

Willmar, Minnesota Controls Nitrification in Distribution System

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Summary

Previous studies, reported in Public Works (October-December, 1997), showed that chloramine was the principal cause of elevated copper levels in water withdrawn from household plumbing after 6 hours of retention. In an effort to reduce chloramine concentrations throughout the Willmar water distribution system, the present study was undertaken to find a practical means for removing ammonium ion from the Willmar groundwater supply. Ammonium ion removal was expected to reduce microbially-mediated nitrification, thereby reducing the formation of nitrite and nitrate ion during distribution. In the absence of reducing agents, it was believed that chloramine residuals would be stabilized so that lower concentrations could be applied to the finished water leaving the treatment plant.

Introduction

Studies conducted in July and August, 1996, provided strong evidence that *chloramine* was the strongest factor influencing the short-term rate of corrosion of copper pipe. The results of these studies indicated that decreasing finished water chloramine to levels approaching 1 mg Cl/l should limit copper corrosion in household plumbing to less than the 1.3 mg Cu/l copper action level.

The barrier to simply decreasing the level of chloramine leaving the treatment plant was the loss (consumption) of disinfectant during distribution. Under normal circumstances, low levels of chloramine can persist for hundreds of hours in finished water. However, when ammonium ion is present in excess, nitrifying organisms colonizing the distribution system piping will oxidize the ammonium ion to nitrite ion and, ultimately, nitrate ion. The depletion of dissolved oxygen is a most readily-measured and sensitive indicator of the progress of nitrification.

In systems undergoing nitrification, reducing agents rapidly react to consume the chloramines in hours instead of days. As a result, elevated levels of chloramine were applied at Willmar's treatment plants to offset the loss of residual during distribution.

Nitrite ion, in particular, is a strong reducing agent. In addition to the discoloration of poultry products, the presence of nitrite ion in a water distribution system could constitute a health concern (methemoglobinemia). Nitrite is therefore regulated at 1 mg N/l. For this reason alone, the control of the activity of the nitrifying organisms is indicated.

The basic control strategy of this study can therefore be summarized, as follows:

- Reduce the concentration of chloramine applied.
- Control chloramine residual loss during distribution.
- Control formation of nitrite during distribution.
- Control nitrifying bacteria in the distribution system.

Oxidation of Ammonium Ion by Ozone

The literature on ozonation indicates that it is possible to *directly* oxidize ammonium ion using *ozone*. The reported reaction is comparatively slow (requires hours of contact in the absence of catalytic agents), is temperature-dependent and is accelerated at higher pH.

The application of ozone to ground water should result in the rapid oxidation of reduced *iron, manganese, sulfides* and a portion of the *organic carbon* present. The partial oxidation of the naturally-occurring organic compounds (humic and fulvic substances) is expected to reduce both color and the formation of disinfection by-products, such as the trihalomethanes.

Finally, ozonation should completely *sterilize* the water leaving the plant. Since ozone will independently oxidize the manganese ion present, the present permanganate feed could be discontinued. However, post-chlorination would still be required to provide a stable distribution system residual since ozone will not persist.

While most waters will not sustain a residual ozone concentration in aqueous solution for long periods, high alkalinity waters allow ozone to persist for hours, enhancing direct reactions with aqueous (dissolved) ozone.

Of the options available, ozonation appeared to offer the promise of combined oxidation and disinfection. A critical need was to determine under what operational conditions the application of ozone to Willmar water might result in ammonium ion oxidation.

Ozonation Pilot Plant Study Results

The principal objective of the proposed study was to evaluate the effectiveness of ozonation as a unit process to augment the treatment presently provided by Willmar.

To perform the tests, a 10 gpm ozonation pilot plant unit was installed at the Southwest treatment plant. The pilot plant utilized a compressed oxygen feed to a corona-discharge ozone generator. The ozonated oxygen was then applied to the aerated plant water through an ozone injector, contactor and degasifier. Following the absorption of ozone, a greensand filter was used to observe the filterability of the ozone-oxidized byproducts.

The study results indicated that ferrous iron was already effectively oxidized by oxygen in the aerated water.

Manganous ion was oxidized to permanganate by ozone, giving the ozonated water the characteristic clear, pink color of permanganate. On filtration through greensand, this permanganate was chemically reduced and the resulting manganese dioxide precipitate effectively removed.

Sulfides, which were low in the influent groundwater, were undetectable in the ozonated water.

While color was significantly reduced, there was only a 20% reduction in total organic carbon.

