Pilot Study of Greater Boston Drinking Water Quality Changes

- Monochloramine and pH change

Xin (Cindy) Huang, Graduate Student, Civil and Environmental Engineering Department, Northeastern University, Boston, MA

Irvine W. Wei, Ph.D., M.AWWA, Associate Professor, Civil and Environmental Engineering Department, Northeastern University, Boston, MA

Windsor Sung, Ph.D., PE, DEE, M.ASCE, Program Manager, Chemistry Quality Assurance Department of MWRA, Southborough, MA

ABSTRACT

A pilot study was conducted from July 2001 to November 2003 to understand the impact of ozonation on monochloramine decay and pH change in the future Massachusetts Water Resources Authority’s (MWRA) drinking water system. The impact of the distribution system, which consists of old cast-iron pipes, was also investigated.

Homogeneous and heterogeneous samples were taken from the Pipe Loop Pilot Plant (PLPP), which represented the best and the worst scenarios respectively, i.e. a very clean distribution system, or dead ends far from the main.

The results suggested that corrosion and biological activity inside the pipe were the major causes of the deteriorated water quality in heterogeneous samples. In homogeneous samples, ozonation may cause faster monochloramine decay and larger decrease of pH. Therefore more chemicals may be needed for pH adjustment and residual disinfectant when the new Walnut Hill Water Treatment Plant (WHWTP) is online.

BACKGROUND

MWRA water system. MWRA provides drinking water to 2.2 million people in the Greater Boston area. The source water comes from the Wachusett and Quabbin reservoirs, which are located approximately 60 and 90 miles west of Boston respectively. The raw water has a low alkalinity (less than 10 mg/L CaCO₃), and a hardness of 8 to 18 mg/L as CaCO₃.

Current water treatment processes include chlorination for primary disinfection, alkalinity and pH adjustment, and chloramination for residual disinfectant. To ensure good water quality without filtration, the WHWTP is under construction and is scheduled to be online in 2005. Ozonation will replace chlorination as the primary disinfection in WHWTP. The impact of this change was the primary objective of the study.
The extensive transmission and distribution system is a very important part of the MWRA's drinking water system. Approximately 45 percent of the MWRA 300-mile distribution system and nearly 50% of the 5,500-mile network of community pipes are old unlined cast iron pipes. These pipes experience corrosion problems as well as biofilm accumulation, which can cause water quality to deteriorate (Sarin et al, 2003; AWWA, 1996; Geldreich, 1996). Thus the impact of the distribution system on the ozonated water became the secondary objective of this study. The impact of other parameters on water quality, such as excess free ammonia, is also discussed in the paper.

**Monochloramine chemistry.** Chloramines have long been used to provide residual disinfectant in distribution systems where it is difficult to maintain free chlorine residual. And more recently chloramines have been used to replace free chlorine because they produce less Disinfection by Product (DBP). It has been used for over 50 years in MWRA’s system (Sung, 2004).

Ammonia combines with free chlorine to produce chloramines. At different chlorine to ammonia nitrogen ratios, different species of chloramines, monochloramine, dichloramine, and trichloramine, may be produced, shown in Equations 1 to 3:

\[
\begin{align*}
NH_3 + HOCl & \leftrightarrow NH_2Cl + H_2O \\
NH_2Cl + HOCl & \leftrightarrow NHCl_2 + H_2O \\
NHCl_2 + HOCl & \leftrightarrow NC1_3 + H_2O
\end{align*}
\]

Monochloramine is the most stable among the three, and is the most desirable one for disinfection purpose. Theoretically the optimum Cl₂:N weight ratio for monochloramine formation is about 5. Less monochloramine will be produced when the ratio is bigger than 5. And when it is approaching 7.5, break point chlorination occurs (Wei et al, 1974), which causes a complete removal of chlorine residual and ammonia nitrogen from solution, shown as Equation 4.

\[
2NH_2Cl + HOCl \rightarrow N_2(gas) + 3H^+ + 3Cl^- + H_2O
\]  

Therefore the chlorine to ammonia-N ratio is crucial to any disinfection facilities where monochloramine is formed as a residual disinfectant. The ratio used in MWRA is targeted at 4.7, at which ammonia is slightly in excess.

