Security Consequences for Consideration When Switching From Free Chlorine to Monochloramine Disinfectants

Dan Kroll[1*], Karl King[1], Mark Ginsberg[2]
[1]Hach HST, Loveland, Colorado, 80529 *e-mail address: DKROLL@hach.com
[2] US Army Corps of Engineers Construction Engineering Research Lab, Champaign, Ill. 61826

ABSATRACT: Switching to Monochloramine as a residual disinfectant has been deemed to be an effective means to meet limits for Disinfection Byproducts (DBPs). Many municipalities have switched indicating that the perceived advantages outweigh the disadvantages. We have become increasingly concerned that there are drawbacks related to security that are overlooked during the decision process. We have studied the interactions of a number of potential threat agents with different levels of various disinfectants while developing an early warning system. The experimental design entailed the gathering of bulk parameter data for a wide variety of agents at different concentrations. This resulted in an extensive database on the reactions of these agents in common drinking water scenarios. This revealed some disadvantages associated with switching to Monochloramine.

KEY WORDS: Free Chlorine, Monochloramine, disinfection by product, monitoring, security terrorism, backflow attack

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INTRODUCTION

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

There are numerous strategies currently in use to decrease DBP exposure to consumers. One of the most popular, inexpensive and easiest to implement is a change from Free Chlorine to Monochloramine as a secondary disinfectant. There are many advantages to using Monochloramine in this role including the following. (EPA 1999)

- Chloramines are not as reactive with organics in forming DBPs.
- 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 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 more harmful than those created by the use of Chlorine. (Choi, 2002; Plewa, 2004; Zhao, 2006)

Apparently deciding that the advantages outweigh the disadvantages, many municipal suppliers of drinking water have opted to change from Chlorine to Monochloramine to help meet EPA regulations. Switching to monochloramine also involves security compromises that are usually overlooked.

The Terrorist Threat to Water: A great deal of attention has recently been focused on the vulnerability of US drinking water supplies to assault by terrorists. That our municipal water systems, as they are currently configured, are vulnerable to attack has been widely recognized. (Hoffbuhr 2002, BBC 2002, Hickman 1999, Kroll 2006, GAO 2003) Most raw water supply sources are somewhat limited in their vulnerability to chemical or biological attack due to the massive volumes of water contained in them, distribution systems, on-the-other–hand, are vulnerable and tempting targets.

Terrorists could assault and compromise a water distribution system by introducing any of a large number of possible threat agents into the pipe network anywhere in the distribution system. The geographical distribution of such an attack may be widespread depending upon where the system is accessed and the pumping methods used. (Allmann 2005). Key infrastructure and iconic locations such as police stations, firehouses, military bases and government buildings could be targeted and contaminated.

Attack using induced backflow is not just a theoretical threat; such events have occurred and others have been thwarted in the planning stages.

- 1980 – A disgruntled employee deliberately contaminated water mains in Pittsburgh by injecting weed killer into fire hydrants. (Rand, No date, Owenby, 1988; Falkenrath, 1998,)

- April 1985-traces levels of plutonium were intentionally introduced into New York City's water supply. (Time Magazine 1985)
- February 2002 – Al Qaeda operatives were arrested with plans to attack the U.S. embassy's water in Rome with a cyanide compound. (BBC 2002)
- December 2002 - Al Qaeda operatives were arrested with plans to attack water networks surrounding the Eiffel Tower neighborhood in Paris, France. (Von Derschau 2002)
- April 2003 - Jordan foiled an Iraqi plot to poison drinking water supplies from Zarqa feeding U.S. military bases along the Eastern desert. (Feuer 2003)
- September 2003 – A FBI bulletin warned of Al Qaeda plans found in Afghanistan to poison U.S. food and water supplies. (CBS 2003)

In addition to terrorist attacks, domestic accidents have resulted in illness and death. Backflow events are recognized as being a significant cause of illness in the US. Between 1981 and 1998 they were responsible for 57 water born disease outbreaks causing 9,734 illnesses. (EPA, 2002)

Chloramination Security Considerations: Due to such potential threats, switching from Free Chlorine to Monochloramines requires analysis of system security. There are several characteristics of Monochloramines should be considered.

a) Monochloramine is less reactive with organics than Free Chlorine. One of the main reasons Monochloramine reduces formation of DBPs is that it reacts with organic materials less vigorously than Free Chlorine. Many potential threat agents are organic compounds. A change from Free Chlorine to Monochloramine both reduces the potential for degradation and attenuation of an organic agent before it reaches consumers. While the use of Free Chlorine by no means offers a failsafe protective blanket, it would, in many cases, react with organic agents more vigorously than Monochloramine, and degrade the agent to some extent.