Most important, there was little oxidation of ammonium ion even with pH values increased by the addition of powdered magnesium oxide (Figure 1). As a result, the ozonation studies were discontinued for lack of demonstrated effectiveness.

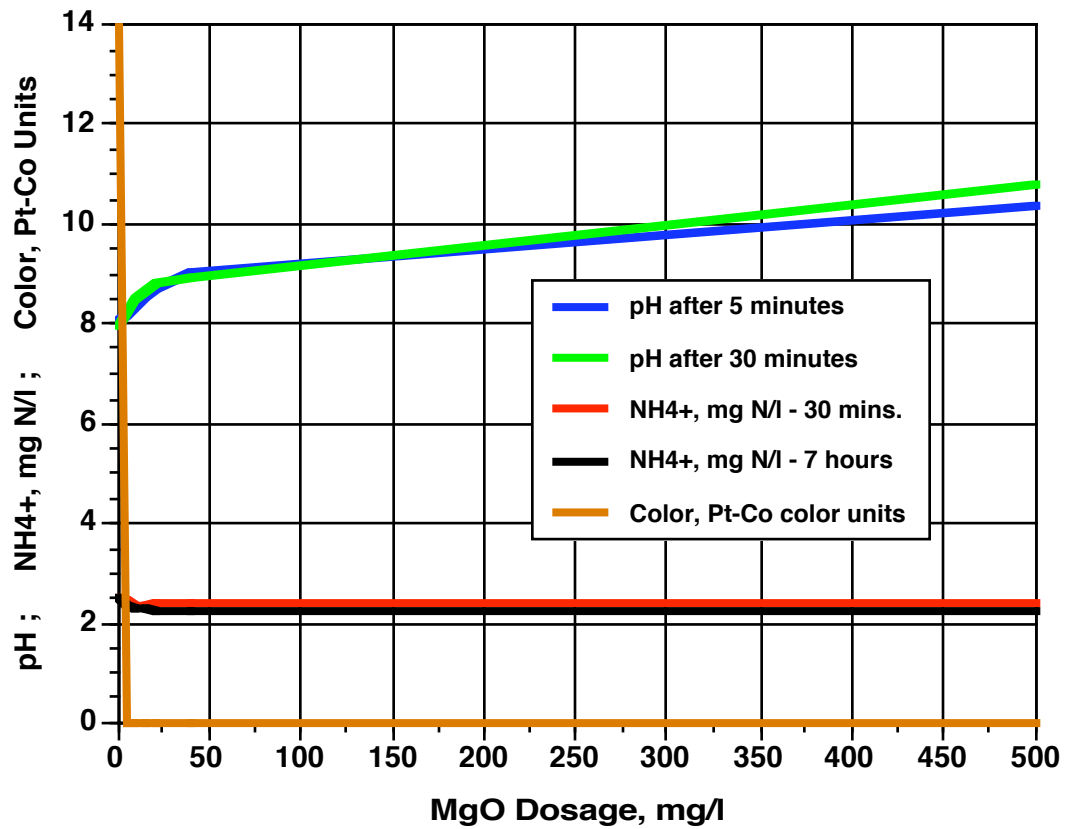


Figure 1. Ozone Oxidation of Ammonium Ion with Addition of MgO to Increase pH



Oxygen Cylinder and Ozonator Generator, Pump, Injector and Contactor (lower left, black), SS Degassing Separator, Ozone Destruct Column (black), Filter Columns in Series (center), Clear Well (right)

Breakpoint Chlorination Studies and Results

Studies of ammonium ion oxidation using chlorine were conducted following the cessation of the ozonation studies. Limited success was anticipated owing to the fact that only about 3.5 minutes of contact time was available following aeration and prior to filtration. Particularly in colder water, the reaction between chlorine and ammonium ion was expected to occur slowly.

However, experimental results showed that ammonium ion was readily oxidized to near-zero levels using chlorine dosages slightly less than the calculated requirement for reaching the breakpoint (Figures 2 and 3). From the results of these studies, a simple algorithm was developed for estimating the dosage of chlorine required to oxidize ammonium ion while maintaining a predominately chloramine residual. This algorithm differs from the well-documented procedure generally used in breakpoint chlorination in that it indicates chlorination to the downward slope prior to the breakpoint where the molar ratio of chlorine to nitrogen is less than 1.5. Operationally, it is somewhat more difficult to maintain consistent chloramine residuals in this region.

Breakpoint ammonia reduction treatment (BART) was successfully implemented in Train #1 of the Southwest water treatment plant early in December 1996. Within 18 hours of start-up, ammonium ion levels in the plant finished water were reduced by about one-half.

