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LITERATURE SEARCH ON POTENTIAL EFFICACY OF AMMONIA BARRIER TO PREVENT ASIAN CARP MOVEMENT THROUGH THE CHICAGO AREA WATERWAY SYSTEM

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Purpose

The May 2010 Asian Carp Control Strategy Framework (Framework) outlined several options that would be considered to try to prevent the passage of Asian carp from the Illinois Waterway to Lake Michigan. Section 2.2.13 of the Framework discussed the potential of using ammonia toxic zones created by the Metropolitan Water Reclamation District of Greater Chicago's (District's) primary effluent to deter Asian carp from passing through the Chicago Sanitary and Ship Canal and the Little Calumet River towards Lake Michigan. The District performed a literature search to investigate ammonia toxicity to Asian carp or surrogate fish, as well as any evidence of ammonia avoidance by fish. The research was conducted to provide insight into what concentration of ammonia would be likely to deter fish movement upstream and to determine the efficacy of using an ammonia toxic zone for this purpose. This interim report summarizes the sources reviewed as well as findings of the literature search.

While there did not appear to be references available that reported the effects of ammonia on Asian carp species in particular, there are many studies regarding ammonia effects on other fish species, including common carp (*Cyprinus carpio*), that may be relevant to the discussion. A search of international journals that are not published in English may yield more information specific to Asian carp; however, this type of search was not performed. Most of the literature available on this topic reports the lethal and sublethal concentrations of ammonia to various fish species as determined by laboratory experiments. A limited number of references include behavioral and physiological observations of fish following exposure to different ammonia levels. There is no precedent in the scientific literature for purposely introducing ammonia as a method to deter fish, so the available information must be used to make inferences regarding the potential efficacy of such an approach.

Sources Used

Scientific literature databases available at the Loyola University Chicago library, such as Academic Search Premier and WorldCat Local, were used to find relevant literature references, as well as *Pegasus*, Loyola University Chicago Libraries' Catalog. Google Scholar and other on-line resources were also employed. Search terms included various keyword combinations of terms, such as ammonia, toxicity, fish, carp, Asian carp, fish avoidance, and fish behavior.

United States Environmental Protection Agency (USEPA) documents that were reviewed as part of this literature search included the "Draft 2009 Update Aquatic Life Ambient Water Quality Criteria for Ammonia—Freshwater" and "1999 Aquatic Life Ambient Water Quality Criteria for Ammonia." Articles published in the following journals were also reviewed:

Aquaculture,
Aquaculture International

Archives of Nature Conservation and Landscape Research
Comparative Biochemistry and Physiology
Ecological Applications
Environmental Toxicology
Indian Journal of Environmental Health
Journal of Fish Biology
Journal of Freshwater Ecology
New Zealand Journal of Marine and Freshwater Research
Transactions of the American Fisheries Society
Water Environment Research
Journal of Zhejiang University Science

Findings

Ammonia Toxicity

Total ammonia concentrations include unionized ammonia (NH_3) and ammonium ion (NH_4^+) in an equilibrium that is mediated by pH and temperature. NH_3 concentrations are higher under alkaline pH conditions. NH_3 is the more toxic species of ammonia since organisms are most permeable to the uncharged ammonia species (Eddy 2005, Passell *et al*., 2007).

There is a wide range of ammonia concentrations reported in the literature that cause acute toxicity in common carp (C*yprinus carpio*). The latest USEPA guidance on ammonia (USEPA, 2009) cites two studies which measured LC50 concentrations for common carp ranging from 16.48 – 31.18 mg/L total ammonia-nitrogen (N) at a pH of eight, which translates to NH_3 concentrations between 0.93 – 1.77 mg/L (Hasan and MacIntosh 1986, and Rao *et al*., 1975), depending on the size of the fish (lower LC50 concentrations were exhibited in smaller individuals). Table 8 of the 2009 draft ammonia criteria document ranks the Genus Mean Acute Values (GMAV) for various organisms. Out of the 27 fish genera included on this list, *Cyprinus* has the tenth lowest GMAV, which is 24.74 mg/L total ammonia-N (1.40 mg/L NH_3).

