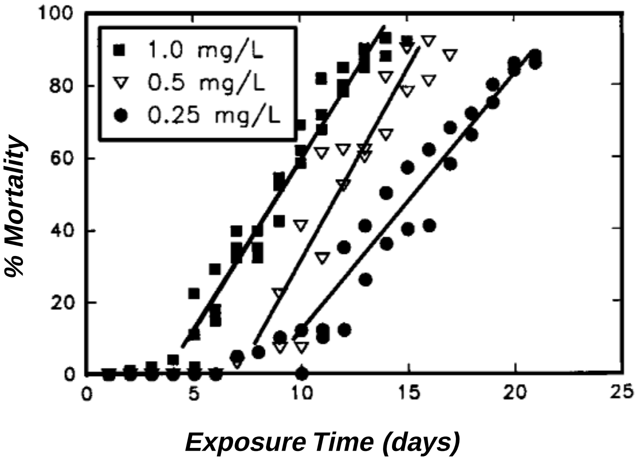


Figure 9: Effect of continuous chlorination on zebra mussels.

tion to the metering pump and to vent the suction line immediately ahead of the metering pump back to the storage tank to reduce gas binding. The high pH of the bleach solution can cause scale to form in transport water lines. Despite these shortcomings, the relatively low price per pound, in the $0.60 per gallon range, and its dual effectiveness as a microbiocide, make bleach a reasonable choice for many utilities. Several studies on the effectiveness of chlorine on Asiatic clams and zebra mussels have been conducted over the years in Europe and the US The data set below presented at the First International Conference on the Zebra Mussel in the Great Lakes in 1989 is typical of the findings (Jenner and Janssen-Mommen, 1989).

A review of several continuous chlorination studies on zebra mussels conducted at 0.5 ppm TRC (Total Residual Chlorine) with a 95% mortality end point was fit to the following curve:

Log (t) = 3.458 - 0.0486 x T
Where: t = time in hours to achieve 95% mortality
T = temperature, 0-25°C

Other researchers have reported similar results with chlorination studies on Asiatic clams (Doherty et al, 1986). Continuous chlorination for a duration of approximately 2-3 weeks at a concentration of 0.5 ppm TRC is required to achieve reasonable effectiveness on Asiatic clams at 20-25°C. Although intermittent 2-hour per day chlorination has been shown to be ineffective (Lyons et al., 1991), semicontinuous chlorination, (e.g. 30 minutes on and 30 minutes off) was found to provide effective control of zebra mussels with reduced chlorine usage (Wianko and Claudi, 1994). However, the effectiveness of the treatment regime dropped off considerably when the off time was an hour or more. Semicontinuous chlorination treatments have also been employed with reasonable success on saltwater macrofouling species in the US and Europe.

Apart from high chemical requirements and the associated costs, continuous chlorination is aggressive to system components, particularly copper alloys. Copper corrosion spikes on the order of 10 to 100-fold can be seen during chlorination using "instantaneous corrosion rate" (linear polarization resistance) techniques (May, 1998).

Ecotoxicological consequences of continuous chlorination are severe, a concept which is not widely appreciated. Safe discharge concentrations for continuously chlorinated effluents are widely acknowledged to be in the range of 0.002 - 0.011 ppm, well below the practical limit of detection of approximately 0.05 ppm (Merkins, 1958; Brungs, 1973; Basch and Truchan, 1974, Brungs and Middaugh, 1984). Several studies have demonstrated a wide range of destructive effects of chlorination on entrained organisms (Morgan and Carpenter, 1977). One study reported a 79% reduction in plankton productivity in passing through a chlorinated once-through cooling system, even at the lowest inlet concentration of 0.1 ppm which was nondetectable in the outfall (Carpenter, et al, 1972). Chlorinated byproducts can also be a concern, and these are reduced only slightly by sulfite treatment. It was reported that chlorinated wastewater effluent can contain 103 chlorinated compounds, of which 72 are mutagenic (Claudi and Mackie, 1994). Principal organohalogenated compounds resulting from chlorination of fresh water are chloroform, chloroacetic acids and chlorophenols. Chloroform is resistant to biodegradation, but is volatile and aerated out of solution over a period of days. Haloacetic acids are not volatile, but biodegrade over several days. Chlorophenols are low volatility but biodegrade, although slowly, in the natural environment. One study of a chlorophenol compound found in chlorinated effluents, 4-chlororesorcinol, showed impairment to Daphnia magna even at 0.001 ppm, the lowest concentration evaluated (Gehrs and Southworth, 1976).

