Alteration of Water Quality

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

ANS Control: Alternation of Water Quality – carbon dioxide (CO_2), ozone, nitrogen, alum, and sodium thiosulfate

Targeted Species: These controls may be effective for use in preventing both upstream and downstream movement of organisms. Specific species recognized as ANS of Concern – CAWS[1] could include those listed below, dependent on the Control.

Oxygen gas is bubbled through a stream to improve water quality. Alternatively, the Controls identified in this fact sheet may be used to degrade water quality to prevent the movement of aquatic nuisance species.

Alum – Algae included in ANS of Concern – CAWS

Sodium Thiosulfate – Annelids, bryozoans, copepods, crustaceans, fish, mollusks, and protozoans included in ANS of Concern – CAWS

Carbon Dioxide – Annelids, bryozoans, copepods, fish, and protozoans included in ANS of Concern – CAWS

Ozone – Algae, annelids, bryozoans, copepods, fish, and protozoans included in ANS of Concern – CAWS

Nitrogen – Annelids, bryozoans, copepods, fish, and protozoans included in ANS of Concern – CAWS

Selectivity: Alum is selective for algae. Sodium thiosulfate, carbon dioxide and ozone are non-selective. Nitrogen and its by-products are non-selective for most aquatic organisms. Activity on the non-selective species is dependent upon concentration, method and timing of application, and length of exposure.

Developer/Manufacturer/Researcher: Carbon dioxide, ozone, nitrogen, alum, and sodium thiosulfate are produced for a variety of commercial purposes. Suppliers are available in most metropolitan areas. The University of Illinois at Urbana-Champaign (UIUC) and the Illinois Natural History Survey are conducting research on oxygen depletion and carbon dioxide treatments on silver and bighead carp (Cory Suski, UIUC, E-mail communication, 2011).

Pesticide Registration/Application: Pesticides, including carbon dioxide, must be applied in accordance with the full product label as registered by the U.S. Environmental Protection Agency (USEPA). Users must read and follow the pesticide product label prior to each application. The registration status, trade name, and availability of pesticides are subject to change. The listing of a

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

pesticide in this fact sheet or Appendix B does not represent an endorsement by the U.S. Army Corps of Engineers or the USEPA regarding its use for a particular purpose.

Brief Description: A variety of chemical compounds can be used to alter water quality to prevent the movement of ANS through an aquatic pathway. Many species can tolerate inhospitable environments for short periods of time. The concentration of a chemical compound and the duration of the exposure must be determined to maximize effectiveness for a specific species. Individuals may be injured but survive sub-lethal doses or inadequate exposure times.

Carbon Dioxide – In a desktop exercise, the U.S. Army Engineer Research and Development Center (ERDC) simulated injecting carbon dioxide gas at the bottom of the Chicago Sanitary and Ship Canal, using a bubbler delivery system, through anchored tubing near the bottom of a waterway. High CO_2 levels usually correlate with low dissolved oxygen (DO), which increases CO_2 toxicity to fish (Fivelstad et al. 1999). The toxicity of CO_2 results from lowering an organism's blood pH (acidemia), creating irreversible cell damage and death. High CO_2 levels can also cause other water quality changes that may impact aquatic species, such as water pH and metal solubility changes.

Ozone – Ozone is commonly used in drinking water and waste water treatment and in industrial settings to disinfect water and disinfect surfaces. The stable form of oxygen is made up of two oxygen atoms, while the unstable ozone is made up of three. When ozone breaks down it gives rise to oxygen free radicals, which are highly reactive and capable of damaging many organic molecules through the process of oxidation. Ozone oxidation is toxic to most small waterborne organisms (Leynen et al. 1998) and has been found to destroy the epithelium covering the gill lamella in bluegill fish. Destruction of the epithelium can cause either immediate mortality or leave the fish highly susceptible to microbial infections (Paller & Heidinger 1979).

There are several ways to create ozone for water treatment, most commonly by using high voltage sparks or intense ultraviolet light. Once created, the ozone gas is then applied using porous diffusers, radial diffusers, or venturi injectors.