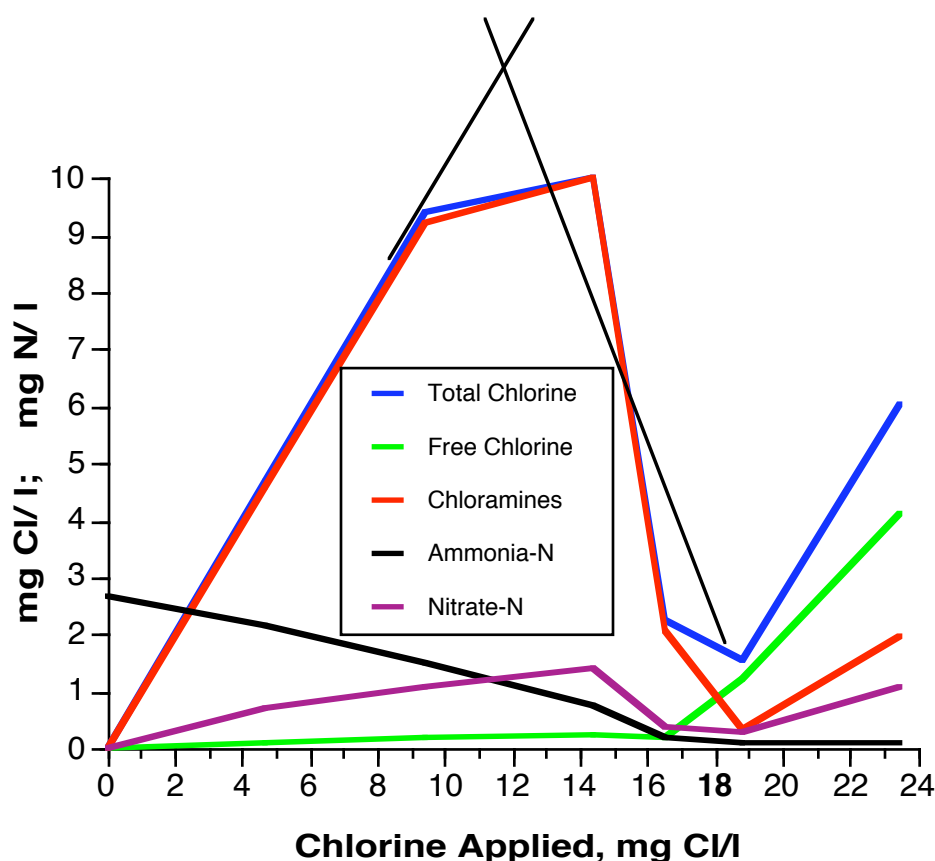


Figure 2. Chlorination to Breakpoint after 30 Minutes Reaction Time -Southwest Plant

