Evaluation of a Proposed Chemical Treatment Lock for the Control of Aquatic Invasive Species in the Chicago Area Waterway System (CAWS)

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PURPOSE: The purpose of this report is to review the concept of developing a special channel near the Chicago Area Waterway System (CAWS) to treat ship and barge traffic headed towards Lake Michigan with chlorinated water, minimizing the movement of aquatic invasive species (AIS) into the Great Lakes. This concept was proposed in a white paper titled *Conceptual Aquatic Invasive Species Treatment System for the Chicago Area Waterways*, which was prepared by CH2M for The Nature Conservancy (CH2M 2016). Victor Medina is an environmental engineer with a strong background in water treatment including disinfection, Jack Killgore and Jan Jeffrey Hoover are research fishery biologists who are experts in AIS, particularly the Asian Carp. All are members of the Environmental Laboratory (EL) of the U.S. Army Engineer Research and Development Center (ERDC).

This project identifies several critical concerns that should be considered before pursuing such a course. All issues could be conceivably addressed with additional studies and/or extensive engineering. That said, some of the identified issues may be challenging to overcome.

BACKGROUND

The Chicago Area Waterway System (CAWS). The CAWS is a complex series of natural and man-made waterways and canals, including the Chicago River, the Chicago Sanitary and Ship Canal (CSSC), the Cal-Sag Channel, and the Calumet River (Figure 1). The system dates back to 1900 and was designed to move stormwater and treated sewage away from the City of Chicago's water supply to the Des Plaines River, which ultimately connects to the Illinois River and then to the Mississippi River (Duncker 2011). The CAWS also allows barge traffic to move from the Mississippi River to Lake Michigan through a series of locks and dams. There is concern that the CAWS serves as a conduit to allow AIS to move from the Mississippi to the Great Lakes (USACE 2014). Two groups of species are of particular concern: the Asian Carp, or bigheaded carp (genus – *Hypophthalmichthys*, there are three species) and the *Apocorophium lacustre*, a shrimp like amphipod which is commonly referred to as a scud (USACE 2014).

Electric fish barriers were constructed in the CSSC near Romeoville to reduce, and possibly prevent, movement of invasive species between Lake Michigan and the Illinois River system (Figure 1). These barriers are currently in operation based on research results from ERDC (Parker et al. 2013; Holliman et al. 2015). However, there is concern that barge traffic can warp the electrical field and small fish can be entrained between barges even while immobilized. A more extensive set of alternatives using both electrical and acoustic deterrents (complex

acoustics may result in avoidance behavior by Asian Carp) are proposed at the Brandon Road Lock and Dam (BRLD) (Figure 1, USACE 2015). The Nature Conservancy has proposed an alternative, the establishment of a chemical chamber using the BRLD, as outlined in a CH2M 2016 white paper. This involves developing a treatment chamber, in which shipping will be treated with chlorine (the process will be described in more detail below).

Figure 1. Diagram of the CAWS system (modified from Duncker 2011).

