Pilot Study of Greater Boston Drinking Water Quality Changes — Impacts of Ozonation and Distribution System

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ABSTRACT

The Massachusetts Water Resources Authority (MWRA) provides drinking water to 2.2 million people in Greater Boston. To ensure good water quality without filtration, the MWRA is about to replace chlorination with ozonation as the primary disinfection at the new Walnut Hill Water Treatment Plant, scheduled to be on-line in 2005. The objective of this study was to understand the influence of ozonation on monochloramine decay and pH change in the MWRA system. The influence of the distribution system, which consists of old cast-iron pipes, on the ozonated water was also investigated.

A pilot plant, including a simulated distribution system with actual 100 year old corroded cast iron pipes, was set up near Wachusett reservoir to simulate the new treatment scheme. Stagnant samples were taken and compared with circulated samples to study the influence of the distribution system. The stagnant samples represented the best scenario, i.e. a very clean distribution system. The circulated samples simulated the worst, where in the real world may be dead ends far from the main.

This study suggested that corrosion and biological activity inside the pipe were the major causes of water quality change in circulated samples. Actual water quality is expected to be somewhere in between the best and the worst scenarios.

BACKGROUND

MWRA water system. The source water comes from the Wachusett and Quabbin reservoirs. It has a low alkalinity (less than 10 mg/L CaCO₃), and a hardness of 8 to 18 mg/L as CaCO₃.
The current water treatment regime consists of chlorination for primary disinfection, then alkalinity and pH adjustment, followed with chloramination for residual disinfectant. The new regime, which will be employed in the new Walnut Hill Water Treatment Plant, departs from the current scheme with the use of ozone for primary disinfection (Website 2, March, 2003). MWRA has an extensive transmission and distribution system. Approximately 45 percent of the MWRA 300-mile distribution system and nearly 50% of the 5,500-mile network of community pipes are unlined cast iron pipe, ranging in age from 40 to 140 years. These pipes experience corrosion problems as well as biofilm accumulation, which cause water quality to deteriorate (Sarin et al, 2003; AWWA, 1996; Geldreich, 1996).

**The Pilot plant.** The Pipe Loop Pilot Plant (PLPP) was designed by Black and Veatch and set up by MWRA for investigating UV and ozone treatment and their impact on water quality. Within the available trains at the PLPP, Train 3 permits simulation of the treatment scheme planned for the MWRA’s Walnut Hill Water Treatment Plant (Black and Veatch Corp., 2001) and was the basis of this work. It included ozonation as primary disinfection, followed by pH and alkalinity adjustment, chlorination, and ammonia addition for chloramine production. The treated water then passed through the pipes.

The pipes used in the PLPP were excavated by Boston Water and Sewer Commission (BWSC) from its distribution system and intended to simulate the worst corrosion conditions in the actual pipe network. The total estimated detention time of thirty six pipes for Train 3 is 5.88 hours, based on a 0.16 m³/hour (0.6gpm) flow. Recirculation pump was installed to enable the system to simulate the circulation time in the MWRA system. The flow diagram is shown in Figure 1.

**Monochloramine decay.** In this study, the monochloramine decay coefficient, kMD, is used to quantify the rate of monochloramine decay. Valentine et al (1998) suggested a second-order monochloramine decay model as shown below.

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

The kMD is evaluated by plotting 1/[NH₂Cl] - 1/[NH₂Cl]₀ versus time t. The slope of the straight line, after converted to (M-h⁻¹), is kMD. It is expected to increase with decreasing pH, increasing temperature, and increasing chlorine to ammonia nitrogen ratio. Natural organic matter (NOM) is expected to accelerate monochloramine decay (Valentine et al, 1998).

**The influence of ozonation.** When Ozone is used as the primary disinfectant, different source water 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).

**The influence of the pipe.** Sarin et al (2003) studied the corroded, unlined cast iron pipes of the MWRA system. Only Fe(III) was found in the top layer of the scales, whereas a high Fe(II) concentration was found inside the scales. Nitrification is found for 63% of the utilities that use chloramines (Harrington et al, 2002). The symptoms of nitrification in the distribution system are loss of residual chloramine, decrease in dissolved oxygen, pH and alkalinity, and increase in HPC (Website 1, January, 2003). Denitrification was found in the distribution system (Lee et al, 1980).
In the present MWRA distribution system, some evidence of nitrification is seen, but typically it does not result in substantial loss of residual chloramine, or increase of HPC. No evidence of denitrification has been observed.

EXPERIMENTATION

Experimental procedure. As shown in Figure 1, samples were collected from six different sampling points throughout the pilot plant at different times. The pipe loops were conditioned at the desirable chemical doses for twenty four hours before the experiment started. Stability of the system was checked before sampling. The sample from point 4 was stored in 6 one-liter amber glass bottles as stagnant sample. They were analyzed at subsequent sampling times, and then compared with the results of the circulated samples. The maximum recirculation time used was ten days.