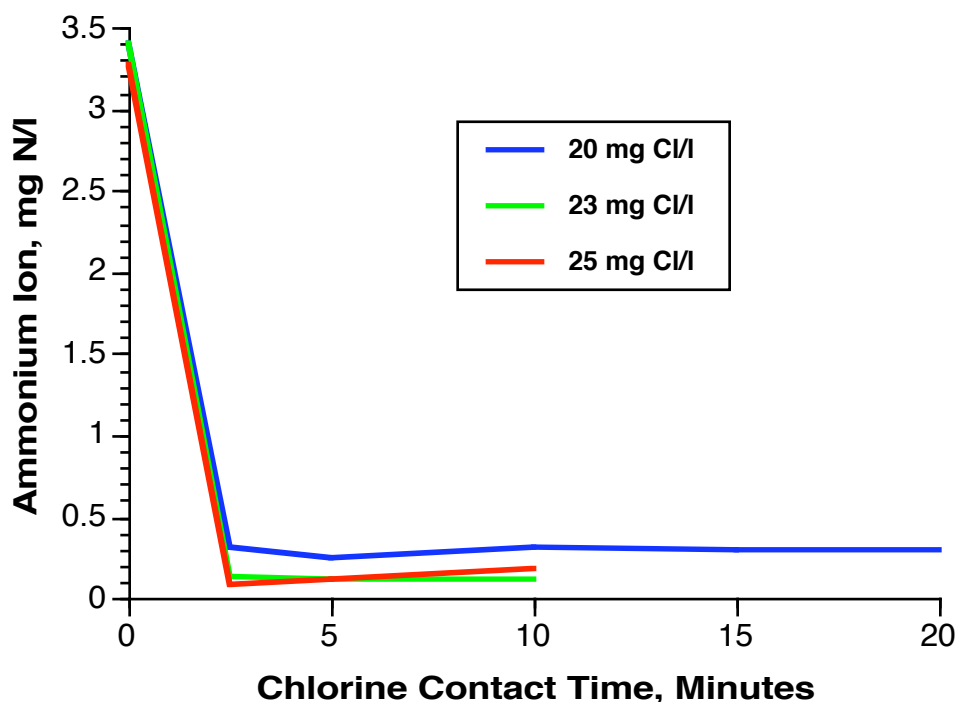


Figure 3. Rate of Ammonium Ion Oxidation by Chlorine -Southwest Plant

Oxidation of Manganous Ion and Organic Matter by Chloramination; Reduction in Color

Subsequently, it was determined that manganous ion was almost completely oxidized in the BART process and removed on the greensand filters. This obviated the need for continuing the addition of potassium permanganate. This result was unexpected because chlorine was not known to be capable of oxidizing manganous ion at neutral pH.

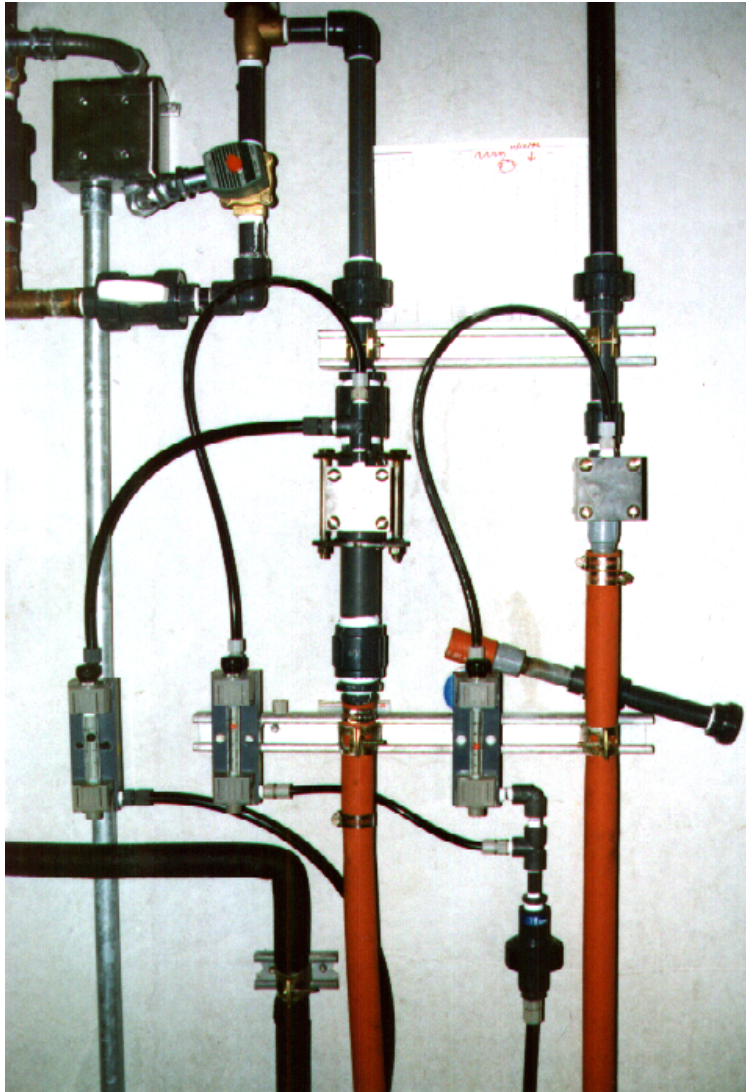
The well water was also decolorized in the BART process, the effluent looking comparable to that obtained by ozonation. This would indicate that chlorine is also capable of partially oxidizing the colored organic matter present in the Willmar well water.

Taste tests were conducted on the filtered water from both the BART and chloraminated treatment trains. No differences in tastes could be detected either in these waters or in local bottled or ozonated waters used for comparison.

Total Organic Carbon Reduction and Trihalomethane Formation

A series of samples was collected in conjunction with both pilot plant ozonation and the initiation of BART to observe the effect of these treatments on the removal of total organic carbon. Neither the BART process nor 'ozonation plus greensand filtration' appeared to have a significant impact on the amount of total organic carbon in the treated water.

The Southwest plant finished and distributed water was also sampled for total trihalomethanes (TTHM). The results indicate that some trihalomethanes, principally, trichloromethane, are formed. However, after blending with chloraminated filter effluent, the clear well and distribution system TTHM levels (10 to 30 μ g/l) were found to be well within established or foreseeable regulatory limits.