The Proposed Nature Conservancy Concept for controlling AIS for the CAS. In a white paper prepared by CH2M, the Nature Conservancy has proposed a chemical treatment approach for controlling AIS (CH2M 2016). This would involve installing a chemical treatment chamber at BRLD. Alternatively, the existing lock could be modified to serve as a chemical treatment reactor. In either case, the size of the chamber would be 600 ft long and 110 ft wide, which is the same dimensions of the lock. The depth would be 13.5 ft, with 4.5 ft for the installation of jet mixing equipment, and 9 ft as the navigable portion. Although not included in this design, the concept envisioned a smaller treatment chamber that could be used for smaller vessels. The treatment chamber will be closed during treatment to isolate the water (Figure 2).
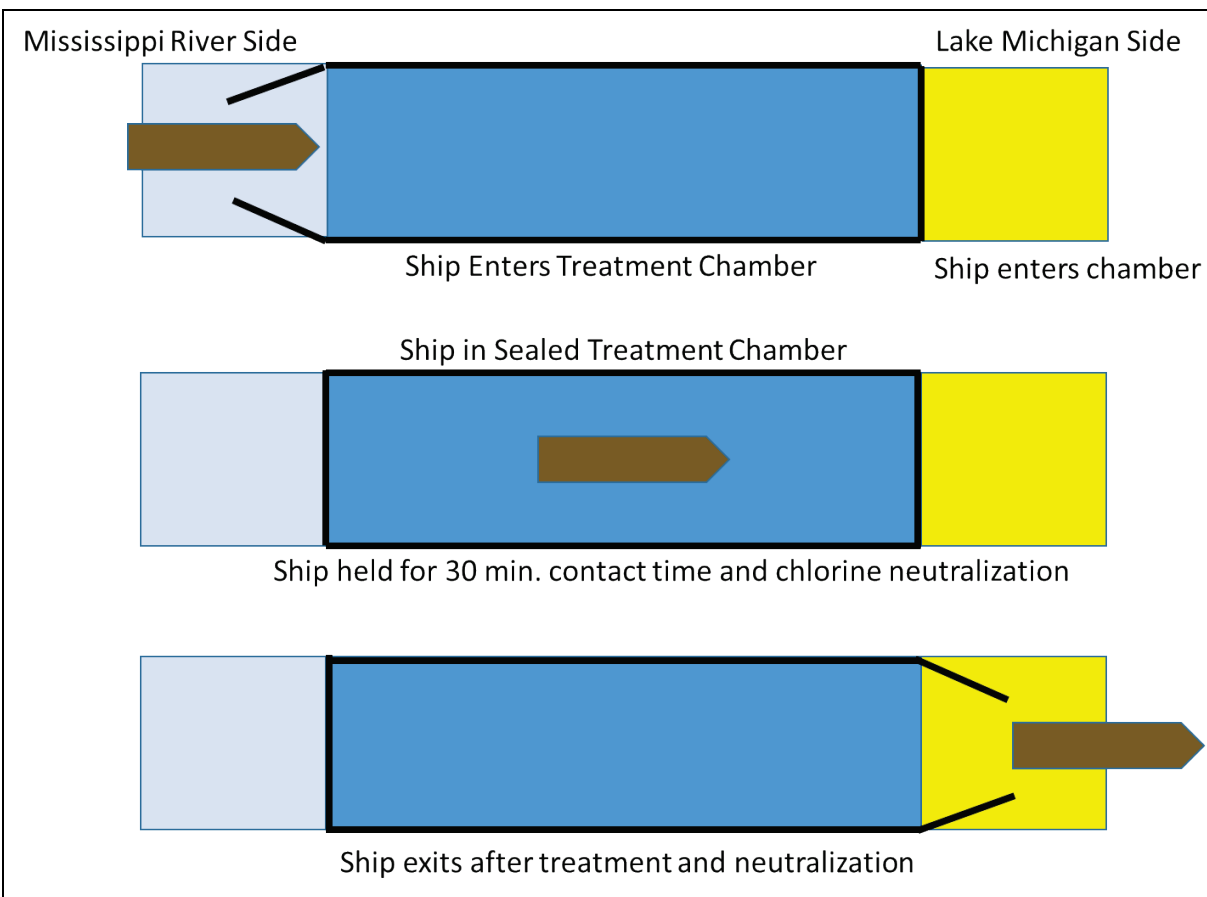
Figure 2.   Conceptual operation of treatment chamber (based on CH2M 2016).

The chemical treatment method chosen was chlorination. The system would use sodium hypochlorite, which is specified in the document as a 12.5% solution. It was determined that this method was easier to manage compared to chlorine gas.

The goal would be to achieve a treatment dose of 10 mg/L free chlorine. The report recognized the need to add additional chlorine to overcome the chlorine demand in the water. An exposure time of 30 minutes or less proposed in the document (CH2M 2016). Discussions with Mr. David Hamilton, P.E., Senior Policy Director of TNC, indicates that they believe a 15 minute exposure time is feasible. After treatment, the water would be treated with a strong reductant, sodium bisulfide, which is commonly used to neutralize chlorine.

Chlorination. Chlorination is a commonly used method for disinfection in drinking water (Hammer 1986; Snoeyink and Jenkins 1980), and as a biocide in swimming pools and fountains. It has a long history of safe use in drinking water system. Chlorine and related products are effective at killing pathogenic microorganisms and it can maintain a residual for an extended period of time, allowing drinking water to be protected in pipe systems. However, chlorine does attenuate over time due to reactions with organic compounds and evaporation.