Ozone dose was controlled by the American Water Works Association Research Foundation (AWWARF) project, which was conducted simultaneously on the other two trains. Train 3 had the ability of switching ozonated water to raw water. The water temperature depended on the room temperature. The chlorine to ammonia-nitrogen weight ratio was targeted at 4.7 to achieve the maximum stability of the monochloramine residual in the distribution system. However, the variability inherited in a pilot study did not allow precise control of some of the parameters, e.g. temperature, chlorine dose, sodium carbonate and bicarbonate dose, chlorine to ammonia nitrogen weight ratio, sampling time and etc.

![Image of treatment scheme and schedule]

Sample analyses. Samples were analyzed on site for temperature, pH, alkalinity, turbidity, Dissolved Oxygen (DO), total chlorine, monochloramine, and ammonia. Total Organic carbon (TOC), UV<sub>254</sub>, nitrate and nitrite were measured at Northeastern University. HPC, total iron, and Disinfection By-products (DBP), i.e. THM and HAA6 were analyzed by MWRA.

RESULTS AND DISCUSSION
Eight experiments were designed, within which three were to study the impact of ozonation and distribution system, and are presented here. Others are covered elsewhere (Huang, 2003).

All of the monochloramine decay figures were plotted from time zero, when ammonia was added to the system. $k_{MD}$ values of stagnant samples were based on the data from all eight days. The $k_{MD}$ of the circulated samples were based on the first day only, when monochloramine was almost completely depleted. The HPC value found in the circulated samples was much higher than those observed in the MWRA system.

Table 1 Experimental conditions of Exp 5, 6, and 7

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Raw water temp $^\circ$C</th>
<th>Raw water pH</th>
<th>Initial TOC, mg/L</th>
<th>Initial UV$_{254}$ Abs/cm</th>
<th>Ozone dose, mg/L</th>
<th>CI/N weight ratio</th>
<th>$[\text{NH}_2\text{Cl}]_0$, mg/L-Cl$_2$</th>
<th>Circulated sample HPC on Day 1, cfu/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.4</td>
<td>7.14</td>
<td>1.99</td>
<td>0.048</td>
<td>0.44</td>
<td>3.9</td>
<td>3.23</td>
<td>4.5</td>
</tr>
<tr>
<td>7</td>
<td>18.5</td>
<td>7.12</td>
<td>2.54</td>
<td>0.078</td>
<td>1</td>
<td>4.7</td>
<td>2.57</td>
<td>445</td>
</tr>
<tr>
<td>6</td>
<td>16.8</td>
<td>6.73</td>
<td>2.37</td>
<td>0.067</td>
<td>0</td>
<td>4.2</td>
<td>2.95</td>
<td>1300</td>
</tr>
</tbody>
</table>

The influence of HPC

Experiment 5 and 7 were conducted to study the influences of different pipe initial conditions on water quality. The condition of the pipe was indicated by the measured HPC value in the bulk water. Stagnant samples represented zero HPC level. While in Experiment 5, the pipes were superchlorinated with 30 mg/L hypochlorite for seven days and achieved a low initial HPC level. As without superchlorination, Experiment 7 represented the high initial HPC level. The experimental conditions for Experiment 5 and 7 are listed in Table 1. The HPC in these two experiments are illustrated in Figure 2. After the monochloramine depletion on Day 4, the HPC in Experiment 5 rose to a larger value than Experiment 7 at the end of Day 8. Thus the low HPC condition of Experiment 5 only existed in the first four days.

Monochloramine decay. As shown in Figure 3, the $k_{MD}$ for the stagnant samples of Experiment 5 and 7 were 18 and 88 (M-h)$^{-1}$, respectively. Lower ozone dose, lower initial TOC, and lower temperature are possible causes of lower $k_{MD}$ for Experiment 5 compared to Experiment 7. The $k_{MD}$ of circulated samples of the two experiments were 5306, 8614 (M-h)$^{-1}$ respectively, as shown in Figure 4. These values are much larger than those of the stagnant samples. As a general trend of all the experiments, all the circulated samples $k_{MD}$ were about two orders of magnitude larger than those of the stagnant samples (Huang, 2003). This indicates the overwhelming impact of HPC level on monochloramine decay. Within the circulated samples, the $k_{MD}$ of Experiment 5 was the smallest among all eight experiments. Even with the lowest raw water temperature and TOC, which may also cause the
lower monochloramine decay, it appears that initial HPC condition of the pipe plays an important role on monochloramine decay in the pipe loop.

**Change of pH.** Figure 5 shows the pH change of the stagnant and circulated samples of both Experiment 5 and 7. In stagnant samples, pH showed a decrease, which may be due to organic acids produced through ozonation. A less initial TOC may cause the less pH decrease in Experiment 5, due to the less organic acid it may produce. The pH increases in circulated samples, which was opposite to the stagnant samples. The increase within one day and the overall pH increase in Experiment 5 circulated samples were lower than that in Experiment 7. Moreover, it was the lowest among all eight experiments. Up till Day 4, Experiment 5 had the lowest HPC in all eight experiments. Apparently, low HPC leads to a small pH increase in circulated pipes. The reason yet remains to be determined.