After monochloramine is formed, there are several reactions which cause monochloramine to decay.

Autodecomposition happens as illustrated by the following generalized Equation 5 (Wilczak et al, 2003, Woolschlager, 2001),

\[
3NH_2Cl \rightarrow N_2 + NH_3 + 3H^+ + 3Cl^-
\]
When monochloramine is added to natural water, it reacts with Natural Organic Matter (NOM) in the water. The conceptualized formula of the reaction is as follows (Wilczak et al, 2003):

\[ \text{NOM} + \text{NH}_2\text{Cl} \rightarrow \text{NH}_4^+ + \text{NOM} + \text{Cl}^- + \text{products} \quad (6) \]

In the water distribution system, there are reducing species which may also consume monochloramine. In cast iron pipes, ferrous iron released from corrosion process can react with monochloramine as follows (Woolschlager et al, 2001),

\[ \text{NH}_2\text{Cl} + 2\text{H}^+ + 2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{NH}_4^+ + \text{Cl}^- \quad (7) \]

The biofilm attached on the pipe wall may be another factor which causes a loss of monochloramine in the distribution system. Complete oxidation of carbon may happen as follows:

\[ \text{C}_5\text{H}_7\text{O}_2\text{N} + \text{NH}_2\text{Cl} \rightarrow \text{CO}_2 + \text{NH}_4^+ + \text{Cl}^- + \text{H}_2\text{O} \quad (8) \]

**Monochloramine decay model.** Monochloramine is found to experience a significant initial drop shortly after its formation, followed by a slower decay afterwards (Valentine et al, 1998; Woolschlager et al, 2001). The initial drop within a certain time, after monochloramine is introduced to the treated water, is defined as the Initial Demand (ID). The slower decay is described kinetically by \( k_{MD} \), which was suggested by Valentine et al (1998) in a second-order kinetic model.

\[
\frac{1}{[\text{NH}_2\text{Cl}]_t} - \frac{1}{[\text{NH}_2\text{Cl}]_0} = k_{MD} \cdot t
\]

where 
- \([\text{NH}_2\text{Cl}]_t\) = monochloramine concentration at time \( t \)
- \([\text{NH}_2\text{Cl}]_0\) = monochloramine concentration at time 0
- \( k_{MD} \) = the monochloramine decay coefficient, in \( \text{M}^{-1}\text{hr}^{-1} \).

The value of \( k_{MD} \) is expected to increase with decreasing pH, increasing temperature, and increasing chlorine to ammonia nitrogen ratio (Valentine et al, 1998). Natural organic matter (NOM) is expected to accelerate monochloramine decay (Valentine et al, 1998). The ID was found to have a linear relationship with organic matter in the source water (Valentine et al, 1998).

When ozone is used for primary disinfection, different source waters may yield different oxidation products. If the source water contains larger organic molecules, ozonation process tends to yield more precursors to the formation of Disinfection By-Product (DBP) as well as the initial monochloramine demand (Wilczak et al, 2003, Singer et al, 1999). It was found that a higher ozone dose for primary disinfection was associated with a faster monochloramine decay (Chin-Leung, 2003).

**The pH change.** The pH change in the treated water has not been thoroughly studied, despite the fact that it is an important factor during corrosion control. Chin-
Leung (2003) found a pH decrease up to 0.7 units during 10 days in a bench scale simulation of the WHWTP. In the bench study, water from the reservoir was treated with ozone and stored in clean BOD bottles at room temperature, after carbonate has been added for pH adjustment and monochloramine was introduced. It simulated the case of a clean distribution system.

When ozonation is used, ozone breaks down big organic molecules (Singer et al, 1999) and may produce small organic acids. This might be responsible for the pH decrease in the bench scale study.