Chlorination is indiscriminant in oxidation reactions. In most waters, there are competing constituents that can consume the chlorine, which is referred to as the chlorine demand

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(Snoeyink and Jenkins 1980). First, reduced inorganic compounds can react with the chlorine. These include reduced sulfur forms (sulfides and sulfites), reduced nitrogen forms (nitrite and ammonia), and various reduced metals. In addition, organic compounds existing in the water will react with the chlorine. To achieve an effective chlorine dose, losses to these reactions must be accounted for. The proposed plan does indicate that it will be necessary to over chlorinate to reach a target of 10 mg/L.

Chlorine releases to natural water bodies, however, can cause environmental damage in some cases. First, it is toxic to fish and other aquatic organisms. In particular, it burns gill tissues, and can be absorbed into the bloodstream in fish and other organisms. Furthermore, chlorine can react with organic compounds in natural waters to form a range of undesirable chlorinated disinfection by-products. Of particular concern are trihalomethanes, of which chloroform is most common (Snoeyink and Jenkins 1980; Figure 3). These compounds are regulated in drinking water as potential cancer causing agents. They can be very persistent and their presence can compromise a source for use as potable water.
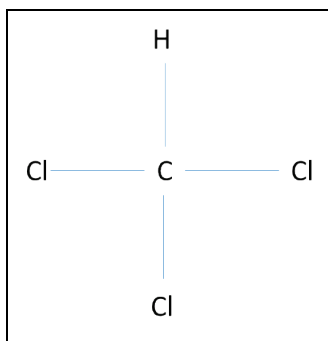

Figure 3. Chloroform, a
trihalomethane
of concern.

Chlorination refers to several different chloride forms that are commonly used to achieve oxidation and disinfection reactions (Snoeyink and Jenkins 1980). These include chlorine gas (Cl_2), chlorine dioxide (ClO_2) and hypochlorite forms (sodium [NaOCl] and calcium [$Ca(OCl)_2$]). In addition, the chlorination process can react with ammonia in the water to from chloramines (NH_2Cl, $NHCl_2$), which tend to have reduced oxidation power, but are also more stable. In some cases, ammonia is intentionally added to stimulate this reaction.

The chlorination method proposed for the BRLD is the use of sodium hypochlorite (NaOCl), commonly called bleach. Sodium hypochlorite has a long history of use for disinfection and is usually very effective. According to the CH2M (2016) white paper, it is attractive for the treatment chamber because it can be applied as a 12.5% solution, simplifying storage and safety issues.

When applied to water, sodium hypochlorite quickly dissociates, forming the hypochlorite ion (Snoeyink and Jenkins 1980):

$$NaOCl \leftrightarrow Na^+ + OCl^-$$

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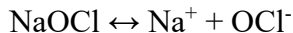
The hypochlorite ion will establish an equilibrium in with hypochlorous acid (HOCl), a weak acid:

$$OCl^- + H^+ \leftrightarrow HOCl, pKa = 7.5.$$

The hypochlorite ion has a pKa (disassociation constant) of 7.5. So, for pH >7.5, OCl^- predominates, and pH<7.5, HOCl predominates. This is important, since HOCl has a disinfection activity about 80 to 100 times higher than OCl^-. So, to achieve the best reactions, acidic conditions must be maintained, usually around pH 3 or 4. The application of sodium hypochlorite increases pH; therefore, acid is commonly added. Interestingly, the application of chlorine gas (Cl_2) undergoes reactions that also form the hypochlorous acid/hypochlorite ion equilibrium. However, the Cl_2 reaction actually lowers pH, so acid addition is not needed. An acid neutralization step is typically added prior to release of the treated water.

The plan proposed by TNC does not include any pH adjustment. The plan is to add enough chlorine to create sufficient toxic condition regardless of pH. This approach is reasonable, however, chlorination is a pH sensitive process, and it might be important to consider this in a more advanced design.

Chlorine toxicity to aquatic organisms tends to focus on the gills, which removes oxygen from the water. Scales and shells can protect organisms from absorbing chlorination compounds through their skin, but organisms with no scales or shells are often more susceptible to chlorination effects.