Nitrogen – Nitrogen supersaturation can cause health deterioration in fish. Supersaturation occurs when the partial pressure of one or more gases becomes greater than the atmospheric pressure and the water contains excess dissolved nitrogen. Once the tissue and organs of fish reach equilibrium with the supersaturated environment, supersaturated gases may leave solution and form nitrogen bubble embolisms. This condition, referred to as gas bubble disease, physically blocks blood circulation in the fish and eventually leads to death.

Alum (aluminum sulfate) – There is a direct relationship between the amount of phosphorus in a lake and the amount of algae growing in the lake. The amount of algae increases as phosphorus levels increase. Alum forms an aluminum hydroxide precipitate on contact with water, which reacts with phosphorus to form an aluminum phosphate compound. This compound binds with phosphorus, making this essential nutrient unavailable to algae. Alum is commonly used in lakes for algae control (Kennedy & Cooke 1982).

Sodium Thiosulfate – Sodium thiosulfate has been investigated as one method of reducing dissolved oxygen in water to prevent the transfer of ANS (Malchoff et al. 2005). Dissolved oxygen is required for aquatic organisms to respire. Dissolved oxygen levels are lethal for many fish species below 0.3 parts per million (Piper et al. 1986). However, it is commonly accepted that Asian carp are tolerant of DO less than 3 parts per million (ppm) (Oregon Sea Grant 2011).

Prior Applications:

Carbon Dioxide – Carbon dioxide has a variety of industrial and food uses, but it is currently not used operationally for controlling ANS movements. Carbon dioxide is being tested experimentally in the laboratory and in lakes to determine physiological and behavioral reactions of silver and bighead carp to different levels of exposure (Cory Suski, UIUC, E-mail communication, 2011).

Ozone – Ozone is commonly used at fish hatcheries and water treatment facilities to prevent contamination from bacteria. It is also used for disinfection of drinking water and treatment of wastewater, and for microbial control or advanced oxidation of trace chemicals.

Nitrogen – Unintentional nitrogen supersaturation commonly occurs in both fish hatcheries and below dams. Nitrogen has not been commonly used to control ANS.

Alum (aluminum sulfate) – Alum is a nontoxic material commonly used in water treatment plants to clarify drinking water. In lakes, alum is used to control the amount of the nutrient phosphorus in the water. The effectiveness of alum treatments depends on the amount of alum applied, the lake's existing chemical conditions (water quality), and the sedimentation rate and external phosphorus loading contributed to the lake from its watershed after the treatment. Depending on these factors, the effectiveness can range from less than 1 year to 21 years (Welch & Cooke 1999). Alum in not used to control algae in large open flowing systems (Kennedy & Cooke 1982).

Sodium Thiosulfate – Sodium thiosulfate has been used in fish hatcheries for dechlorination following disinfection (Waldrop et al. 2009) and for reducing dissolved oxygen in boiler systems (Cavano 1997).

General Effectiveness: The effectiveness of the aforementioned Controls depends on the concentration and exposure time. If applied in an open flowing system, exposure time is greater for upstream movement as compared with downstream movement. Many species can tolerate inhospitable environments for short periods of time. Species that are exposed to sub-lethal concentrations or for too short of time, may be injured but may survive. Application of high concentrations of gases in an open, flowing system may be difficult to control.

With respect to fish, the effectiveness of dissolved gases for controlling ANS fish depends upon the species of fish, size of the fish, and duration of exposure. In general, most fish begin to experience stress when dissolved oxygen levels are less than 5 ppm, nitrogen levels are greater than 100% saturation (supersaturation), or carbon dioxide levels are greater than 10 ppm (Piper et al. 1986). However, many of the fish species within the CAWS are tolerant to a broad range of gas concentrations and may not be affected by moderate exceedance of these thresholds. Field and laboratory studies indicate that many fish species tolerate substantially lower levels of DO. Smale and

Rabeni (1995) showed that headwater fishes survived short-term when exposed to 1.5 ppm DO, and it is commonly accepted that Asian carp are tolerant of DO less than 3 ppm (Oregon Sea Grant 2011). Sub-lethal levels of carbon dioxide are currently being studied to determine if they act as a behavioral barrier for invasive species of fish in the CAWS.