**Modification of Treatment Process for Ammonium Ion Oxidation:
Chlorine Injectors for Increased Application of Gaseous Chlorine**

Long-Term Evaluation of Response of Willmar Distribution System to Plant-Scale Implementation of BART for Ammonium Ion Oxidation (December 1996 - August 1997)

The oxidation of ammonium ion by the addition of slightly less than the stoichiometric requirement of chlorine to reach breakpoint was initiated in Train #1 of the Southwest water treatment plant early in December 1996. Train #2 of the plant continued to receive the same treatment (chloramination) as previously. Both treatment trains were adjusted to treat approximately one-half of the plant flow so that the finished water was an equal blend of the two trains.

Distribution System Monitoring Program

Since BART represented a marked departure from past treatment practice, a comprehensive distribution system monitoring program was planned so that the effects of this treatment could be assessed over a long period. The period of evaluation would span both the winter (cold water temperatures) and summer (warm water temperatures) seasons and provide information on whether and how rapidly the distribution system responded to reduced ammonium ion levels. It was hypothesized that it might take months to observe a significant reduction in the activity of nitrifying bacteria which had colonized the surface of distribution system piping over many years.

Almost immediately upon full-scale implementation, higher chloramine residuals began to appear in regions of the distribution system served by the Southwest plant where they had previously been low. This was particularly evident at the Northwest chlorine booster station. As a result of reduced chloramine demand in the system, the chlorine feed at the booster station could be discontinued, thereby saving chemical storage, feed and maintenance costs.

As a result of this early, beneficial response, BART treatment was subsequently initiated in Train #1 of the Northeast water treatment plant.

Distribution System Monitoring Program

On the same day as the initiation of BART, a comprehensive, monthly sampling of twelve representative sites in the distribution system was undertaken to establish a base-line from which the long-term effects of the ammonium ion removal could be scientifically assessed. Analyses were conducted for pH, temperature, dissolved oxygen, total and free chlorine (chloramine was calculated as the difference), ammonium, nitrite and nitrate ions. The following series of figures illustrate the response of the distribution system to the BART treatment.

Figures 4 and 5 show the rapid decrease of ammonium ion in the distribution system to an average of 1 mg N/l. If necessary, additional ammonium ion reductions can be achieved by treating a higher proportion of the plant flow.

While ammonium ion levels dropped immediately, nitrite and nitrate levels, shown in Figures 6-9, declined over a two-month period with nitrite averaging 0.13 mg N/l and nitrate averaging 0.55 mg N/l thereafter. A seasonal rise in nitrite and nitrate levels, observed at some sampling locations, indicate that some nitrification is still occurring in the distribution system.

The observed general decrease in nitrification may have been due to the increased persistence of the chloramine residual throughout the distribution system. As shown in Figures 10-11, despite applications being significantly reduced at the treatment plant plus the elimination of chlorination at the booster station, chloramine concentrations still generally exceed 0.5 mg Cl/l throughout the distribution system.