Chlorination for drinking water is commonly to levels of 0.2 to 2 mg/L, but can be as high as 5 mg/L (*https://www.corrosionpedia.com/definition/1102/total-chlorine*). Levels for skin contact typically range from 1 to 3 mg/L (Contra Costa Health Services 2014). Levels higher than 3 mg/L could result in irritations like red eye or swimmers itch (APEC Water 2018). However, levels as high as 10 mg/L are reported to be acceptable (Contra Costa Health Services 2014)

ANALYSIS OF CHLORINE TOXICITY DATA

According to CH2M (2016), a residual chlorine concentration of 10 mg/L for a 30 minute exposure should be sufficient to destroy AIS in the treatment lock. Zillich (1972) and Brungs (1973) supports the assessment that 10 mg/L would be toxic to most aquatic organisms. Additional data was provided by Mr. David Hamilton of the TNC, and is summarized in Table 1. In our professional judgment, Table 1 effectively summarized available literature to support the contention a 30-min exposure to 10 mg/L would be fatal to species of fish that have been tested and therefore should be fatal to Asian Carp. 10 mg/L is greater than all concentrations associated with LD50, 10 times greater than most concentrations (see Table 1), and almost 100 times greater than many concentrations (USEPA, 1985). Many of the species tested are cypriniform fishes (minnows and carps), most of which have lower LD50s than most perciform fishes (sunfishes, darters), suggesting that cypriniform data may be applicable to other taxonomically related taxa (like Asian Carp).

In addition, Heath (1977) studied the effects of chlorine on several fish species, including common carp (*Cyprinus carpio*). The free chlorine concentrations were much lower than those proposed for

the treatment chamber, <1 mg/L. Still the paper suggests that carp are relatively resistant to chlorination compared to the other species, although no reason was given for this difference.

Both the 100% mortality and the LC50 do not necessarily mean that the fish were killed within the given exposure time. The exposure time relates to the time the fish were exposed to the chlorine, but it is common that exposed were then transferred to another tank (recovery tank) and observed for 24 to 72 hours. Some of the fish may die in the exposure time, but others may die after. The LC50% and the 100% mortality number are calculated on the survival of these fish both during the exposure and in the recovery tanks. So, this also needs to be accounted for in applying this data to a treatment chamber intended to kill organisms prior to release.

Table 1. Summary of Chlorine Toxicity. Data provided by David Hamilton, TNC, and checked by ERDC team.								
Results from chlorine toxicity tests on aquatic species Total Residual Concentration (mg/l) that causes 100% mortality								
Species	size	exposure time (min)	10 °C	15 °C	20 °C	25 °C	30 °C	reference
Rainbow trout	juvenile	30	1.6	1.5	0.69			Brooks and Seegert (1977)
Yellow perch	YOY	30	15	7.1	2.1	1.6	0.95	Brooks and Seegert (1977)
Spottail shiner	adult	30			0.83			Seegert and Brooks (1978)
Alewife	juvenile	30					0.63	Seegert and Brooks (1978)
Total Residual Concentration (mg/l) that causes LC50 (50% mortality)								
Rainbow trout	juvenile	30	0.99	0.94	0.6			Brooks and Seegert (1977)
Yellow perch	YOY	30	8	3.9	1.11	0.97	0.7	Brooks and Seegert (1977)
Emerald shiner	55 mm	15				0.57		Brooks and Bartos (1984)
Emerald shiner	55 mm	30				0.44		Brooks and Bartos (1984)
Channel catfish	96 mm	15					1.27	Brooks and Bartos (1984)
Channel catfish	96 mm	30					1.12	Brooks and Bartos (1984)
Spottail shiner		30	2.41	1	0.53			Seegert and Brooks (1978)
Smelt	adult	30	1.27					Seegert and Brooks (1978)
Alewife	juvenile	30		2.27			0.3	Seegert and Brooks (1978)

DISCUSSION

Mixing

The proposed process relies on delivering a chlorine concentration of 10 mg/L throughout the treatment lock. Mixing is a challenging task in water treatment. Flash mixing vessels are typically cylindrical to minimize dead spaces (Hammer 1986). Square tanks, although easier to build, generally result in dead spaces where mixing is incomplete. Rectangular basins are still more challenging. The fact is that the lock was not designed to be an efficient mixing basin. It is a very elongated rectangle (110 ft x 600 ft); so, it is likely that dead spaces would occur that may

allow organisms to escape treatment. These areas would most likely be in the corners, although they could occur in other places as well.