Although sulfite treatment reduces chlorinated effluent toxicity by reacting rapidly with free chlorine (HOCl and OCl-) and more slowly with chloramines, fish often avoid sulfite-treated "dechlorinated" effluents, with good reason. Flow-through bioassays of dechlorinated effluents have shown lethal effects to inland silversides and sublethal effects on sticklebacks and scallops (Hamel and Garey, 1979). "Dechlorination" of chlorine in pond water was found to be insufficient to prevent toxicity even with a 3-times stoichiometric dose of sulfite in flow-through studies (Fisher and Burton, 1995). Other analyses indicated that a 5-fold molar excess of sulfite with 25 uniform injection points would be required to achieve a 96% reduction of a 0.5

ppm free chlorine residual (FAC) within a 40-foot discharge canal at a water velocity of 6.2 fps, and that a stoichiometric dose would provide minimal reduction (Tan et al., 1980; Berker and Whitaker, 1977). The excess sulfite imposes a chemical oxygen demand on the receiving stream.

Although Berker and Whitaker (1977) provide a comprehensive treatise on the removal of fast-reacting free chlorine, they do not address the much slower-reacting chloramines, particularly those resulting from the chlorination of amino nitrogen groups which comprise a significant proportion of naturally occurring aquatic nitrogen compounds. Dechlorination half-life times on the order of several minutes to 3 hours were reported for various chloramines in the presence of sulfite concentrations ranging from stoichiometric to 30-times stoichiometric (Stanbro and Lenkevich, 1982). The false impression that a stoichiometric concentration of sulfite is adequate to detoxify chlorinated effluents appears to be rooted in artifacts of the current analytical and biological test methods. Chloramines are not detectable with standard analytical methods in the presence of excess sulfite (Helz and Kosak-Channing, 1984). Standard analytical methods such as amperometric titration and DPD measure chloramines by first reacting iodide with the chloramine to form iodine. In the absence of sulfite, iodine is the oxidant species titrated or measured by the method. However, in the presence of sulfite, the iodine reacts rapidly with the sulfite in the test apparatus giving the false impression that no "total chlorine residual" is present and that dechlorination reactions are "instantaneous" with stoichiometric levels of sulfite (Stanbro and Lenkevich, 1982; Helz and Kosak-Channing, 1984). Common bioassay methods such as EPA's Whole Effluent Toxicity (WET) test use an effluent sample typically composited over several hours, then shipped off-site to a contract lab for testing a day or more later. Slow reacting halogenated species are consumed by sulfite and other demand in the sample jug while awaiting testing.

Although scholarly debates may persist on environmental issues related to chlorination and dechlorination, the practical utility chemist's definition of "environmentally acceptable" remains simply, "Can I get it listed on my permit?" Perhaps out of concern for alternative compounds that are less familiar to them, many regulatory agencies still permit and even recommend continuous chlorination, provided that the effluent is continuously treated with a stoichiometric quantity of a sulfur (IV) reducing agent.

Chloramines

Based on limited research, monochloramine appears to offer similar, or better, efficacy in controlling zebra mussels and other macrofouling organisms than chlorine (Matisoff, et al, 1990). In studies involving only juvenile Asiatic clams, an LT50 exposure time of 2.5 days at 63.7°F was reported for a monochloramine concentration of 1.27 ppm. The LT50 was reduced to 0.6 days at 74.8°F at a concentration of 1.13 ppm (Cameron, et al, 1989). The authors propose the following relationship for the exposure time to achieve 100% mortality on juvenile Asiatic clams exposed to monochloramine:

$$\text{Log}(t) = 1.102 - 0.618 \times \log(C) - 0.018 \times (T)$$

Where: t = LT100 (days)
C = Monochloramine concentration (ppm)
T = Temperature (°C)

Monochloramine is a weaker oxidizer than free chlorine, and consequently does not produce other chlorinated organics. For this reason, as well as for its persistence in the distribution system, it is often used in the disinfection of drinking water,. The relatively lower oxidizing potential of the chloramine does not seem to affect its performance as a molluscicide. It has also been used successfully to control bryozoans in Belgian power stations. Monochloramine can be produced on-site by mixing solutions of sodium hypochlorite and ammonium chloride. Disadvantages