In a corroded cast iron pipe, there are a few potential processes which may cause pH change. The biofilm attached on the pipe wall may act as a bioreactor and consume the organic acids produced during ozonation. This might cause an increase in pH, as shown conceptually in Equation 10,

\[
\text{Biomass} + \text{Organic Acids} \rightarrow \text{Biomass} + H_2O + CO_2 \tag{10}
\]

As illustrated in the monochloramine chemistry section, a common product of the oxidation reduction reactions between monochloramine and various reducing species is ammonia. As monochloramine is used up, ammonia is produced and accumulated until nitrification starts to happen. This might contribute to an increase in pH before nitrification. Harrington et al (2002) observed pH increase in two of the three trains of their pilot distribution system in 4 days.

Denitrification can happen under anoxic condition, which may exist inside the biofilm attached on the pipe wall. As shown in Equation 11, denitrification could be another mechanism which contributes to a pH increase,

\[
2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \tag{11}
\]

Corrosion could be another cause of pH increase in old cast iron pipes. A mechanism suggested by Kuch (AWWARF, 1996) may happen under low flow conditions close to the pipe wall.

\[
2FeOOH_{(s)} + Fe_{(s)} + 2H^+ = 3Fe^{3+} + 4OH^- \tag{12}
\]

**EXPERIMENTATION**

The Pipe Loop Pilot Plant (PLPP). The PLPP was designed by Black and Veatch\(^3\) as a collaboration project of the AWWA Research Foundation, and constructed and operated by MWRA for investigating the impact of UV and ozone treatment on water quality. Within the three trains at the PLPP, Train 3 permitted simulation of the treatment scheme planned for the MWRA’s WHWTP (Black and Veatch Corp., 2001) and was the basis of this study. Train 3 included ozonation for primary disinfection, followed by pH and alkalinity adjustment, chlorination, and ammonia addition for chloramine production. The treated water then passed through a pipe rack.
The pipes used in the PLPP were excavated by Boston Water and Sewer Commission (BWSC) from its distribution system and used to simulate the corrosion conditions in the actual distribution network. The total estimated detention time of thirty six pipes for Train 3 is 5.88 hours, based on a flow rate of 0.16 m$^3$/hour (0.6 gpm). A recirculation pump was installed to enable the system to simulate the circulation time in the MWRA system, which can have a maximum of up to 10 days. The schematic flow diagram is shown in Figure 1.

![Figure 1 Treatment Scheme and Sampling Points](image)

**Experimental procedures.** Ten experiments were carried out in this study over a two year period. The pipe loops were conditioned at the desirable chemical doses for twenty four hours before each experiment started. Stability of the system was checked before sampling. As shown in Figure 1, samples were collected from six different sampling points throughout the Train 3 at different times.

On Day 0 of an experiment, water samples were taken from each of the sampling point. The sample from point 4 was stored in 6 one-liter amber glass bottles, from which homogeneous samples were collected at subsequent sampling times and compared with heterogeneous samples drawn from the end of the pipe (sampling point 5). The maximum recirculation time used was ten days. The homogeneous samples, taken before the water contacted with the pipes, simulated a very clean distribution system, or the best scenario. Whereas the heterogeneous samples, taken after the water contacted with the pipes, simulated the conditions such as dead ends far from the water main.
Within the ten experiments, the first one was to get familiar with the pilot system. The second and the third experiments were to study the influence of chlorine to ammonia ratio, which is not the focus of this paper. These three experiments will not be included here but are covered elsewhere (Huang, 2003).

Sample analyses. Parameters analyzed on site were temperature, pH, alkalinity, turbidity, and Dissolved Oxygen (DO). Total chlorine, monochloramine, and total ammonia were also monitored by using Hach Odyssey DR/2500 spectrophotometer. Total Organic carbon (TOC), UV254, nitrate and nitrite were measured at Northeastern University. HPC, DBP, and total iron were analyzed by MWRA. The methods used are listed in Table 1. Only some of the parameters are discussed in this paper.