The mixing issue would be further exacerbated by the addition of the ship or barge in the lock. Furthermore, since these vessels can be of different size and geometry, the mixing issue is not a trivial one to address. Spaces between barges and tugs could create dead zones in which mixing does not reach. Mixing could be addressed by adding chlorine in excess, which would allow for diffusion to allow chlorine to move into the dead areas. But this would then exacerbate any issues involving chlorine release or corrosion (see below).

The mixing issue also affects the plan to neutralize the chlorine. The idea is to use a strong reductant, sodium bisulfite. Inefficient mixing in the neutralization process could allow for unreacted chlorine and unreacted bisulfite to escape the system. Sodium bisulfite is not considered an important environmental contaminant, but it is reactive, it can effect eyes and mucous membranes at high concentrations, and it can have a bad odor.

The proposed CH2M plan includes a detailed discussion of mixing, and it is clear that this issue is understood as being important. The article discusses both mechanical and jet mixing and settles on jet mixing as the best alternative. Two configurations of jet mixing nozzles were explored, consisting of 18 and 16 nozzles respectively. The author's professional opinion is that such an extensive mixing system could be sufficient to achieve sufficient mixing. However, further modeling, either physical or numerical, to confirm this is recommended by this group.

Assumption that a chemical treatment system can be fully contained. The success of the proposed treatment concept assumes that the treatment structure can completely isolate the chlorination processes until the reaction is completed and the chlorine could be neutralized by sodium bisulfate. Locks are well designed systems to allow navigation around river structures and accommodate water level differences. However, they are not designed to be completely water tight. Some water loss may occur, and this effect should be quantified.

Corrosive effects on ships and treatment chamber structure. Chlorine is a strong oxidizer. As such, it can be very corrosive. Controlling corrosion in drinking water systems that use chlorination is a critical design and operational consideration. In terms of design, flash mixing areas and reaction vessels are constructed using corrosion resistant materials. In operation, pH is carefully monitored and controlled (usually above pH 8). Alkalinity is also maintained to allow thin coatings of calcium carbonate to deposit on pipe surfaces, protecting them from corrosion. Even with these safeguards in place, corrosion does occur.

This issue could be addressed by a survey of building materials in the treatment chamber coupled with corrosion testing as needed. The treatment chamber should also be carefully monitored during operations. Similarly, shipping vessels should be surveyed for materials susceptible to corrosion. Of particular concern would be exposed metal and seal materials.

Potential for releases affecting human health. The chemicals proposed for this project can have severe human health effects. There is extensive experience using these chemicals in water treatment and other industrial processes, but risk does exist. Applying chlorine as a concentrated bleach form does reduce risk as opposed to gaseous chlorine application, but

concentrated bleach can also be an inhalation and exposure hazard. The concentrated bleach would be most hazardous to staff that directly handle it. However, once mixed in the lock, exposure issues should be minimized substantially.

Other. After conducting our analysis, ERDC reviewed a document prepared by the Chicago District in 2016 titled *Comments on Draft Conceptual Aquatic Invasive Species Treatment System for the Chicago Area Waterways*. Many of the critical issues identified by the ERDC analysis were also mentioned in the Chicago District Analysis. Some additional issues include:

- Cleanout of killed organisms after treatment. Putrefaction could make this a very unpleasant task. The proposed plan would be to use the treatment chamber after water jets and noise disruption, which would reduce the number of large organisms killed in this process.

- Regulatory approval and compliance challenges.

- Costs not accounted by the CH2M Hill whitepaper, such as road costs and if changes to the lock are required.

- Potential for vaporous release of chlorine that may affect lock workers and vessel personnel. The potential for this is reduced, but not fully eliminated, by the use of sodium hypochlorite solution, as these solutions can be hazardous if inhaled.

- Potential effects on water craft and people.

ALTERNATIVES TO CHLORINATION: One of the challenging issues of chlorination is its relatively long attenuation. Approaches with much faster attenuations might be valuable, some examples are:

- Ozone – Ozone is a powerful oxidant that has been widely used for disinfection. It has the advantage in that it does not form trihalomethanes. However, it is generally energy intensive.