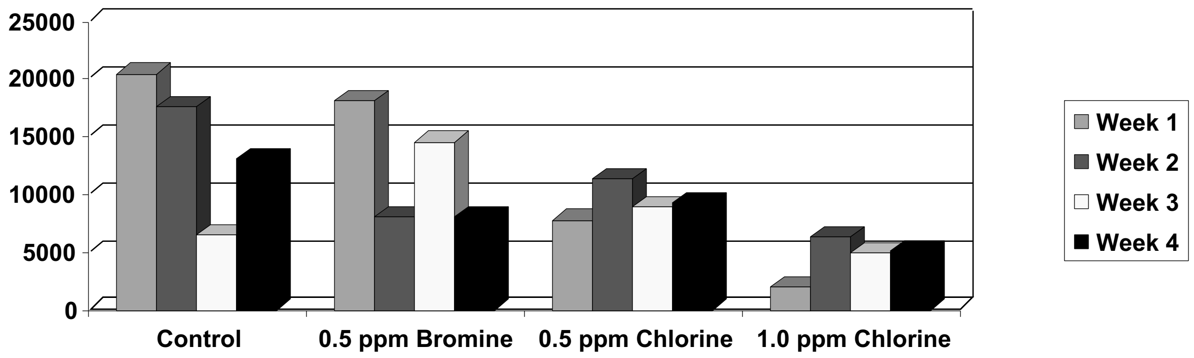


Figure 10: ***Weekly zebra mussel larvae setting with 2-hr/day bromination and chlorination during 4 consecutive weeks***

include the need to feed two chemicals and the environmental considerations related to discharging ammonia in lieu of chlorinated byproducts.

Bromine

In fresh water systems, sodium bromide is frequently added in-line with bleach in order to generate sodium hypobromite in situ via a simple displacement reaction. The process was developed by the Wallace and Tiernan Company in 1946. Bromine reacts with water to form hypobromous acid, which is in equilibrium with the hypobromite ion. This chemistry is similar to that of chlorine, except that the pKa for bromine is approximately 8.5, one unit higher than that of chlorine. The undissociated acid is a better germicide, probably because its electrical neutrality allows it to penetrate bacterial cell walls. Comparison studies have shown bromine to be somewhat less effective than chlorine as a molluscicide (Lyons et al., 1991).

The ecotoxicological profile for bromine is similar to that of chlorine. It is somewhat more prone to form THM's than is chlorine. Rook and Jolley have shown in many publications that the presence of bromide salts can result in high THM's in chlorinated drinking water, a fact of increasing concern to water purveyors given the large volumes of bromide now used for industrial cooling water treatment. In some states, power plants are restricted to lower TRO (Total Residual Oxidant) levels in their discharge when bromine chemistry is in use. Bromine may not be attractive for use solely as a molluscicide, but if employed in a dual capacity as a microbiocide it can be a reasonable control alternative. Bromine has the additional feature of being less corrosive to copper alloys than chlorine, which can be significant for continuous halogenation. Brominated amines are much stronger oxidants than the corresponding chlorinated amines, rendering them more effective as microbiocides and reducing their reaction times with sulfite. For example, the reaction half time between sulfite and N-bromoalanylalanylalanine was 15 seconds as compared to 3 hours for the corresponding N-chloro compound (Stanbro and Lenkevich, 1982).

Chlorine Dioxide

Chlorine dioxide is an explosive gas that must be generated in situ. Chlorine dioxide (ClO_2) can be synthesized by several routes, but the most common in cooling water applications is by the action of bleach and/or hydrochloric acid on a 25% sodium chlorite ($NaClO_2$) solution. Once one gets over the initial reservations of mixing three hazardous ingredients on site to produce an explosive one, chlorine dioxide does offer some advantages relative to chlorine. Chlorine dioxide requires lower dosages and shorter exposure times than chlorine. A 0.2 ppm concentration can produce 100% mortality on zebra mussels in only 8 days as compared to more than 3 weeks for chlorine (Khalanski, 1993). A 1.0 ppm residual will produce 99% mortality in a 4-day exposure as compared to 14 days for chlorine (Matissoff, et al, 1996). The exposure time required as a function of dose to achieve 100% mortality for chlorine dioxide was found to fit the following expression for water temperature in the 60-75°F range (Jenner et al., 1998):

$$T = 4.47 - 3.79 \times \log (ClO_2)$$

Where: t = exposure time in days
ClO_2 = chlorine dioxide concentration in ppm

Aside from the necessity for mixing three hazardous chemicals on site, the main disadvantage of chlorine dioxide is cost. The 25% sodium hypochlorite solution costs $0.50 to $1.00 per pound depending on whether generation equipment and service are included. With the additional reagents, the total cost is in the range of $2.50 -$5.00 per pound of active chlorine dioxide.

The toxicity of chlorine dioxide to a broad range of nontarget species is similar to that of chlorine. Chlorine dioxide does not produce THM's, and the AOX production is half or less that of chlorine. One drawback is that the primary reaction product of chlorine dioxide is chlorite, the starting material. Chlorite is a weak oxidizer, and does not react readily ("dechlorinate") with sulfur (IV) compounds even at a 10-fold molar excess of sulfite (Burton and Fisher, 1995). Yet it has an LC50 on Daphnia, an EPA marker organism, of only 71 ppb (Fisher and Burton, 1993a and 1993b). Due to this, some states have restricted the discharge of the chlorine dioxide to unworkable concentrations.

