To Switch or Not to Switch—Potential Security Considerations in the Free Chlorine Versus Monochloramine Debate for Drinking Water Disinfection

Dan Kroll, Hach Homeland Security Technologies

Hach Homeland Security Technologies • 5600 Lindbergh Drive Loveland, Colorado 80539 • 970-663-1377 • DKROLL@hach.com

Abstract

As part of a recent development endeavor to design a early warning system for the drinking water distribution system, Hach Homeland Security Scientists, in coordination with experts from the Army Corps of Engineers Research and Engineering Laboratory and the Edgewood Biological and Chemical Command, have had cause to study the interactions of a wide variety of potential water borne threat agents with different levels of either free chlorine or monochloramine present.

This resulted in the accumulation of what is most likely the World's most extensive database on the reactions of these agents in common drinking water scenarios and their effect on the bulk parameters being monitored. This revealed some highly interesting and significant findings on the security repercussions of the Free Chlorine/Monochloramine debate.

These studies have lead to several significant findings that have security implications.

1. *Monochloramine is less reactive than free chlorine with many threat agents. This leads to concerns for both degradation of potential threats and their early detection.*
2. *Monochloramine is a less efficient disinfectant than free chlorine, especially, in the short contact time that may be encountered in a back flow attack.*
3. *Monochloramine use may lead to terrorist alteration of attack strategies making an attack more difficult to detect.*

The findings in these studies have significant repercussions as to the safety and security of our Nation's water supplies. Details of the studies are discussed along with recommendations to help alleviate the potential risk.

Introduction

In recent years there has been a push in the water treatment industry to move away from water disinfection using Chlorine towards procedures using Chloramine. The underlying cause behind this move is the concern that Free Chlorine reacts with organic materials contained in the water to form disinfectant byproducts (DBPs), primarily Trihalomethanes (THM) and Haloacetic Acids (HAA), which are carcinogenic in nature. The EPA has placed strict regulations on the amount of DBPs that are allowed to be present in finished drinking water. (EPA 1998, EPA 2006)

There are many advantages to using Monochloramine in this role including the following. (EPA 1999)

- Chloramines are not as reactive with organics in forming THMs and HAAs.
- Monochloramine residuals are more stable and longer lasting than Free Chlorine or Chlorine Dioxide residuals, providing better protection against bacterial regrowth in systems with large storage tanks or dead-end water mains.
- Monochloramine residuals have been shown to be more effective in controlling bacteria in biofilms because of their superior ability to penetrate biofilm.
- Because Chloramines do not tend to react with organic compounds, properly operated systems using Chloramines will experience fewer incidences of taste and odor complaints.
- Chloramines are inexpensive.
- Chloramines are easy to make.

There are also a number of disadvantages associated with the use of Monochloramine. (EPA 1999)

- The disinfecting properties of Chloramines are not as strong as other disinfectants, such as Chlorine, Ozone, and Chlorine Dioxide.
- Chloramines may not have adequate oxidizing power to oxidize some inorganic species.
- When using Chloramine as the secondary disinfectant, it may be necessary to periodically convert to Free Chlorine for biofilm control in the water distribution system.
- Excess Ammonia in the distribution system may lead to nitrification problems, especially in dead ends and other locations with low disinfectant residual.
- Monochloramines are less effective as disinfectants at high pH than at low pH and many systems maintain a high pH to prevent corrosion throughout the distribution network.
- If Chlorine dosage in the preparation of Monochloramine is not properly controlled, Dichloramine may form resulting in taste and odor problems.
- Chloramines must be made on site using some form of Chlorine.

Other potential disadvantages to using Monochloramine that have recently come to light.

- The potential for Monochloramines to release lead from pipes. (Switzer et. al 2006)
- The potential for Monochloramine to form other DBPs that may be as harmful or more harmful as those created by the use of Chlorine. (Choi, 2002; Plewa, 2004; Zhao, 2006)

Chloramination Security Considerations

Monochloramine is less reactive with organics than Free Chlorine

- The security repercussions of this difference are often overlooked, and are two-fold in nature. First, many potential threat agents are organic compounds. A change from Free Chlorine to Monochloramine concomitantly reduces the potential for degradation and attenuation of an applied organic agent before it reaches consumers.
- Secondly, and perhaps more importantly, one of the key factors relied upon by many municipalities to detect distribution system contamination including such a terrorist attack is the unexpected loss or reduction of the normal Free Chlorine residual.