- Hydrogen peroxide – Hydrogen peroxide is a very powerful oxidant that can be used for disinfection and destruction of harmful algae (Barrington et al. 2013). It is relatively short lived, and degrades into water and oxygen. However, hydrogen peroxide can only be provided as a liquid, which makes storage and handling challenging.

- Superoxide radical – ERDC has tested a reactor that generated superoxide radicals, the KRIA Water Treatment System (Medina et al. 2016a). It was very effective in treating algae (Medina et al. 2016b), and can superoxygenate water.

- Cavitation – Cavitation creates turbulence that may damage or destroy AIS and it also generated radicals. Cavitation has been used in the treatment of cyanobacteria (Li et al. 2013; Li et al. 2015; Medina et al. 2016b; Wu et al. 2012). Both superoxide and cavitation are intriguing, but have far less data associated with them.

These might be interesting alternatives, although they certainly may have critical issues of their own.

RECOMMENDATIONS: Prior to implementation of a chemical treatment chamber, the ERDC team recommends the following:

- A series of toxicity studies with Asian Carp and *A. lacustre* to determine their chlorine toxicity up to 30 minute exposures. The goal should approach 100% mortality with the 15- to 30-minute exposure. The study should include delayed mortality effects.

- A study investigating chlorine interactions with materials of the lock, to explore chlorine consumption and corrosion.

- A study on chlorine interactions with water from the lock to investigate chlorine demand and transformational products.

- A model of the lock (computer or physical) to investigate mixing, including effect of ships and barges.

These recommendation are consistent with findings in the CH2M document.

In this document, we have presented several concerns regarding the proposed treatment chambers, and have recommended several studies to be conducted. However, if it is determined that such a system would be beneficial and costs are accounted for, none of the engineering issues appear to be impossible to accomplish.

REFERENCES

Advanced Purification Engineering Corp. (APEC) 2018. *Proper chlorine levels for a healthy pool*. *http://www.freedrinkingwater.com/water-education3/proper-chlorine-levels-for-a-healthy-pool.htm* (Retrieved on 3 Jan 2018).

Arthur, J. W., and J. G. Eaton. 1971. Chloramine toxicity to the amphipod *Gammarus Pseudolimnaeus* and the fathead minnow *Pimephales prometas*. *Journal of the Fisheries Research Board of Canada* 28(12):1841–1845. *https://doi.org/10.1139/f71-278*.

Barrington, D. J., E. Reichwaldt, and A. Gharouani. 2013. The use of hydrogen peroxide to removal cyanobacteria and microcystins from waste stabilization ponds and hypereutrophic systems. *Ecological Engineering* 50:86–94. *https://doi.org/10.1016/j.ecoleng.2012.04.024*.

Brooks, Arthur. S. and James M Bartos. 1984. Effects of free and combined chlorine and exposure duration on rainbow trout, channel catfish, and emerald shiners. *Transactions of the American Fisheries Society*. 113:786–793. *https://doi.org/10.1577/1548-8659(1984)113<786:EOFACC>2.0.CO;2*.

Brooks, A. S., and G. L. Seegert. 1977. The effects of intermittent chlorination on rainbow trout and yellow perch. *Transactions of the American Fisheries Society*. 106(3):278–286.

Brungs, W.A. 1973. Effects of residual chlorine on aquatic life. *Water Pollution Control Federation* 45(10):2180–2193. *http://www.jstor.org/stable/25038016*.

CH2M. 2016. *Conceptual aquatic invasive species treatment system for the Chicago Area Waterways*. WT0916161147MKE. Prepared for the Nature Conservancy. Milwaukee, WI. *https://www.nature.org/ourinitiatives/regions/northamerica/unitedstates/ohio/newsroom/the-nature-conservancy-proposes-an-ais-prevention-solution-to-stop-invasive.xml*. (accessed on 2 Jan 2018).

Contra Costa Health Services. 2014. Public Swimming Pool and Spa Operating Requirements. Environmental Health Division. Concord, CA. *https://cchealth.org/eh/recreational-health/*. (accessed on 2 Jan 1018).

Duncker, J. 2011. *The Chicago Area Waterway System, Asian Carp, and the Great Lakes*. PowerPoint presentation slides. USGS – Illinois Water Science Center. *https://acwi.gov/monitoring/webinars/CAWS_AsianCarp_20111013.pdf*

Hammer, M. 1986. *Water and wastewater technology*. Second Edition. New York, NY: Wiley.