Hydrogen Peroxide

Hydrogen peroxide is a strong oxidant that does not produce chlorinated byproducts. It is short lived in the environment, breaking down quickly to water and oxygen. Hydrogen peroxide was evaluated for its effectiveness in controlling Asiatic clams and zebra mussels as part of an EPRI project on nontoxic chlorine alternatives (Petrille and Miller, 2000). Peroxide was found to be reasonably effective against zebra mussels in short duration exposures at high dosages. Surprisingly, the zebra mussels did not respond by closing their shells, and many were observed to gape open wider. By contrast, Asiatic clams responded by closing their shells and avoiding contact at concentrations greater than 5 ppm. There was no difference in peroxide effectiveness on zebra mussels as a function of shell size. Larger Asiatic clams required longer exposure times than smaller ones. LC90 values for

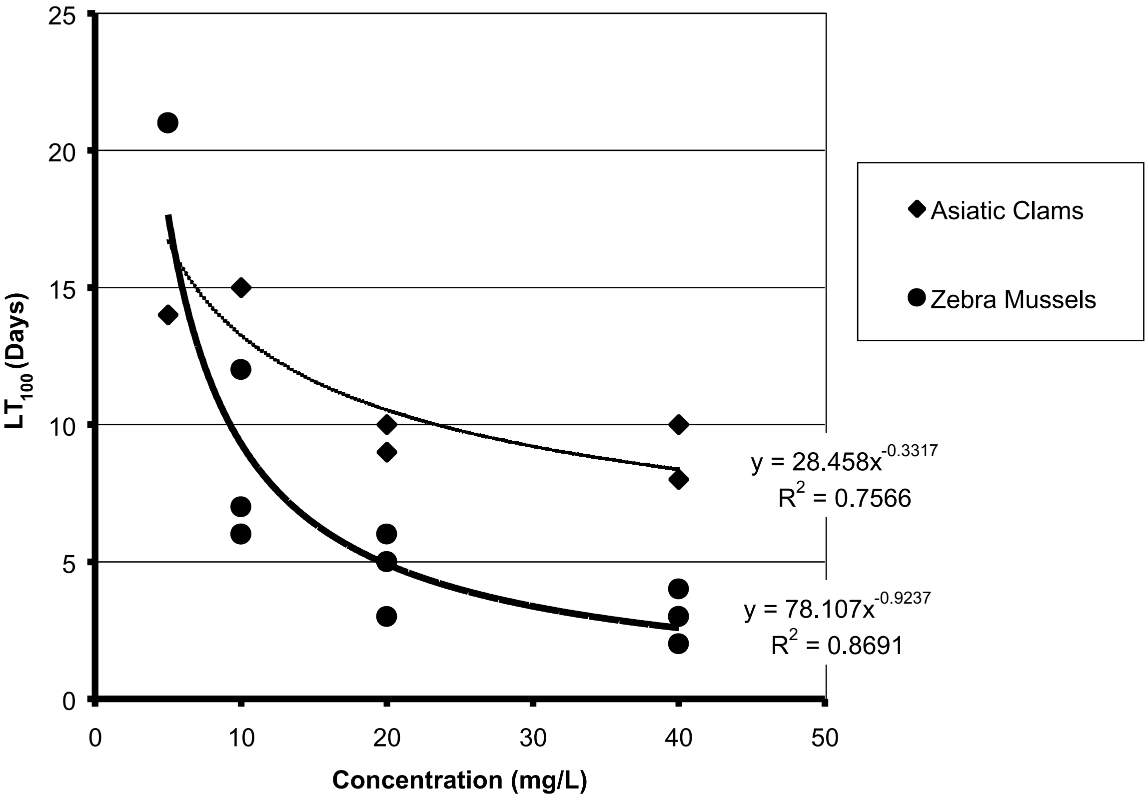


Figure 11: Peroxide exposure time required to produce 100% mortality on Asiatic clams and zebra mussels at 68°F (Petrille and Miller, 2000).

zebra mussels were determined to be 10.7, 7.7, and 5.3 ppm after 7, 14, and 21 days of continuous exposure. At hydrogen peroxide concentrations of 10, 20, and 40 ppm, the exposure time required to produce 100% mortality was found to be 7.75, 4.75, and 3.0 days on zebra mussels and 13.5, 9.5, and 9.0 days on Asiatic clams, respectively. The relative performance of hydrogen peroxide on zebra mussels and Asiatic clams at 68°F is shown in Figure 11.