Carbon Dioxide – Application of CO_2 in high concentrations would potentially be effective against many invasive animal species, but it is non-selective and would also affect non-target species in the treatment area. Fish utilize special sensory cells on their gill arches to determine the presence of carbon dioxide (Perry & Reid 2002). Some early life stages of fish are more CO_2 tolerant than other fish in later life stages (Kikkawa et al. 2003). High levels of dissolved oxygen could inhibit the effectiveness of CO_2 because fish can tolerate considerably higher levels of CO_2 for short periods, even when dissolved oxygen is near saturation (Ross et al. 2001; Ishimatsu et al. 2005). High CO_2 levels would also stimulate growth of some aquatic plant species (Idso et al. 1987).

Ozone – Depending on concentration and exposure time, ozone is capable of killing ANS. The chemical is toxic to all life stages of fish, however, it is less toxic to eggs than to the larval stages of several fish species (Asbury & Coler 1980).

Nitrogen – Nitrogen gas is less lethal to fish than CO_2 and ozone. Adult fish are more tolerant of nitrogen supersaturation than young fish (Ebel 1969).

Alum (aluminum sulfate) – Alum treatment of an open flowing system may not be an effective method to control algae. Nutrient inactivation using alum is only appropriate where internal loading (sources from within the lake, such as decomposing organic material or resuspension of bed sediments) is a significant phosphorus source (Cooke et al. 2005). In systems that have a continuous elevated phosphorus loading from external sources, such as wastewater treatment plants and urban runoff (fertilizers), alum treatment may not be effective (Welch & Cooke 1999). Additionally, under anoxic conditions, phosphorous can be re-released, which can decrease the effectiveness of alum.

Sodium Thiosulfate – Factors determining the rate at which sodium thiosulfate reacts with water include the purity of the water (the potential for side reactions), the residence time in a system, the location of the chemical feed, the applied concentration, the temperature of the water, and the water's pH.

Operating Constraints: In a flowing system, maintaining an effective concentration and exposure time for these Controls may be constrained by the system's non static conditions such as fluctuations in volume and flow velocity during dry and wet weather conditions, inconsistent flow direction, variability in water density throughout channel depth, removal of water by users, addition of effluent from dischargers to the waterway, and the variability of sediment conditions along the targeted area. In addition, control of gas application in an open environment would be difficult at best, due to the tendency of the gases to move into the atmosphere.

Carbon Dioxide – In its desktop exercise, ERDC calculated approximately two atmospheres of pressure created; CO_2 solubility in water was measured in the range of 2500 mg/L. ERDC estimated that achieving a concentration of 100 mg/L CO_2 in the Chicago Sanitary and Ship Canal at the Electric

Fish Barrier site in Lockport, IL would require approximately 2,100,000 pounds of CO_2 per day. The largest tank truck available holds only 40,000 pounds of liquid CO_2. Supplying the aforementioned quantity of gas to the channel would require 35 tank truckloads of CO_2 per day (equal to a semitrailer delivery to the barrier site every 41 minutes). The largest bulk storage tank currently available is 70,000 pounds, so onsite storage would not be a practical solution.

CO_2 is a greenhouse gas, and introducing the quantity of CO_2 identified by ERDC would reduce the pH of the waterway to below five. If applied in an open system, prolonged exposure to acidified water from elevated CO_2 concentrations may injure submersed structures and channel walls and may alter sediment chemistry releasing sediment bound contaminants into the water column. Introducing the required quantity of CO_2 into the waterway may reduce the water's temperature. Due to its gaseous properties, CO_2 may prove to be ineffective in open flowing systems.

Ozone – Ozone must be produced onsite. Ozone may prove to be ineffective in open flowing systems, due to its gaseous properties and high reactivity. If applied in an open flowing system, diffused ozone, a reactive gas, may impact nearby plants and buildings, and pose a risk to human health. Ozone is a component of photochemical smog; however, unlike other chemical disinfectants or biocides, ozonation does not leave any objectionable by-products. Upon degradation in a waterway, ozone would increase dissolved oxygen in the waterway.

Nitrogen – The operating constraints of nitrogen are similar to those of carbon dioxide. Supersaturation of open flowing systems may not be possible. Nitrogen gas infusions may increase ammonia levels in a waterway and could spur nuisance plant growth in nitrogen limited systems.