<table>
<thead>
<tr>
<th>Parameter Analyzed</th>
<th>Method used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>Standard Method (APHA et al, 1998)</td>
</tr>
<tr>
<td>Total chlorine</td>
<td>Method 10101 (Hach, 2003)</td>
</tr>
<tr>
<td>Monochloramine</td>
<td>Method 10171 (Hach, 2003)</td>
</tr>
<tr>
<td>Total ammonia</td>
<td>Method 10023 (Hach, 2003)</td>
</tr>
<tr>
<td>TOC</td>
<td>SM5310C</td>
</tr>
<tr>
<td>Nitrate, nitrite</td>
<td>EPA300.1</td>
</tr>
<tr>
<td>HPC</td>
<td>SM9215B</td>
</tr>
<tr>
<td>THM</td>
<td>EPA524.2</td>
</tr>
<tr>
<td>HAA</td>
<td>EPA552.2</td>
</tr>
<tr>
<td>Total iron</td>
<td>EPA 200.7</td>
</tr>
</tbody>
</table>

Limitations of the experiments. The variability inherent in a pilot study did not allow precise control of some of the parameters, e.g. chlorine dose, sodium carbonate and bicarbonate dose, chlorine to ammonia nitrogen weight ratio. Due to the nature of the project, some other parameters were not under our control. For example ozone dose was controlled by the American Water Works Association Research Foundation (AWWARF) project, which was conducted simultaneously on the other two trains. The actual water temperature within the pipes was impacted by room temperature, which was not controlled.

RESULTS AND DISCUSSION

The experimental conditions of the seven experiments are listed in Table 2.

As shown in Figure 2, an initial drop of monochloramine concentration was found in most of the homogeneous samples subjected to ozonation. Thus in this study, the difference of the initial monochloramine concentration and the concentration at about...
one hour after its addition was used as ID. Then starting from one hour and beyond, $1/[\text{NH}_2\text{Cl}]_1 - 1/[\text{NH}_2\text{Cl}]_{1\text{hr}}$ versus time $t$ were plotted. The slope of the straight line, after unit conversion, is $k_{MD}$ in (M-h)$^{-1}$.

**Figure 2** Monochloramine Change in Homogeneous Samples

**Figure 3** Monochloramine Change in Heterogeneous Samples
Figure 3 shows the monochloramine decay pattern in heterogeneous samples. It is very different from that in homogenous samples. Monochloramine dropped dramatically within Day 1 and was almost depleted in three days. The ID was overwhelmed by the fast decay. No ID was evaluated for heterogeneous samples. 1/[NH₂Cl]ₙ - 1/[NH₂Cl]₀ versus time t were plotted only over a 1 day period for heterogeneous samples before the complete depletion of monochloramine. The regression lines were forced to go through the origin.

Impact of excess free ammonia concentration on monochloramine ID and \( k_{MD} \). The homogeneous samples of Experiment 4 & 5 are used to illustrate the impact of initial monochloramine concentration on ID and \( k_{MD} \).

As shown in Table 2, the ozone doses and operational temperature ranges of Experiments 4 and 5 were very close. The TOC were 1.65 and 1.99 mg/L respectively. The chlorine contact time of Experiment 5 was half of that of Experiment 4. The longer chlorine contact time will leave less NOM for monochloramine consumption. With more initial TOC and less chlorine contact time, a larger ID and faster monochloramine decay were expected for Experiment 5.