The ecotoxicological profile for hydrogen peroxide is its primary advantage. The primary disadvantage of peroxide is cost. Nevertheless, peroxide may be a good fit for smaller systems or off-line treatments in environmentally sensitive areas.

Ozone

Ozone (O_3)- is a strong oxidizer produced by passing an electric arc through pure oxygen or air. It is too unstable to be transported, is not easily stored and must be generated on site. Ozone has been used as a disinfectant in smaller cooling water applications and has a good environmental profile, making it a reasonable candidate for freshwater macrofouling control. (Seawater contains 65 ppm of bromide, which would react instantly with ozone to produce hypobromous acid). The most noteworthy application of ozone to a once-through utility cooling system was considered a failure due to the oxidation and deposition of manganese on the condenser tubes (Sugam, 1985). Ozonation for the control of adult zebra mussels has been studied in North America by Lewis and colleagues (1991; 1993) for Ontario Power Generation, and in Europe by Duvivier (1996) and his colleagues at LABORELEC. In general, despite its oxidizing power, ozone was found to be somewhat less effective than chlorine, with the possible exception of very high dosages for short periods. A 2 ppm dose required an exposure time of approximately 8 days at 68°F. A 0.32 ppm dose required an exposure time of 39 days to achieve 100% mortality at 70°F. Jenner (1998) and his colleagues examined several sets of ozone effectiveness data for zebra mussels and fit them to the following expression:

$$O_3 \text{ (ppm)} = 17.731 \times t^{-1.1127}$$

Where: t = exposure time in days

The major advantage of ozone is its environmental profile. Ozone has a short half life, actually oxidizes and removes potentially harmful organics, and obviously does not produce halogenated byproducts in fresh waters with negligible bromide content. Disadvantages are the relatively high dosages and contact times, and the very significant capital and operating costs of an ozone generator. Rapid dissipation of the ozone residual would also be a major disadvantage for service water systems and fire protection systems having long piping runs and residence time, where the residual would be depleted before it reached all areas of the system.

Potassium Permanganate

Permanganate has been used to control zebra mussels in potable water systems. However, its usefulness in utility systems is limited by its tendency to form manganese dioxide deposits which are both insulating and corrosive. Although Fraleigh (1993) and his colleagues found that 0.25 ppm of permanganate prevented growth and settlement of zebra mussels, intermittent treatments of nearly 30 days were required to produce only 50% mortality (Van Benschoten, et al, 1993). Potassium permanganate seems likely to be relegated to certain specialty applications in the power industry, such as fire suppression systems.

Nonoxidizing Chemicals:

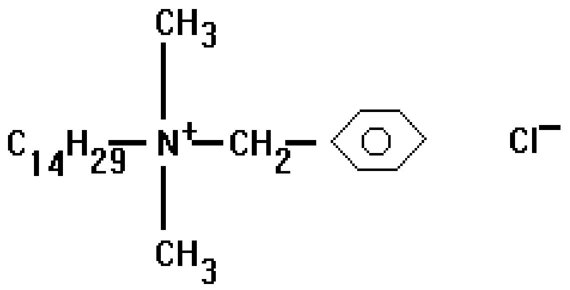
As a class, the nonoxidizing chemicals have the potential to be far more specific to the target organism than oxidizing chemicals. Whereas the oxidizers burn indiscriminately, a nonoxidizing compound can be selected to specifically attack the target species, while doing little harm to nontarget aquatic species, particularly fish. Moreover, the nonoxidizers do not react with naturally occurring organics to produce a potpourri of chlorinated or oxygenated substances. All of the antimicrobial compounds registered in the US for cooling water use have been evaluated for macrofouling control. These include:

- Quaternary amines
- Tertiary amines
- Long chain aliphatic amines
- Polyquaternary amines
- Dodecylguanidine (DGH)
- (Decylthio)ethanamine (DTEA)
- Glutaraldehyde
- Isothiazolones
- Trifluoromethyl nitrophenol (TFM)
- Bromonitrostyrene (BNS)
- Bromonitropropane diol (BNPD)
- Dibromo nitrilopropionamide (DBNPA)

Figure 12: Photograph illustrating the selectivity of a quaternary amine. Compound produces 100% mortality on zebra mussels without harming trout fry. (0.5 ppm ADBAC, 96-hr., 65°F).