Peyghan and Takamy (2002) report LC50 concentrations of total ammonia-N as high as 123 mg/L (NH_3 = 0.69 mg/L) for adult common carp (average weight 570 grams) at pH 7-7.2, causing the authors to conclude, "Our data indicate that common carp in comparison with other fish species used in aquaculture has a higher LC50, and we may consider this fish as one of the most resistant fishes to ammonia toxicity in aquaculture. The differences in metabolic pathways and the ability of carp in changing ammonia to urea may be the reason for this high tolerance." Similarly, Eddy (2005) proposed that, "Common carp seem to tolerate rather than avoid ammonia," describing that some fish species, including common carp, can convert glutamate and ammonia to glutamine, which can then be stored in tissues until toxic ammonia conditions in the environment have ceased.

The available literature on ammonia toxicity described above indicates that NH_3 concentrations would likely have to range from 0.69 – 1.77 mg/L in order to be lethal to common carp.

Ammonia Avoidance

While many experiments have been dedicated to determining the degree to which various fish species are able to tolerate ammonia, there have been few studies observing fish behavior and avoidance in response to high levels of ammonia. None of the identified literature looked at common carp or Asian carp species. Fish behavior is an important consideration since, "Avoidance behavior can provide the first line of defense against adverse conditions and may reduce or eliminate the probability of death." (Richardson *et al*., 2001). Richardson et al. observed inanga (*Galzias maculates)*, common smelt (*Retropinna retropinna*), and common bully (*Gobiomorphus cotidianus*) in glass fluvaria at two ammonia concentrations as high as 25 times the Criteria Maximum Concentration reported in the 1998 USEPA ammonia criteria document. Neither of the experimental ammonia concentrations caused avoidance in inanga or common bully fish. Common smelt did exhibit ammonia avoidance, but this experiment was unable to identify a threshold concentration for such behavior. It was apparently difficult to maintain consistent levels of NH_3 because pH reductions caused a decrease in this more toxic form. These experiments also showed ammonia-related lethality in the fish that did not exhibit avoidance behavior, suggesting that an ammonia barrier may end up killing rather than deterring fish in the environment.

Fava and Tsai (1976) observed that blacknose dace (*Rhinichthys atratulus*) did not avoid total ammonia even at concentrations as high as 270 mg/L (NH_3 = 3.34 mg/L). Xu *et al.* specifically controlled NH_3 concentrations and found that tilapia (*Oreochromis niloticus*) exhibited avoidance behaviors only at the highest NH_3 treatment concentration of 2.65 mg/L.

However, none of the fish used in the studies described above are particularly good surrogates for Asian carp since they are all comparatively small; smelt, inanga, dace, and tilapia are schooling fish, and bullies are demersal. The avoidance behavior of schooling fish species may differ from that of solitary fish.

Passell *et al.,* (2007) used modeling to assess potential ammonia toxicity to fish in the Rio Grande River in New Mexico and shed some light on potential complications that may arise from attempting to use ammonia downstream of water reclamation plants as a fish barrier: "The dynamic reactions that take place when total ammonia in sewage discharge mixes with a receiving river and equilibrates between NH_4^+ and NH_3 complicate the effort to calculate the toxicity and both the spatial and temporal dimensions of the resulting NH_3 plume." While this article poses that ammonia may serve as a barrier to migrating fish, it does not discuss the efficiency of such a barrier, since this outcome is seen as a negative environmental consequence.

While a contaminant barrier may cause avoidance behavior in some fish species which prevents their passage, it would be an inconsistent, unreliable method to keep every individual Asian carp from passing through. There are indications that fish avoidance of higher ammonia concentrations have led to habitat fragmentation in the environment (Passell *et al.*), but it may not stop every fish, particularly of a species that is relatively tolerant of ammonia. Several of the reviewed articles suggest that if ammonia is high enough to cause behavioral modification, this concentration may also be sufficient to kill the fish before it has the opportunity to leave the toxic zone. Thus, such a barrier would effectively create a kill zone rather than an avoidance zone.

The scant literature available on fish avoidance behavior to ammonia indicates that a range of 2.65 – 3.34 mg/L NH_3 may be required in order to elicit an avoidance response in studied fish species.