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Ozone dose</th>
<th>Cl₂ contact</th>
<th>Mono Initial Conc.</th>
<th>Cl₂/N weight ratio</th>
<th>TOC</th>
<th>UV254</th>
<th>Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>min</td>
<td>mg/L</td>
<td></td>
<td></td>
<td>Abs/cm</td>
<td>°C</td>
</tr>
<tr>
<td>Exp4</td>
<td>0.47</td>
<td>72</td>
<td>1.24</td>
<td>4.3</td>
<td>1.65</td>
<td>0.031</td>
<td>9-15</td>
</tr>
<tr>
<td>Exp5</td>
<td>0.44</td>
<td>36</td>
<td>3.23</td>
<td>3.9</td>
<td>1.99</td>
<td>0.043</td>
<td>8-16.5</td>
</tr>
<tr>
<td>Exp6</td>
<td>0</td>
<td>36</td>
<td>2.95</td>
<td>4.2</td>
<td>2.35</td>
<td>0.066</td>
<td>17-18.8</td>
</tr>
<tr>
<td>Exp7</td>
<td>1</td>
<td>36</td>
<td>2.57</td>
<td>4.7</td>
<td>2.54</td>
<td>0.078</td>
<td>18.9-20.5</td>
</tr>
<tr>
<td>Exp8</td>
<td>0.8</td>
<td>72</td>
<td>1.96</td>
<td>4</td>
<td>2.45</td>
<td>0.076</td>
<td>23-21</td>
</tr>
<tr>
<td>ExpA</td>
<td>1</td>
<td>30</td>
<td>2.96</td>
<td>4.3</td>
<td>2.16⁺</td>
<td>0.051</td>
<td>12.4-12.7</td>
</tr>
<tr>
<td>ExpB</td>
<td>0</td>
<td>30</td>
<td>3.25</td>
<td>4.5</td>
<td>2.18⁺</td>
<td>0.053</td>
<td>11.5-14.5</td>
</tr>
</tbody>
</table>

Note: + Data was from MWRA.

Experiment 5 had a higher monochloramine initial concentration but lower chlorine to ammonia nitrogen weight ratio. These gave Experiment 5 a higher excess ammonia concentration than Experiment 4, as shown in Figure 4. Thus theoretically a smaller ID and slower monochloramine decay were expected.

As shown in Table 3 and Figure 5, Experiment 5 experienced a higher ID, 0.05(mg/L)⁻¹, as compared to 0.03 (mg/L)⁻¹ in Experiment 4, and a smaller \( k_{MD} \) than Experiment 4 (20 vs. 101 (M-h)⁻¹). This suggested that initial TOC and chlorine contact time have more impact on ID than initial excess free ammonia. Yet when it comes to \( k_{MD} \), excess free ammonia concentration becomes more important.
Figure 4 Excess Free Ammonia in Homogeneous Samples

Table 3 Monochloramine ID and $k_{MD}$ in Homogeneous Samples

<table>
<thead>
<tr>
<th>Exp #</th>
<th>$k_{MD}$, (mg-d/L)$^{-1}$</th>
<th>$k_{MD}$, (M-h)$^{-1}$</th>
<th>$R^2$</th>
<th>ID (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp4</td>
<td>0.0342</td>
<td>101</td>
<td>0.99</td>
<td>0.03</td>
</tr>
<tr>
<td>Exp5</td>
<td>0.0069</td>
<td>20</td>
<td>0.90</td>
<td>0.05</td>
</tr>
<tr>
<td>Exp6</td>
<td>0.0121</td>
<td>36</td>
<td>0.86</td>
<td>0</td>
</tr>
<tr>
<td>Exp7</td>
<td>0.0335</td>
<td>99</td>
<td>0.94</td>
<td>0.22</td>
</tr>
<tr>
<td>Exp8</td>
<td>0.0343</td>
<td>101</td>
<td>0.98</td>
<td>0.01</td>
</tr>
<tr>
<td>ExpA</td>
<td>0.0101</td>
<td>30</td>
<td>0.81</td>
<td>0.03</td>
</tr>
<tr>
<td>ExpB</td>
<td>0.0069</td>
<td>20</td>
<td>0.78</td>
<td>0</td>
</tr>
</tbody>
</table>
The comparison shows that the more excess free ammonia the smaller the kMD. The impact of excess free ammonia on ID was not clear. When the Cl₂:N ratio is less than 5, at a certain ratio, higher monochloramine initial concentration means more excess free ammonia. Thus a lower kMD is expected.

Impact of ozonation on monochloramine ID and kMD. Experiments 6 & 7, A & B were carried out back to back respectively. Experiments 6 and B were without ozonation. The homogeneous samples of those experiments were used to study the impact of ozonation on monochloramine decay.