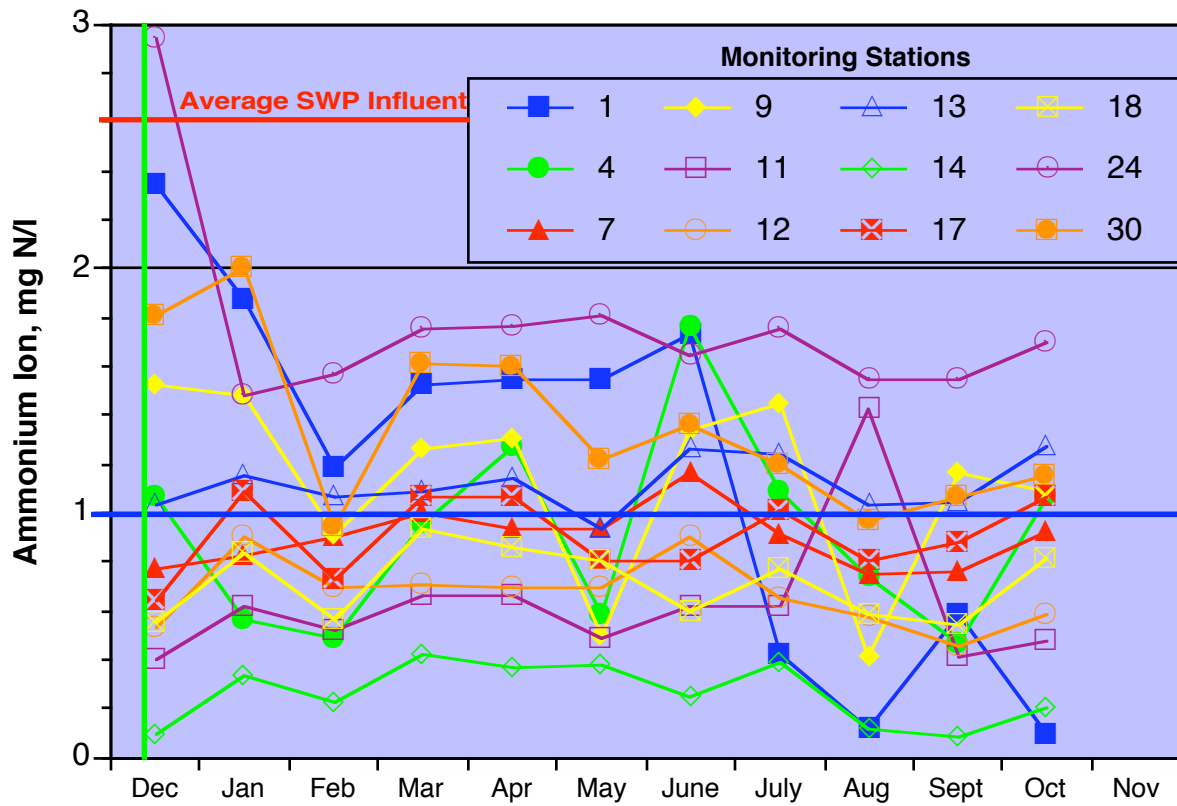


Figure 4. Distribution System Ammonium Ion after BART - Willmar, MN

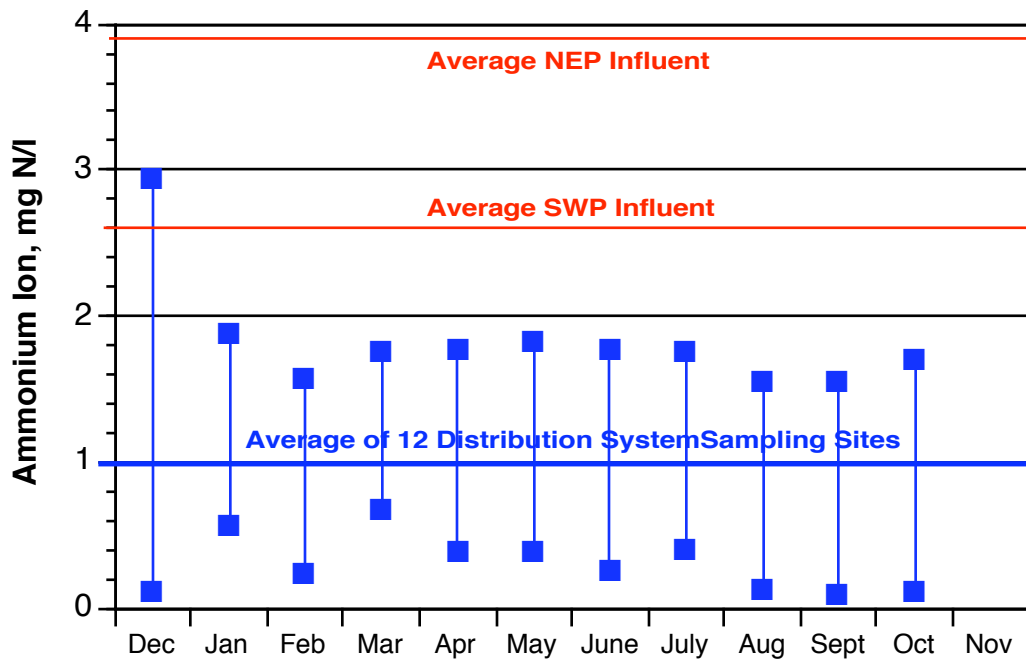


Figure 5. Range of Ammonium