- Tetrakishydroxymethyl phosphonium sulfate (THPS)
- Benzothiazoles (MECT, and others)

All of the above compounds have reasonable environmental profiles with respect to persistency and mammalian effects. Of the group, the amines have proven to be particularly effective and selective against macrofouling organisms. The success of the amine compounds is due to the fact that the mollusks do not sense them at lethal concentrations, as they do the oxidizing compounds. The mollusks do not close their shell and continue siphoning in the amine. The amines appear to damage the gill tissue and interfere with the mollusks' ability to osmoregulate, as evidenced by swelling of the soft tissue and an increase in tissue water content (Bidwell et.al., 1993). Exposed Asiatic clams, for example, swell to such an extent that they frequently are unable to retract their foot into their shell.



$$C_{14}H_{29}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-CH_2-C_6H_5 \quad Cl^-$$

Figure 13: ADBAC (n-alkyl dimethylbenzyl ammonium chloride)

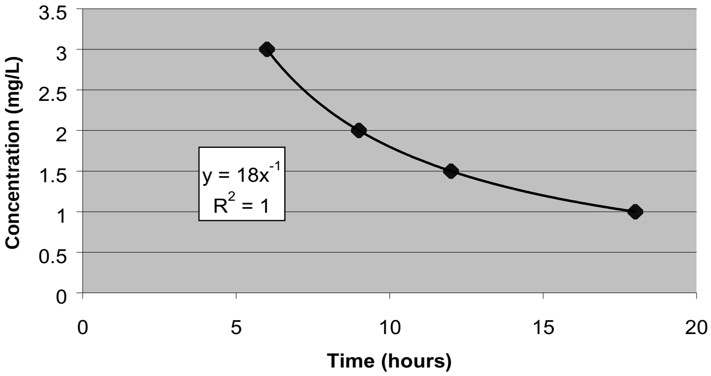


Figure 14: ADBAC quat effectiveness on zebra mussels at 68°F

Quaternary Amines

The most widely used of these compounds are the quaternary amines, which were first applied and registered in the US for mollusk control in 1986 (Lyons et al.). One reason for their success is their remarkable selectivity to the target organisms, as illustrated in Figure 12. It is possible to place rainbow trout fry and adult zebra mussels in the same aquarium, dose the aquarium with quaternary amine, and kill the zebra mussels without harming the trout. By contrast, chlorine would be lethal to the trout fry at 1/100 the dose that would be effective on the zebra mussel.

The most common and biodegradable of the quaternary amines is ADBAC (n-alkyl dimethylbenzyl ammonium chloride). The structure of ADBAC is shown below.

alkyl chain = 12-16 carbon for bactericidal and molluscicidal applications.

ADBAC is a familiar material which has been used in a broad spectrum of household and industrial applications for more than 50 years, with current annual US consumption estimated at 30-40 million pounds. The term "quaternary" refers to the nitrogen group being attached to 4 alkyl groups. ADBAC with an alkyl chain length of approximately 18 carbons, is often referred to as "stearalkonium" chloride and is the principle ingredient in many hair conditioners and fabric softeners. In these applications the cationic charge is used to neutralize the naturally occurring negative charges on hair and fabric that are responsible for combing difficulties and "static cling." ADBAC with an alkyl chain length of predominantly 12-14 carbons is often referred to as "benzalkonium chloride," and is widely used as a preservative in a variety of personal care products including eye drops and nasal sprays. It is the active ingredient in many household disinfectants and in antiseptics for direct application to cuts and scratches at a concentration approximately 500 times higher than that required for effective mollusk control programs. ADBAC with an alkyl chain length of 12-16 carbons has been used to control microbiological slime in algae in cooling towers since the mid-1950's. Today, the largest antimicrobial usage for ADBAC is as a swimming pool algaecide, where the compound has been in use for more than 30 years. Effective dosages in