Heath, A. G. 1977. Toxicity of intermittent chlorination to freshwater fish: Influence of temperature and chlorine form. *Hydrobiologia* 56(1):39–47.

Holliman, F. M., K. J. Kilgore, and C. Shea. 2015. *Development of operational protocols for electric barrier system on the Chicago Sanitary and Ship Canal: Induction of passage-preventing behaviors on small sizes of silver carp*. ERDC/ANSRP-15-1. Vicksburg, MS: U.S. Engineer Research and Development Center. *https://erdc-library.erdc.dren.mil/xmlui/handle/11681/5087*.

Hubert, T. D., M. A. Bogaard, and K. T. Fredricks. 2016. *Identify potential lock treatment options to prevent movement of aquatic invasive species through the Chicago Area Waterway System (CAWS)*. U.S. Geological Survey open file report 2016-1001. *https://doi.org/10.3133/ofr20161001*.

Li, P., Y. Song, S. Yu. 2013. Removal of *Microcystis aeruginosa* using hydrodynamic cavitation: Performance and mechanisms. *Water Research* 62:241–248.

Li, P., Y. Song, S. Yu, H-D Park. 2015. The effect of hydrodynamic cavitation of *Microcystis aeruginosa*: Physical and chemical factors. *Chemosphere* 136:245–251.

Medina, V. F., A. B. Morrow, R. Wade, and C. Thomas. 2016a. *Testing of the KRIA ionizing water treatment system for waters contaminated with Diesel, PCBs, and nutrients (nitrogen forms)*. ERDC/EL TR-16-03. Vicksburg MS: U.S. Army Engineer Research and Development Center. *http://acwc.sdp.sirsi.net/client/en_US/search/asset/1048390.*

Medina, V. F., C. S. Griggs, and C. Thomas. 2016b. Evaluation of the destruction of the harmful cyanobacteria, *Microcystis aeruginosa*, with a cavitation and superoxide generating water treatment reactor. *Bulletin of Environmental Toxicology and Contamination*. 96(6):791–796. Doi: 10:1007/S00128-016-1742-6.

Parker, A. D., P. B. Rogers, J. G. Stewart, D. G. Glover, S. T. Finney and R. L. Simmnonds. 2013. *Fish behavior and abundance at the electric dispersal barrier in the Chicago Sanitary and Ship Canal, Illinois, USA*. Presentation Slides for the 2013 International Conference on Aquatic Invasive Species. *http://www.icais.org/pdf/2013abstracts/4Thursday/B-10/1050_Parker.pdf*.

Seegert, G. L., and A. S. Brooks. 1978. The effects of intermittent chlorination on Coho Salmon, Alewife, Spottail Shiner, and Rainbow Smelt. *Transactions of the American Fisheries Society* 107(2):346–353.

Snoeyink, V. L., and D. Jenkins. 1980. *Water Chemistry*. New York, NY: John Wiley and Sons.

United States Army Corps of Engineers (USACE). 2014. *The GLMRIS Report: Great Lakes & Mississippi River Interbasin Study Report*. *http://glmris.anl.gov/documents/docs/glmrisreport/GLMRIS_Report.pdf.*

United States Army Corps of Engineers (USACE). 2015. *Great Lakes and Mississippi River Interbasin Study – Brandon Road. Feasibility Study Project Management Plan*. *http://www.mvr.usace.army.mil/Portals/48/docs/PM/GLMRIS%20-%20BR%20PMP%201%20May%202015.pdf*

United States Environmental Protection Agency (USEPA). 1985. *Ambient Water Quality Criteria for Chlorine - 1984*. EPA 440/5-84-030. Washington, DC. Office of Water Regulations and Standards Criteria and Standards Division.

Wu, Z., H. Shen, B Ondruschka, Y. Zhang, W. Wang, D. H. Bremner. 2012. Removal of blue-green algae using the hybrid method of hydrodynamic cavitation and ozonation. *Journal of Hazardous Materials* 235–236:152–158. *https://doi.org/10.1016/j.jhazmat.2012.07.034*.

Zillich, J. A. 1972. Toxicity of combined chlorine residuals to freshwater fish. *Water Pollution Control Federation* 44(2):212–220. *http://www.jstor.org/stable/25037299*.