Ion Concentrations after BART

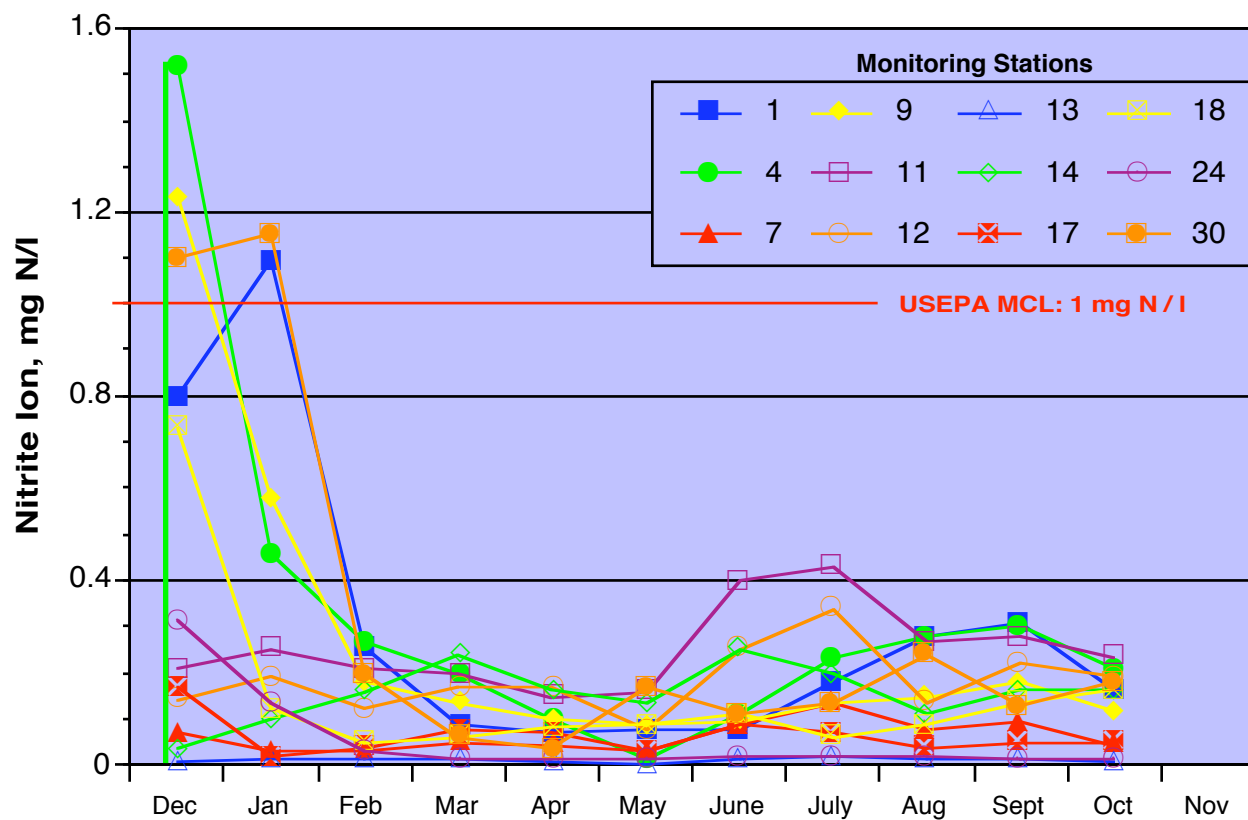


Figure 6. Distribution System Nitrite Ion after BART Dec. '96 - Nov. '97

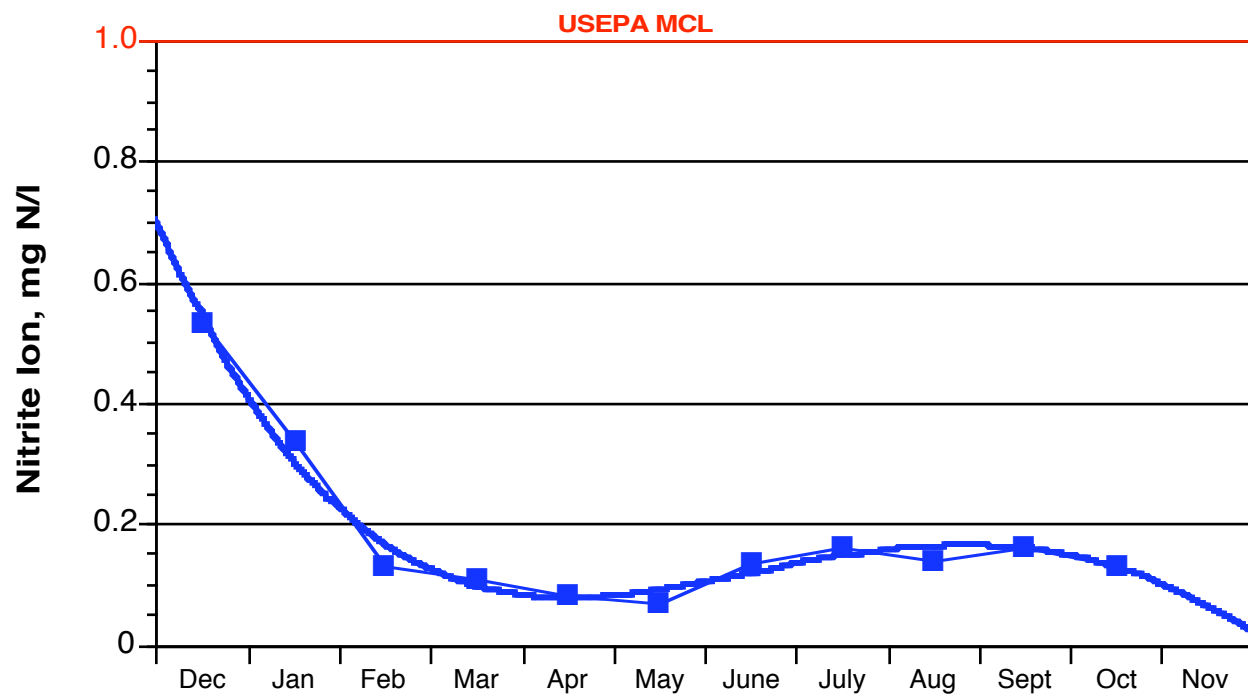