b) Monochloramine concentration is a poor indicator of an attack: 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. Although there are organic compounds that do not induce a distinct drop in Free Chlorine level upon exposure (see Study Section below) many organic agents will. A large number of chemicals that cause a Free Chlorine residual drop when added to chlorinated water do not cause a decrease in Total Chlorine levels when Monochloramine is the disinfectant. Consequently a change from Free Chlorine to Monochloramine masks a key parameter that used in detecting threat agent within the distribution system. It may significantly reduce the probability of early detection of an attack, thus delaying the triggering of both protective and remedial actions.

c) **Monochloramine is a less effective bacteriological disinfectant than Free Chlorine**. It has long been known that Monochloramine is less effective than Free Chlorine in destroying bacterial contaminants. Wattie and Butterfield conducted a series of comprehensive experiments as far back as the 1940's to determine the relative effectiveness of Free Chlorine versus Monochloramine as a biocide. Results from these experiments demonstrated conclusively that under relatively demand free, laboratory-controlled conditions, Free

Chlorine inactivated enteric bacteria much faster than Chloramines (Wattie and Butterfield, 1944.)

This is a crucial factor from a security standpoint. Biological threat agents are a likely choice in a terrorist attack. If an attack via backflow or pumping is launched close to the intended target the proximity of the attack site to the target determines 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. Experts have long debated the exact method that an aggressor would take to attack a water system using a biological agent. Would the perpetrators be more likely to use a purified and washed culture, or would they use a bulk culture that still contained growth media? While either mode of attack would be possible, there are many arguments pointing to the concept that an attack would most likely take the form of a dirty attack that still contained the growth media. It is difficult to wash the media from a culture without substantially reducing the number of viable bacteria therein. When cells are washed they have a tendency to undergo lysis due to the difference in osmotic pressure across their cell membranes. Also, washing and preparation of the cells would require much more handling of the infectious material and would increase the risk to the perpetrators. So, if such an attack were to occur, the chances are that the aggressor would use raw unwashed cultures or even raw sewage, both of which would exert a noticeable demand on a Free Chlorine residual. While some biological agents are resistant to chlorine, the most ubiquitous and easy to obtain agents are readily inactivated by chlorine. (Kroll 2006; Burrows and Renner, 1999) Some biotoxins are also inactivated by Free Chlorine, such as botulinum toxin (Wannemacher, 1993) This means that in a chlorinated system, an effective biological attack would require that either enough biomaterial or toxin to overcome the chlorine residual, or a reducing agent such as Sodium Thiosulfate would have to be co-injected with the contaminant to destroy the Free Chlorine residual.

These observations have several implications for the potential detection of a biological attack. 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 to be overcome. The use of a substantially smaller dose would result in reduced effects on a variety of parameters that could indicate the 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 usually be slower than a reaction with Free Chlorine (if it occurs at all), thus making the recognition of decreasing residual disinfectant concentrations much more difficult.

METODOLOGY

For the past several years, scientists at Hach Homeland Security Technologies (HST) have been actively pursuing research to develop an early warning system to detect the presence of potential threats to the water supply. The goal of this research and development effort was to provide a continuous, real-time contaminant detection and operating-condition monitoring platform that could provide early detection of chemical or biological agents in the on the drinking water distribution system.

The Hach HST system employs a dynamic, intelligent, heuristic software application to calculate a trigger signal by analyzing the data from basic bulk water parameter monitoring sensors (pH, Conductivity, Turbidity, TOC and Chlorine Residual {Free or Total}) and interprets the significance of water quality deviations from the established baseline. It applies a mathematical analysis of all parameter measurements to recognize data patterns and deviations, and classifies agents found in an on-board Agent Library that has been populated with unique "fingerprints" of likely threat agents and other contaminants.

One of the key aspects to successes of the Hach research was the population of a master Agent Library with the 5-parameter signatures, each belonging to one of a multitude of recognized threat agents in various water matrices. Much of the work was performed at the Hach Laboratory located in Loveland, Colorado. For agents that could not be tested at the Loveland facility, a Cooperative Research and Development Agreement (CRADA) was entered into by Hach HST, the Army Corps of Engineers Research and Development Laboratory in Champaign, Illinois, and the Edgewood Chemical and Biological Center to perform the work at the Edgewood biosafety facility in Aberdeen, Maryland. Populating the agent library entailed gathering bulk parameter monitoring data for a wide variety of agents at different concentrations when they were injected into water sources containing differing amounts and types of disinfectants. The research also revealed significant findings on the security consequences of the Free Chlorine/Monochloramine choice.