**Impact on DBP.** Figure 6 and 7 illustrate the difference in Total THM and HAA change. Both THM and HAA have been shown to be biodegradable (Baribeau et al. 2000, Zhou and Xie 2002). In both stagnant samples, which had zero HPC, both Total THM and HAA experienced a slight increase over time. With a high initial HPC level in circulated samples of Experiment 7, both THM and HAA were consumed by heterotrophs inside the pipe loop and decreased during the eight days. With low initial HPC level within the first four days, in Experiment 5, the THM and HAA increased in circulated samples. This was probably due to the reaction between monochloramine and the more organic matters contributed by the dead bacteria cells. After the HPC rose after Day 4, Total HAA started to decrease yet Total THM kept increasing to the end of Day 8. The pipe loop with biofilm attached to the pipe wall apparently reacts as a bioreactor and consumes organic matter, including HAA. The more HPC the more HAA it will remove.

**Biological activity.** Nitrification was expected in the circulated samples. The free ammonia and nitrate concentration change were shown in Figure 8 and 9. Free
ammonia consists of ammonium ion and ammonia. Experiment 5 had higher initial free ammonia, which caused its lower chlorine to ammonia ratio. The increase of free ammonia in both stagnant samples may be due to the monochloramine decomposition. In circulated samples the increase may be due to the ammonium produced when monochloramine reacted with other reducing species in the pipes as well as its auto-decomposition.

In Experiment 7 circulated sample, free ammonia decreased after Day 1, which might be a result of both biological uptake and nitrification. With less HPC level for the first four days, there was no significant decrease in eight days for Experiment 5 circulated samples.

Both Experiment 5 and 7 showed a nitrate decrease in circulated samples and no change in stagnant samples. The decreasing nitrate indicates the potential of denitrification (Lee et al. 1980). Denitrification could conceivably take place within the biofilm under the anoxic condition. Since denitrification causes pH to rise, this observation is consistent with the pH change in Figure 5.

**The influence of ozonation**

Experiment 6 and 7 were conducted to study the influence of ozonation. The experimental conditions of the two experiments are listed in Table 1. There was no ozonation used in Experiment 6. The HPC levels of the two experiments are about the same during the 8 days as shown in Figure 10.
**Monochloramine decay.** The $k_{MD}$ of the circulated samples were 8761 and 8614 (M-h)$^{-1}$ for Experiment 6 and 7. This shows that, in circulated samples, compared to HPC, ozonation has an insignificant impact on monochloramine. Thus only monochloramine decay in stagnant samples is discussed here.

As shown in Figure 11, the $k_{MD}$ of Experiment 7 and 6 for stagnant samples were 88 and 29 (M-h)$^{-1}$. Experiment 6 has slower monochloramine decay. Compared to other experiments, the stagnant sample $k_{MD}$ of Experiment 6 is less than most of other experiments which used ozonation. Ozonation caused faster monochloramine decay, which agreed with the bench scale study (Chin-Leung, 2003). It is likely that ozonation yields small-molecule organic products, which are easier to react with monochloramine (Singer et al, 1999).

**Change of pH.** Figure 12 shows the pH change of stagnant and circulated samples in 8 days.

In stagnant samples, ozonation expedited pH decrease. More small-molecule organic acids produced by ozonation might be responsible for this. In circulated samples, ozonation resulted in more pH increase within Day 1 as well as in 8 days. The organic acids, produced by ozonation, might be consumed by biological uptake and denitrification in the circulated samples, and thus leading to more increase in pH.

**Impact on DBP.** Raw water TOC and monochloramine dose reflect the potential of DBP formation. With about the same initial TOC, Experiment 6 had more initial monochloramine dose and smaller $k_{MD}$ than Experiment 7. In stagnant samples, without the HPC influence, no significant difference was observed for Total THM and HAA6 for the two experiments, as shown in Figure 13 and 14. With similar HPC
condition, in circulated samples, Experiment 7 had less Total THM and HAA6. The less monochloramine dose in Experiment 7 may account for this difference. Nevertheless the impact of ozonation on DBP per se cannot be delineated.

CONCLUSIONS
This study is based on the pilot MWRA water treatment system. The results suggest that under the worst scenario, e.g. highly corroded distribution pipes, biological condition of the pipes is the main factor of water quality change. Higher HPC are associated with higher monochloramine decay, pH increase, and iron release. Ozonation seems to promote pH increase. Nitrification and denitrification may occur under such conditions.

Under the best scenario, represented by the stagnant samples, ozonation expedited monochloramine decay, and pH decrease.

The impacts of increasing HPC and ozone dose are summarized in Table 2.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>pH Change</th>
<th>HPC</th>
<th>Ozone</th>
<th>kMD</th>
<th>DBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circulated</td>
<td>pH increase</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td>Stagnant</td>
<td>pH decrease</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>t</td>
</tr>
</tbody>
</table>

Note: -: no significant impact; t: increase; t: decrease

This study suggests that a larger monochloramine initial dose and more pH adjustment chemical may be required during the future operation of Walnut Hill Water Treatment Plant. The corroded distribution system appears to be the key factor of the deteriorated water quality after the water leaves the treatment plant.

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