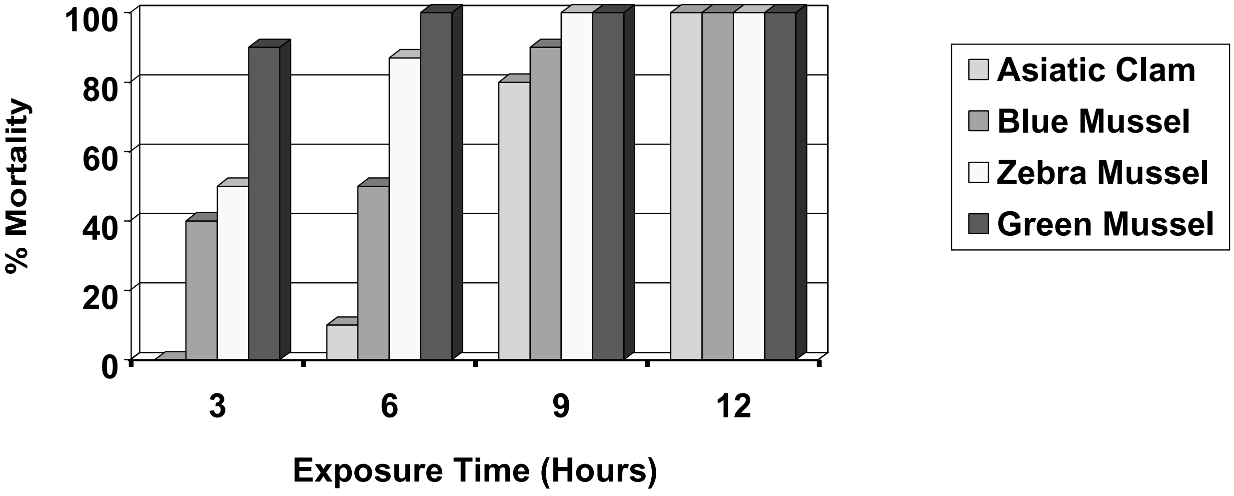


Figure 15: Dose-response data for 2 ppm ADBAC against mollusks at 77°F

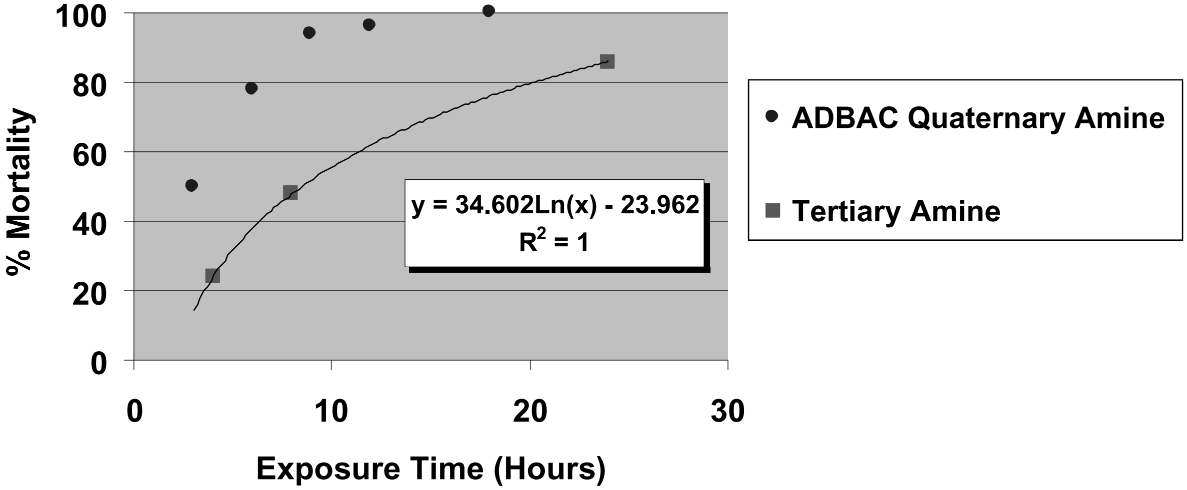


***Figure 16:** Efficacy of 18 ppm hydrothol 191 (2.2 ppm tertiary amine) on zebra mussels at 68°F. 2.0 ppm ADBAC shown for comparison.*

swimming pools are the same as those required for mollusk control, 1-3 ppm. One ADBAC molluscicide has recently been NSF certified for use in potable water systems, attesting to the safety of these compounds.

Another reason for ADBAC's widespread use in macrofouling control is that it is effective using only brief exposures; hours vs. days or weeks for oxidizers. Figure 14 illustrates the time required to achieve 100% effectiveness against zebra mussels using 1-3 ppm of ADBAC at 68°F.

The time and dosage required to produce 100% mortality on adult zebra mussels for 1-3 ppm active was fitted to the following expression:

ADBAC (ppm) = 18/t (hours)

ADBAC is also effective against Asiatic clams, as well as saltwater mollusks, as shown in Figure 15.

The ability to control mollusks using only short exposures gives rise to a number of advantages over chlorine and other oxidizers. These include:

- Less chemical released to the environment
- Product concentrations can be monitored and verified during the entire application
- Permanent installation of tankage, dikes and feed equipment is generally not required
- Reduced impact on entrained plankton
- Costs are lower since far less chemical is required

Costs savings and environmental benefits are particularly significant when the fast acting characteristics of the surfactants can be used to treat a portion of the system "off-line" in a nonflowing condition. This is often the case for fossil fueled units, where one pump bay can be taken out of service overnight during periods of light load, or during an outage, at least once per year.

ADBAC is also particularly well suited for application to fire protection systems. The material can be dosed to the system at the front end while hose coils are opened on the back end. Once a residual is detected, the hose coil is shut off for at least 12 hours. The product can be allowed to remain in the system to provide protection against microbially influenced corrosion (MIC).