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 were then collected for at least 1 hour while the system was allowed to react.

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 at the Edgewood facility to verify that the beaker signatures corresponded to data from an actual flowing system.

RESULTS

A summary of significant findings is shown in Tables 1 and 2. Table 1 lists the limits of detection of the developed 5 parameter system for various potential threat agents in a matrix of 1 mg/L Free Chlorine, 2 mg/L Monochloramine or no disinfectant present at all. The names of the tested compounds have been replaced by general categories for security reasons. The data has also been normalized by taking the detection level of the conditions under which it is lowest and dividing the other detection levels by that number to get a factor for that compound. For example if the detection level of a given compound was 2 mg/l in chlorine matrix 5 mg/l in no disinfectant and 3 mg/l in monochloramine it would be reported as Chlorine (low) no disinfectant (2.50) and monochloramine (1.50).

Table 1

Agent Type	MDL Chlorine	MDL No Chlorine	MDL Chloramine	Agent Type	MDL Chlorine	MDL No Chlorine	MDL Chloramine
Bacteria	Low	1.39	1.31	Insecticide	Low	1.16	1.74
Biotoxin	Low	1.11	1.55	Insecticide	Low	1.24	1.45
Fungicide	Low	1.25	1.21	Insecticide	1.25	1.30	Low
Heavy metal	1.10	2.88	Low*	Insecticide	Low	2.46	1.72
Heavy metal	2.22	8.59	Low*	Insecticide	Low	15.34	1.48
Heavy metal	Low	2.47	2.98	Insecticide	Low	1.18	1.04
Heavy metal	2.12	2.17	Low*	Insecticide	Low	7.12	2.36
Heavy metal	1.27	1.78	Low*	Nematocide	Low	5.26	2.01
Heavy metal	5.91	27.06	Low*	Organometal	1.17	1.30	Low
Heavy metal	Low	2.89	2.04	Pesticide	Low	1.21	1.30
Herbicide	1.10	1.40	Low	Pesticide	Low	1.01	1.01
Herbicide	1.33	1.38	Low	Preservative	Low	1.52	2.10
Herbicide	Low	Low	Low	Rodenticide	Low	1.13	1.06
Herbicide	Low	1.24	1.07	Street drug	Low	1.21	1.05
Herbicide	1.05	1.07	Low	Street drug	Low	Low	1.16
Herbicide	Low	1.68	1.36	TIC	Low	1.06	Low
Herbicide	Low	1.03	1.94	TIC	Low	1.39	1.63
Herbicide	Low	3.16	2.07	TIC	1.31	4.92	Low
Insecticide	Low	1.52	1.36	TIC	Low	2.90	2.43
Insecticide	Low	1.37	1.06	TIC	1.78	1.78	Low
Insecticide	Low	1.14	1.14	TIC	1.02	1.04	Low
Insecticide	Low	8.75	5.50	TIC	Low	8.63	4.46
Insecticide	Low	1.21	1.06	TIC	1.03	1.28	Low
Insecticide	1.43	1.54	Low	TIC	1.27	1.37	Low
Insecticide	1.09	3.36	Low	TIC	1.05	1.33	Low
Insecticide	1.53	2.52	Low	TIM	1.24	1.63	Low
Insecticide	1.15	1.20	Low	TIM	Low	2.73	1.82
Insecticide	1.18	1.38	Low	TIM	Low	2.26	2.70
Insecticide	Low	5.58	5.77	TIM	1.04	2.46	Low
Insecticide	Low	1.22	1.06	CWA	Low	1.14	1.39
Insecticide	1.02	11.91	Low	CWA	Low	2.01	1.95
Insecticide	1.11	1.16	Low	CWA	1.68	1.95	Low
Insecticide	Low	1.16	1.18	BWA	Low	1.48	1.11
Insecticide	Low	7.83	1.26	BWA	Low	1.56	1.40
Insecticide	Low	1.63	1.78	BWA	3.04	8.56	Low

Notes: The yellow highlighted areas represent reactions in which the kinetics were very slow or erratic and may cause problems in detection of the compound. MDL is "minimum detection limit" expressed as a factor of the lowest detection limit for that Compound. TIC is Toxic Industrial Chemical. TIM is Toxic Industrial material. CWA is a chemical warfare agent. BWA is a biological warfare agent.