Monochloramine is a less effective bacteriological disinfectant than Free Chlorine

- This is a crucial factor from a security standpoint. Many potential threat agents are biological in nature. As stated above, the most likely anticipated drinking water attack scenario would be injecting a contaminant through a backflow event somewhere within the distribution system. The injection could be very close to the intended target area, population, or individual. The proximity of the attack site to the potential target would play a key role in determining the residence time of the contaminant in the water pipes before it reaches the consumers. If the residence time is very short, there may not be adequate contact time for Monochloramine to inactivate or attenuate the potency of the threat agents used in the attack.
- Another consideration has to do with the nature of a biological attack. To be effective, a biological attack would either need to contain enough biomaterial or toxin to overcome the chlorine demand so that an infectious dose would be left unaffected by the Free Chlorine, or a reducing agent such as Sodium Thiosulfate or Ascorbic Acid would have to be co-injected with the contaminant to destroy the Free Chlorine residual.
- If the aggressors were aware that a target system was protected with Monochloramine only, they could choose not to co-inject a reducing substance, as it would not be needed, therefore no substantial drop in total chlorine levels may be observed. Also, the aggressors may use a smaller dose of the biological material because no Free Chlorine demand needs be overcome. The use of a substantially smaller dose would result in reduced affects on a variety of parameters that could be indicative of such an attack including pH, Conductivity, Turbidity, Total Organic Carbon (TOC) and Chlorine. Finally, if the terrorist were to use a substantial dose of a dirty culture, the attack may still be more difficult to detect because the reaction of the Monochloramine with the media would most likely be slower than a reaction with Free Chlorine (if it occurs at all), which would make the recognition of any decreasing residual disinfectant concentrations problematic.

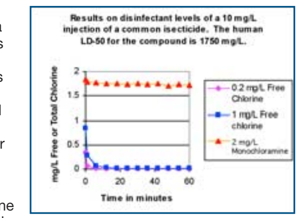
Experimental Design

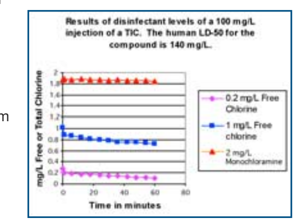
Most of the pertinent information was produced via beaker studies. These studies were conducted by injecting several known concentrations of the various agents into beakers of tap water that had been adjusted to represent various disinfectant and water quality regimes.

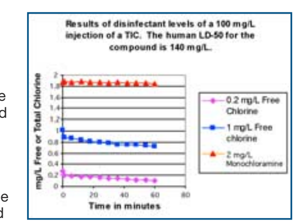
Both high and low concentrations of Free Chlorine (1-1.5 mg/L and 0.2mg/L) and Monochloramine (2 mg/L and 0.2 mg/L) were tested in the various water matrices. The beaker data from the parameters in question was then collected for at least 1 hour while the aqueous system was allowed to react.

For example the first chart at the right shows the chlorine demand curve for a 10 mg/L injection of a common insecticide into standard tap water with different levels of Free Chlorine and monochloramine present.

Similar data was collected for all 5 test parameters and more than 80 potential chemical and biological agents in Chloraminated and Free Chlorine containing water at various concentrations. In addition to beaker studies pipe loop work was conducted and the Edgewood facility to verify that the beaker signatures corresponded to data from an actual flowing system.







Above are a few examples showing the injection of the various categories of threat agent cause a clear and rapid drop in free chlorine levels but negligible effect on monochloramine levels.

Summary of Significant Findings

MINIMUM DETECTION LIMITS EXPRESSED AS A FACTOR OF THE LOWEST MDL FOR THAT COMPOUND

Compound Type Tested	Chlorine	No Chlorine	Chloramine
Bacteria	Low	1.39	1.31
Biotoxin	Low	1.11	1.55
Fungicide	Low	1.25	1.21
Heavy metal	1.10	2.88	Low*
Heavy metal	2.22	8.59	Low*
Heavy metal	Low	2.47	2.98
Heavy metal	2.12	2.17	Low*
Heavy metal	1.27	1.78	Low*
Heavy metal	5.91	27.06	Low*
Heavy metal	Low	2.89	2.04
Herbicide	1.10	1.40	Low
Herbicide	1.33	1.38	Low
Herbicide	Low	Low	Low
Herbicide	Low	1.24	1.07
Herbicide	1.05	1.07	Low
Herbicide	Low	1.68	1.36
Herbicide	Low	1.03	1.94
Herbicide	Low	3.16	2.07
Insecticide	Low	1.52	1.36
Insecticide	Low	1.37	1.06
Insecticide	Low	1.14	1.14
Insecticide	Low	8.75	5.50
Insecticide	Low	1.21	1.06
Insecticide	1.43	1.54	Low
Insecticide	1.09	3.36	Low
Insecticide	1.53	2.52	Low
Insecticide	1.15	1.20	Low
Insecticide	1.18	1.38	Low
Insecticide	Low	5.58	5.77
Insecticide	Low	1.22	1.06
Insecticide	1.02	11.91	Low
Insecticide	1.11	1.16	Low
Insecticide	Low	1.16	1.18
Insecticide	Low	7.83	1.26
Insecticide	Low	1.63	1.78
Insecticide	Low	1.16	1.74
Insecticide	Low	1.24	1.45
Insecticide	1.25	1.30%	Low
Insecticide	Low	2.46	1.72