Alum (aluminum sulfate) – Guidelines for alum application require that the pH remain within the 5.5-9.0 range (Kennedy & Cooke 1982). Alum would work only in the non-flowing connections of the CAWS. Alum coagulates dissolved and suspended solids in water, and these coagulated solids then settle. If applied in an open system, coagulated solids, if not collected and removed, would settle and add to the sediment layer within the waterbody.

Sodium Thiosulfate – Most prior applications of sodium thiosulfate have been employed in closed systems, and therefore, this control may not be effective in an open flowing system. The addition of oxygen depleting substances will reduce dissolved oxygen concentrations within a body of water; however, in an open system, the water will also absorb oxygen from the atmosphere continuously. This may result in larger input requirements of sodium thiosulfate.

Cost Considerations: The following are general cost considerations for these controls.

Carbon Dioxide –

Implementation: Implementation would include the construction of a CO_2 generation plant or procurement of a delivery contact. Planning and design activities in this phase may include research and development of this Control (regarding concentration and exposure times, effectiveness for specific species), modeling, site selection, site-specific regulatory approval, development of plans and specifications, and real estate acquisition. Design will also include analysis of this Control's impact to existing waterway uses including, but not limited to, flood risk management, natural resources, navigation, recreation, water users and dischargers, infrastructure impacts from acid degradation, and required mitigation measures.

Operations and Maintenance: Operations and maintenance would include maintenance of the piping and bubbler system and continuous monitoring of water quality to ensure effective mixing. Possible canal wall maintenance and downstream pH adjustment may be necessary.

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

Ozone –

Implementation: Ozone equipment size and cost varies by the amount of water being treated. Implementation costs may include the construction of an ozone generation and treatment plant, and distribution system. Planning and design activities in this phase may include research and development of this Control (regarding concentration and exposure times, effectiveness for specific species), modeling, site selection, site-specific regulatory approval, development of plans and specifications, and real estate acquisition. Design will also include analysis of this Control's impact to existing waterway uses including, but not limited to, flood risk management, natural resources, navigation, recreation, water users and dischargers, and required mitigation measures.

Operations and Maintenance: Operations and maintenance would include maintenance of the ozone generation plant and treatment plant. Additionally, the onsite generation of ozone is energy intensive, therefore, energy would be an ongoing operation cost.

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

Nitrogen – The cost considerations for nitrogen are expected to be similar to those of carbon dioxide.

Alum (aluminum sulfate) –

Implementation: The implementation cost for alum treatment is greatly varied, depending upon the amount of water being treated, site characteristics (i.e. ease of access), equipment requirements and whether the pH must be adjusted.

Planning and design activities in this phase may include research and development of this Control (regarding concentration and exposure times, effectiveness for specific species), modeling, site selection, site-specific regulatory approval, development of plans and specifications, and real estate acquisition. Design will also include analysis of this Control's impact to existing waterway uses including, but not limited to, flood risk management, natural resources, navigation, recreation, water users and dischargers, and required mitigation measures.

Operations and Maintenance: Operations and maintenance would include application of the chemical and monitoring of phosphorous levels to determine when reapplication is required.

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

Sodium Thiosulfate –

Implementation: A supplier would need to be found and a method of application developed for each system to ensure the target concentration is met throughout the water column.

Planning and design activities in the implementation phase may include research and development of this Control (regarding concentration and exposure times, effectiveness for specific species), modeling, site selection, site-specific regulatory approval, development of plans and specifications, and real estate acquisition. Design will also include analysis of this Control's impact to existing waterway uses including, but not limited to, flood risk management, natural resources, navigation, recreation, water users and dischargers, and required mitigation measures.

Operations and Maintenance: Operations and maintenance would include application of the chemical(s) monitoring to ensure the targeted dissolved oxygen concentration is met and tested to ensure effectiveness of application in open flowing systems.