There are a large number of potential agents where the limit of detection is appreciably increased in a Monochloramine based system versus a Free Chlorine based system. This data represents results from a fully deployed Early Warning System simultaneously measuring pH, Conductivity, Turbidity and TOC in addition to Free or Total Chlorine (dependent upon the disinfectant present). In a rudimentary detection system that was relying on disinfectant residual alone for agent detection, these results would be even more pronounced for the relative differences between Free Chlorine and Monochloramine. In such a system with no disinfectant, the agents would be undetectable. There were also a sizable number of compounds in which the kinetics of the reaction with Monochloramine was either very slow or erratic in nature. This could lead to further problems in detection of the substances. These compounds are highlighted in yellow in the table.

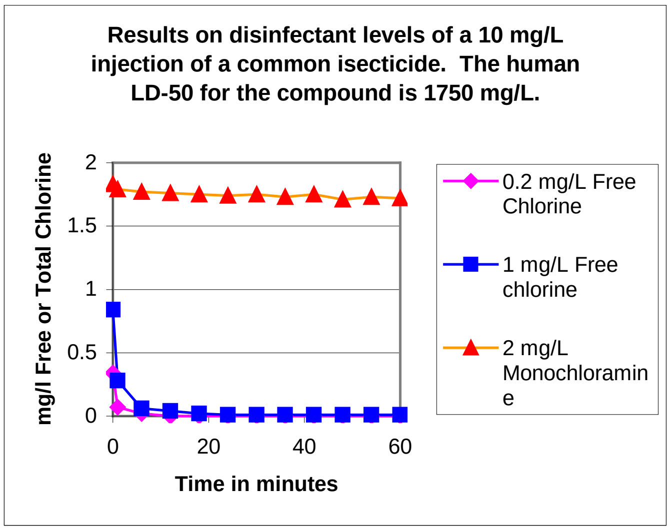

Figure 1. The injection of the insecticide causes a clear and rapid drop in Free Chlorine levels but negligible effect on Monochloramine levels.

Table 2 categorizes the reaction strength of both high and low Free Chlorine levels with that of Monochloramine. A strong reaction is denoted by a rapid (less than 10 minutes) and complete or near complete degradation of the disinfectant residual. A moderate reaction is denoted by a slow (greater than ten minutes) and/or incomplete (only a partial degradation) of the disinfectant residual. A weak reaction is 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). The reaction level strength is not definitive proof of the degradation of the compounds in question by reaction with the listed disinfectant as no analysis of the solutions was done for remaining product or the degradation products of any possible reaction. Strong results, however, are indicative of a proclivity to react with the compound whether or not it is being beneficially degraded while a weak reaction would tend to indicate that little or no degradation is likely to be occurring. As the table clearly shows, there are a wide variety of potential agents that have the tendency to react with Free Chlorine at various levels, but that are largely immune to reaction with Chloramines.

Table 2

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).

Table 3

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 - Number 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 – Percent of parameters where chlorine provides more sensitivity than using no disinfectant
H – % of parameters where Chloramine provides more sensitivity than using no disinfectant

DISCUSSION and CONCLUSIONS:

While the findings in this study are by no means unexpected, it does represent the first time that the reactions of these various and diverse potential threat agents have been documented in multiple disinfectant regimes. This helps to shed some light on the security aspects of the Free Chlorine/Monochloramine question that may have been overlooked in the past. While Monochloramine has some redeeming qualities in its role of reducing the formation of DBPs, it has some definite security related drawbacks. Recognition of these factors helps to accentuate the conflicting role that many people in the commercial and regulatory sectors of water industry are forced to play when making decisions as they pertain to weighing the risks of increased potential for exposure to carcinogenic materials versus the risk of a serious water attack or accidental contamination.

The general industry consensus is that the risk of a severe incident involving an intentional or accidental backflow event is real and has the potential to cause mass casualties. (Hickman 1999; GAO 2003; Kroll 2006) In light of these findings, it is advisable to consider the security aspects of switching to Monochloramine. Several recommendations should be given serious consideration:

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 available. 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.

The findings in this study have significant repercussions for the safety and security of our Nation's water supplies. The research, however, is not complete. The studies done to date have given us a snapshot as to the differing effects Monochloramine and Free Chlorine have on threat agent chemistry. Unfortunately, due to time and budget constraints, no analysis of the actual fate and breakdown products was performed nor has ability of these treatment processes to destroy or ameliorate the effects of these agents been studied. Hopefully, continued research will be deemed important enough to the Nation's safety to generate public sector funding.

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