Preliminary Conclusions

In 2010, total ammonia-N in the primary treated effluent from the southwest side of the Stickney Water Reclamation Plant (WRP) ranged from 3.66 – 36.41 mg/L (approximately 0.03 – 0.23 mg/L NH_3), with a daily mean of 19.78 mg/L, while the west side ranged from 2.49 – 19.50 mg/L (approximately 0.03 – 0.22 mg/L NH_3) with a daily mean of 11.88 mg/L. The Calumet WRP had a daily mean total ammonia-N concentration of 10.24 mg/L and a range of 3.16 - 19.87 mg/L (approximately 0.09 – 0.30 mg/L NH_3). At both WRPs, even the higher range of NH_3 concentrations during 2010 was much less than the values reported to cause fish avoidance or toxicity. Recall that in laboratory experiments the LC50 of NH_3 in common carp ranged from 0.69 – 1.77 mg/L, while 2.65 – 3.34 mg/L NH_3 was required to elicit avoidance behavior in various studied fish. Therefore, the NH_3 concentration necessary to provide a potential fish deterrent is 2 to 15 times higher than the *maximum* NH_3 concentrations found in primary effluent from the Stickney and Calumet WRPs.

It appears unlikely that after primary treatment or secondary treatment without nitrification the Stickney and Calumet WRPs wastewater discharge would consistently exhibit a high enough ammonia concentration to serve as either an efficient avoidance or kill zone for fish.

The most important factor contributing to the extent of toxicity in the ammonia zone would be pH. Maintaining appropriate or desired levels of ammonia may require modulating the pH, since higher pH values favor the more toxic, unionized form of ammonia. This may be a problem in the environment. Mean pH at Harlem Avenue in the Chicago Sanitary and Ship Canal downstream of the Stickney WRP ranged from 7.11 – 7.41 between 2005 – 2009. In the Little Calumet River at Halsted Street downstream of the Calumet WRP, the mean pH ranged from 7.11 – 7.51 during those years. Ammonia would be less toxic to fish at these pH levels compared to the acute toxicity values reported in the USEPA 2009, which were normalized to pH 8. The GMAV reported in the USEPA 2009 for total ammonia-N translates to approximately 1.40 mg/L NH_3. In order for NH_3 concentrations to approach this lethal threshold in the Chicago Area Waterway System (CAWS), pH would have to be increased to about 8.5, on average. However, when total ammonia-N discharged from the WRPs was in the lower range, pH would have to be in excess of 9.0 in order for NH_3 to reach lethal limits in the environment.

If primary effluent rather than secondary effluent without nitrification were used to create a fish barrier, then biochemical oxygen demand (BOD) could act in synergy with ammonia to deter fish. Significant amounts of BOD are present in the primary effluent at the Stickney and Calumet WRPs (mean five-day BOD ranged from 85 – 136 mg/L in 2010). BOD discharged into the CAWS could decrease dissolved oxygen (DO) concentrations in the barrier zone.

However, carp are known to gulp air from the water surface under low DO conditions, so low DO is not considered a viable way to deter Asian carp. While the combination of low DO and elevated ammonia may be more efficacious for a fish barrier than ammonia alone, this is not studied in the literature.

Disclaimer

It should be noted that the District does not condone the technique of using partially treated effluent in an effort to deter movement of aquatic nuisance species. This literature search was among many studies discussed by the Asian Carp Regional Coordinating Committee to potentially decrease the risk of aquatic nuisance species transfer between the Great Lakes and the Mississippi River basins.

Practical considerations for an ammonia toxic zone to prevent Asian carp migration upstream include determining the required length of such a zone, which is entirely unanswered by the current body of literature on fish avoidance. The acute toxicity studies cited in this literature search ranged in duration from two to four days. DeGrandchamp *et al.* found that electronically tagged bighead and silver carp in the lower Illinois River traveled an average of 6.83 and 10.61 km/day, respectively. Extrapolating the average travel distance for silver carp to four days (the length of three out of the four cited acute toxicity tests), the length of a deterrent fish barrier may need to be approximately 42 kilometers (26 miles) in order to provide necessary exposure time.

Also, it is uncertain where and how ammonia would be removed from the waterways. Furthermore, the effects of such a measure would impact all aquatic life, not just Asian carp. There are regulatory implications that would have to be addressed since the ammonia-laden discharges would violate the Clean Water Act and water quality standards. Effluent that has only undergone primary treatment could potentially contain other pollutants, such as metals and BOD at concentrations that would violate water quality standards. Discharging such pollutants may affect local indigenous aquatic life as well as cause unintended downstream consequences. To overcome this concern, effluents could undergo secondary treatment without nitrification, but there would still not likely be enough ammonia in these effluents to consistently and reliably deter Asian carp or other fish.

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