As shown in Table 2, Experiments 6 and 7 had the same chlorine contact time, close temperature range, and similar TOC. The initial monochloramine concentrations of Experiments 6 and 7 are 2.95 and 2.57 mg/L. The chlorine to ammonia nitrogen ratios of the two experiments are 4.2 and 4.7.

With a lower initial monochloramine concentration and higher chlorine to ammonia ratio, Experiment 7 had less excess free ammonia than Experiment 6, as shown in Figure 6, and was expected to have a larger kMD.

As shown in both Table 3 and Figure 5, Experiment 7 had a much larger kMD than Experiment 6, 99 versus 36 (M-h)⁻¹. Although ozonation may have impact on kMD, the larger kMD in Experiment 7 than in Experiment 6 appears to be due to the impact of excess ammonia.

The ID of Experiment 7 was 0.22 mg/L. Yet there was no ID for Experiment 6. This was suspected to be due to ozonation.
Experiments A & B had the same chlorine contact time, similar TOC, and close temperature range. Although Experiment A had a smaller chlorine to ammonia nitrogen ratio and lower initial monochloramine concentration, the excess free ammonia concentration of the two experiments was about the same, as shown in Figure 6. The $k_{MD}$ of Experiment A was slightly greater than that of Experiment B. Experiment A had ID of 0.03 mg/L. Yet there was no ID in Experiment B. These may be due to the impact from ozonation.

![Figure 4 Excess Free Ammonia in Homogeneous Samples](image)

When ozonation is not used, the complex organic molecules in raw water may have less potential to react with monochloramine and result in a less or no ID. When ozonation is used, it breaks the complex molecules down into simpler ones (Singer et al, 1999), which may be easier to react with monochloramine. Ozonation seems to lead to higher ID and $k_{MD}$, although its impact on $k_{MD}$ is not as significant as the excess free ammonia concentration.

The bench scale study showed a faster monochloramine decay with higher ozone dose (Chin-Leung, 2003), which is consistent with the finding in this study. Wilczak et al (2003) also found an increased chloramines demand contributed by ozonation.

**Impact of distribution system on monochloramine $k_{MD}$**. The influence of the distribution system was studied through the comparison between the homogeneous and heterogeneous samples.

As shown in Table 4 and Figure 7, the $k_{MD}$ of the heterogeneous samples of all the six experiments were at least two orders of magnitude larger than those of the homogeneous samples, indicating much faster decay in the heterogeneous samples.
on Day 1 is defined as the initial pH drop. The linear decrease afterwards is described using a coefficient $k$ unit/day.

Homogeneous samples of Experiments 6 & 7 and A & B are used to illustrate the impact of ozonation on pH change. The experimental conditions of the experiments are listed in Table 2. The pH drop in one day and the decrease coefficient after one day are listed in Table 5.

![Graph showing pH change in Homogeneous Samples](image)

**Figure 6 pH change in Homogeneous Samples**

As shown in Table 5, with ozonation, Experiment 7 had more pH drop within one day as well as faster decrease in the remaining 8 days, compared to Experiment 6. When comparing Experiment A and B, there was no significant difference between the pH drops within one day, but the decrease afterwards in Experiment A (the one had ozonation) was faster than in Experiment B (the one without ozonation). The overall pH decrease for all the experiments are within 0.5 pH units in 8 days.

**Table 5 Initial pH drop and k in Homogeneous Samples**

<table>
<thead>
<tr>
<th>Exp #</th>
<th>pH Change</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unit</td>
<td>unit/day</td>
</tr>
<tr>
<td>Exp6</td>
<td>-0.08</td>
<td>-0.0039</td>
</tr>
<tr>
<td>Exp7</td>
<td>-0.13</td>
<td>-0.0344</td>
</tr>
<tr>
<td>ExpA</td>
<td>-0.04</td>
<td>-0.0355</td>
</tr>
<tr>
<td>ExpB</td>
<td>-0.06</td>
<td>-0.0262</td>
</tr>
</tbody>
</table>
During a water treatment process utilizing oxidation, such as ozonation and chlorination, complex organic molecules are broken down into small-molecules, which may include small-molecular organic acids. These acids may be responsible for the decrease of pH in homogeneous samples. Since ozone has a higher oxidation potential than chlorine, ozonation may result in the production of more of these acids and expedite pH decrease as compared to chlorination alone.