ADBAC meets international standards for ready-biodegradability and has been shown to be 50% mineralized to CO_2 in 9 days by unacclimated organisms when used as the sole source of carbon and nutrient (Post et al., 1996). The quaternary amines are characterized by a positively charged hydrophilic nitrogen "head" attached to a hydrophobic "tail," generally a linear fatty acid. Once the cationic charge contacts naturally occurring anionic silt and substrates, the charge is neutralized by adsorption and the compounds no longer express toxicity. Degradation studies in a cooling tower with the blowdown closed demonstrated a 90% reduction in ADBAC concentration over a period of 12 hours (Post et al., 1996). ADBAC readily intercalates the swelling clays that typify US soils, which binds and immobilizes it. Studies conducted on several sediment dwelling species have confirmed that the adsorbed ADBAC does not impair survival or growth. On large direct discharge applications in sensitive areas where the demand from the natural water is insufficient, bentonite clay is often deliberately added to inactivate the remaining residual. However, there is a growing awareness that the low degree of toxicity to fish may not warrant the addition of clay in most applications. Of the many aquatic species evaluated, only zooplankton are impaired by low levels of

ADBAC. Zooplankton are replenished quickly in the environment and are of little ecological concern for the very short seasonal applications required for ADBAC. In fact, since plankton pass through the intake screens, the primary effect on planktonic organisms occurs within the plant piping system and can be related directly to the duration of the treatment program. In that respect, ADBAC applications of only 12 hours will have 1/40th the effect on plankton as a 20-day continuous chlorination treatment.

Tertiary Amines

Tertiary amines supplied as the salt of the aquatic herbicide, endothall, have also been applied for zebra mussel control in the US (Green, R.F., 2000). The compound reportedly degrades rapidly in the environment. Efficacy of the tertiary amine against zebra mussels is significantly less than the ADBAC quaternary amine as shown in Figure 16 (Petrille, 1995).

The efficacy of a dosage of 2.2 ppm of active tertiary amine (18 ppm product) as a function of exposure time can be fitted to the following expression:

Mortality (%) = 34.602 x Ln(t) - 23.96
Where: t = exposure time in hours

Compared to the quaternary amine, the tertiary amine is less selective to the target organism relative to fish, although still far more selective than oxidizing compounds. The table below provides published aquatic effects data on fathead minnow and rainbow trout (Mudge, et al., 1986; Keller, et al., 1988):

Table 2: Hydrothol 191 (tertiary amine endothall) Toxicity to Nontarget Organisms

Aquatic Organism	Whole Product LC50	LC50 As Tertiary Amine Equivalent
Fathead Minnow	0.39 mg/L	0.12 mg/L
Rainbow Trout	1.7 mg/L	0.50 mg/L

Like the quaternary amines, the tertiary amine is removed from the water column by adsorption onto naturally occurring silt and surfaces. The NPDES permissible discharge concentration for the tertiary amine endothall salt depends on the amount of demand and dilution downstream of the sample point, as well as the permitting authority, but has ranged from 20 ppb as amine (Howe, 1999) to 1 ppm as amine (Green, 2000).

Long chain aliphatic amines

An aqueous emulsion of long chain aliphatic amines has been used successfully against zebra mussels by Electricité de France (EDF). At 3.5 ppm, the material is effective against zebra mussels in 19 hours (Khalanski, 1993). Like the fatty acid quaternary and tertiary amines, these compounds are reportedly adsorbed out of solution, biodegradable, and relatively short-lived in the environment. Proposed concentrations to protect nontarget freshwater organisms are 1-3 ppm for brief exposures of less than 1 hour and 0.25 ppm for continuous treatments lasting more than 36 hours (Khalanski, 1997).

Polyquaternary amines

Polyquaternary amines have also been proposed for use against macrofouling but are less effective, requiring exposure times similar to those of the oxidizing compounds. At a concentration of 2 ppm, an exposure time of 13 days was required to produce 100% mortality on zebra mussels (McMahon, et.al, 1989). The same study reported that 2 ppm of TCMTB, a benzothiazole, also required an exposure time of 13 days to produce 100% mortality.

Summary

There are a wide range of effective mechanical, physical, thermal and chemical methods available to electric utility professionals today in their battle against macrobiological fouling. No one method is likely to be the best in all situations. At most sites, a combination of methods may be the best approach, although several stations rely primarily on one method. The only completely unacceptable approach to the problem is to do nothing at all, and allow the plant to reach an advanced state of macrofouling. At that point the only options are to shut down intentionally for manual cleaning or to await the inevitable "cleaning by catastrophe."

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