MINIMUM DETECTION LIMITS AT FAR OF 1 PER YEAR NORMALIZED AND EXPRESSED AS A FACTOR OF THE LOWEST MDL FOR THAT COMPOUND

Compound Type Tested	Chlorine	No Chlorine	Chloramine
Insecticide	Low	15.34	1.48
Insecticide	Low	1.18	1.04
Insecticide	Low	7.12	2.36
Nematocide	Low	5.26	2.01
Organo-metal	1.17	1.30	Low
Pesticide	Low	1.21	1.30
Pesticide	Low	1.01	1.01
Preservative	Low	1.52	2.10
Rodenticide	Low	1.13	1.06
Street drug	Low	1.21	1.05
Street drug	Low	Low	1.16
Toxic industrial and agricultural chemical	Low	1.06	Low
Toxic Industrial Chemical	Low	1.39	1.63
Toxic Industrial Chemical	1.31	4.92	Low
Toxic industrial chemical	Low	2.90	2.43
Toxic industrial chemical	1.78	1.78	Low
Toxic industrial chemical	1.02	1.04	Low
Toxic industrial chemical	Low	8.63	4.46
Toxic industrial chemical	1.03	1.28	Low
Toxic industrial chemical	1.27	1.37	Low
Toxic industrial chemical and pesticide	1.05	1.33	Low
Toxic industrial material	1.24	1.63	Low
Toxic industrial material	Low	2.73	1.82
Toxic industrial material	Low	2.26	2.70
Toxic industrial material	1.04	2.46	Low
Warfare agent	Low	1.14	1.39
Warfare agent	Low	2.01	1.95
Warfare agent	1.68	1.95	Low
Warfare agent, Biological	Low	1.48	1.11
Warfare agent, Biotoxin	Low	1.56	1.40
Warfare agent, Biotoxin	3.04	8.56	Low

Notes: The red highlighted areas represent reactions in which the kinetics were very slow or erratic and may cause problems in detection of the compound
**In the case of heavy metals the monochloramine is not reacting with the metals but the iodide contained in the reagents used to test for the total chlorine monochloramine levels is causing a secondary reaction that aids detection.*

REACTION STRENGTH OF THE COMPOUNDS TESTED IN VARIOUS DISINFECTION REGIMES

Reaction Strength	Low Chlorine	High Chlorine	Monochloramine
Strong	42	37	7
Moderate	13	15	15
Weak	14	17	47

Strong: *denoted by a rapid (less than 10 minutes) and complete or near complete degradation of the disinfectant residual.*

Moderate: *denoted by a slow (greater than ten minutes) and/or incomplete (only a partial degradation) of the disinfectant residual.*

Weak: *denoted by either no change in disinfectant residual, a change that would be very hard to discern form background or extremely slow kinetics (greater than 45 minutes for a discernable drop).*

REACTION STRENGTH OF THE COMPOUNDS TESTED IN VARIOUS DISINFECTION REGIMES

A	B	C	D	E	F	G	H
All agents	69	59%	83%	41%	21%	100%	80%
Agents of particular concern from a security standpoint	18	61%	52%	39%	18.2%	100%	83%

A= *Parameters described on the row to the right*
B= *# of parameters*
C= *Percent of parameters where the use of chlorine provides more sensitivity compared to monochloramine*
D= *Average Percent decrease in sensitivity for those less sensitive with monochloramine*
E= *Percent of parameters where the use of chlorine provides less sensitivity compared to Chloramine*
F= *Average percent decrease in sensitivity for those less sensitive using chlorine rather than monochloramine*
G= *% of parameters where chlorine provides more sensitivity than using no disinfectant*
H= *% of parameters where Chloramine provides more sensitivity than using no disinfectant*

Conclusions

1. *While it is unlikely that areas that have made the switch to Monochloramine will revert back to Free Chlorine they should be cognizant of the limitations of relying upon Monochloramine residual levels as an early warning of contamination. While the system being tested in these experiments showed a marked decrease in its detection level of several compounds in Monochloraminated systems the detection levels were still well below the levels likely to cause immediate harm. This is due to the fact that the system utilizes more than simple disinfectant residual levels to detect compounds. The presence of other parameters, such as TOC, allows the system to detect contamination even with no change in disinfectant levels. This would not be true in a system where residual disinfectant levels alone are used for an early warning system,*
2. *Major terrorist targets such as large urban areas, military bases, icon facilities etc. that have not already switched should seriously consider not making the switch from Free Chlorine to Monochloramine if other means of decreasing DBPs are capable of being implemented. Security considerations and not just cost should be taken into account.*
3. *A minimal chlorine residual should be maintained in all parts of the system to help elicit some degradation of threat agents if they are encountered and to facilitate detection of these agents. This level should be maintained as high as possible while taking into account odor and taste considerations*
4. *Where feasible, chlorine-monitoring stations should be linked to chlorine booster stations to maintain chlorine concentrations throughout the system.*
5. *All water utilities that have converted to chloramines should have a contingency plan to convert to free chlorine in certain national security situations. Coordination between water utilities and the appropriate state and federal authorities (Homeland Security, etc.) should be established in advance to assist in making this decision.*