Impact of distribution system on pH. As shown in Table 6 and Figure 9, pH increased in all heterogeneous samples. All the 7 experiments showed the same trend (Huang, 2003). For comparison purpose, only the data of four out of the seven are shown below.

Table 6 Initial pH increase and k in Heterogeneous Samples

<table>
<thead>
<tr>
<th>Exp #</th>
<th>pH Change</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unit</td>
<td>unit/day</td>
</tr>
<tr>
<td>Exp6</td>
<td>0.18</td>
<td>0.0251</td>
</tr>
<tr>
<td>Exp7</td>
<td>0.25</td>
<td>0.0351</td>
</tr>
<tr>
<td>ExpA</td>
<td>0.24</td>
<td>0.1006</td>
</tr>
<tr>
<td>ExpB</td>
<td>0.17</td>
<td>0.0762</td>
</tr>
</tbody>
</table>

Figure 7 pH change in Heterogeneous Samples

As stated before, there are several potential mechanisms which may explain the increase of pH in the heterogeneous samples.
The organic acids, produced by ozonation, might be consumed by biological uptake and denitrification in the heterogeneous samples. The ammonia produced from monochloramine decay could be another reason of pH increase. The Kuch mechanism might add to this increase as well. The data showed a decrease of nitrate (a symptom of denitrification) and an increase of the total iron (a potential result from the Kuch mechanism reaction), which are consistent with the above interpretations (Huang, 2003).

The experiments were not originally designed to quantify the impact of each mechanism, nor were they carried out exactly as originally designed. Thus the above interpretations remain our best educated guesses based upon the data collected.

In all seven experiments, the pH increase in one day was within 0.5 units. And the total increase of pH in 10 days was within 0.9 units.

Impact of ozonation on pH in heterogeneous samples. Interestingly, in Table 6 and Figure 9, Experiments 6 & 7, A & B showed the impact of ozonation on the heterogeneous samples. The experiments with ozonation, which are Experiment 7 and A, both had a larger pH increase within day one and a faster increase afterwards, compared to those without ozonation, which are Experiment 6 and B respectively. Ozone seemed to cause a slightly larger initial pH increase as well as a faster increase afterwards. Further studies may be needed to understand the mechanisms.

CONCLUSIONS

The results suggest that in a relatively clean MWRA transmission system, monochloramine will experience an initial drop after a short interval and a slow decay afterwards. The $k_{MD}$ of monochloramine will be in the range of 10 to 100 (M-h)$^{-1}$. The pH followed the same trend as monochloramine decay. It may decrease up to 0.5 units. In a relatively clean pipe, ozonation seems to expedite monochloramine decay, as well as pH decrease. Thus more chemicals may be needed to keep sufficient monochloramine level in the distribution system, and to maintain the pH level for corrosion control.

In corroded cast iron pipes, monochloramine has a much faster decay and could be depleted in three days. A $k_{MD}$ in the order of 1000 (M-h)$^{-1}$ may occur in some dead ends far from the main. The pH may increase up to 0.9 units, and ozonation seems to expedite this process.

ACKNOWLEDGEMENT

The authors acknowledge the assistance of James Muri, Mary Bezek, Lisa Wong, and all their crew members at MWRA. The authors also acknowledge the support of Civil and Environmental Engineering Department of Northeastern University.

This paper represents personal opinions of the authors and not those of the MWRA.

REFERENCES


Footnotes:
1 MWRA, Charlestown Navy Yard, 100 First Ave, Boston, MA 02129
2 The generalized equations are for conceptualization and do not show balanced stoichiometry.
3 Black & Veatch, 11401 Lamar Avenue, Overland Park, KS 66211.
4 It may be noted that Experiment A had lower TOC than Experiment 7, which might contribute to the lack of initial pH drop in Experiment A.