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

Citations:

Asbury, C, & R. Coler. 1980. Toxicity of dissolved ozone to fish eggs and larvae. *Journal Water Pollution Control Federation*, vol. 52(7), pp. 1990-1996

Cavano, R.R. 2007. Sulfites for Oxygen Control. Scranton Associates Incorporated. Accessed October 18, 2011. http://www.scrantonassociates.com/techarticles/soc.pdf

Cooke, G.D., E.B. Welch, S. Peterson, & S.A. Nichols. 2005. Restoration and Management of Lakes and Reservoirs, Third Edition. CRC Press, Taylor & Francis Group. Boca Raton, FL. 591 pp

Ebel, W.J. 1969. Supersaturation of nitrogen in the Columbia River and its effect on salmon and steelhead trout. Fishery Bulletin, vol. 68:1

Fivelstad, S., A.B. Olsen, H. Kloften, H. Ski, & S. Stefansson. 1999. Effects of carbon dioxide on Atlantic salmon (*Salmo salar)* smolts at constant pH in bicarbonate rich freshwater. *Aquaculture*, vol. 178, pp. 171-187

Ishimatsu, A., M. Hayashi, K.S. Lee, T. Kikkawa, & J. Kita. 2005. Physiological effects of fishes in a high- CO_2 world. *Journal of Geophysical Research* 110: 10.1 029/2004JC002564

Idso, S.B., B.A. Kimball, M.G. Anderson, & J.R. Mauney. 1987. Effects of atmospheric CO_2 enrichment on plant growth: the interactive role of air temperature. *Agriculture, Ecosystems & Environment* vol. 20(1), pp. 1-10

Kennedy, R. & G. Cooke. 1982. Control of lake phosphorus with aluminum sulfate: dose determination and application techniques. Water Resources Bulletin, vol. 18, pp. 389-395

Kikkawa, T., A. Ishimatsu, & J. Kita. 2003. Acute CO_2 tolerance during the early developmental stages of four marine teleosts. *Environmental Toxicology*, vol. 18, pp. 375-382

Leynen, M., L. Duvivier, P. Girboux & F. Ollevier. 1998. Toxicity of ozone to fish larvae and *Daphnia magna*. *Elsevier, Ecotoxicology and Environmental Safety*, vol. 41(2), pp. 176-179

Malchoff, M, J.E. Marsden, & M. Hauser. 2005. *Feasibility of Champlain Canal aquatic nuisance species barrier options.* Lake Champlain Sea Grant

Oregon Sea Grant. 2011. Aquatic invasions! a menace to the west, species guide. Accessed December 18, 2011. http://seagrant.oregonstate.edu/themes/invasives/toolkit/Asian-Carp.pdf

Paller, M.H & R.C. Heidinger. 1979. The toxicity of ozone to the bluegill. *Journal of Environmental Science and Health Part A: Environmental Science and Engineering*, vol. 14(3), pp. 169-193

Perry S.F. & S.G. Reid. 2002. Cardiorespiratory adjustments during hypercarbia in rainbow trout *Oncorhynchus mykiss* are initiated by external CO_2 receptors on the first gill arch. *Journal of Experimental Biology,* vol. 205, pp. 3357-3365

Piper, R.G., I.B. McElwain, L.E. Orme, J.P. McCraren, L.G. Fowler, & J.R. Leonard. 1986. Fish hatchery management. Unites States Department of Interior, Fish and Wildlife Service, Washington, D.C.

Ross, R.M., W.F. Krise, L.A. Redell, & R.M. Bennett. 2001. Effects of dissolved carbon dioxide on the physiology and behavior of fish in artificial streams. *Environmental Toxicology*, vol. 16(1), pp. 84-95

Smale, M.A. & C.F. Rabeni. 1995. Hypoxia and hyperthermia tolerances of headwater stream fishes. Transactions of the American Fisheries Society. vol. 124, pp. 698-710

Suski, C.D. October 25, 2011. University of Illinois at Urbana-Champaign. E-mail communication. suski@illinois.edu.

United States Environmental Protection Agency. 2008. Non-indigenous species migration through the Chicago Area Waterways (CAWs): Comparative Risk of Water Quality Criteria. U.S. EPA Office of Science and Technology, Washington D.C.

Waldrop, T., M. Gearheart, & C. Good. 2009. Disinfecting recirculating aquaculture systems: post-harvesting cleaning. *Hatchery International*. Courtenay, B.C: Capamara Communications in cooperation with the Aquaculture Engineering Society, 2009. http://www.hatcheryinternational.com/HI-jan-feb09.pdf

Welch, E.B. & G.D. Cooke. 1999. Effectiveness and longevity of phosphorus inactivation with alum. *Journal of Lake and Reservoir Management*, vol. 15, pp. 5-27