Figure 7. Average of Nitrite Ion Concentrations after BART

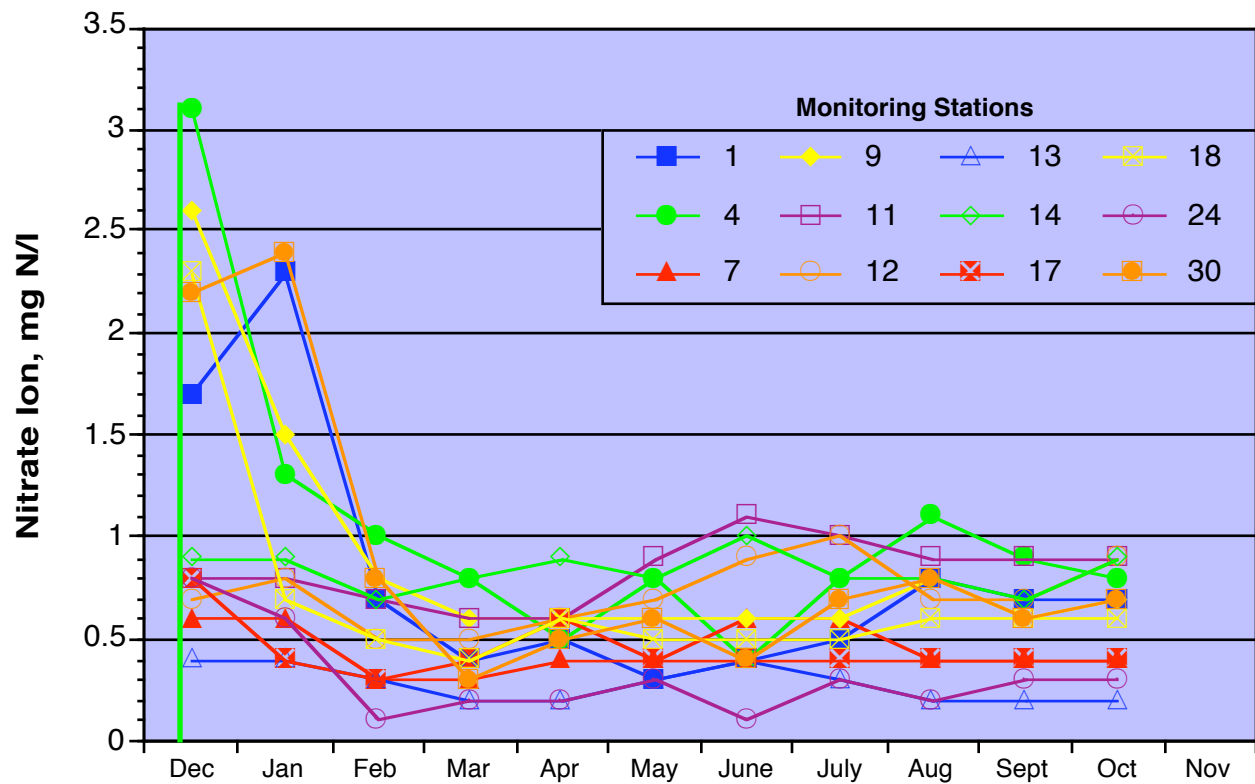


Figure 8. Distribution System Nitrate Ion after BART Dec. '96 - Nov. '97

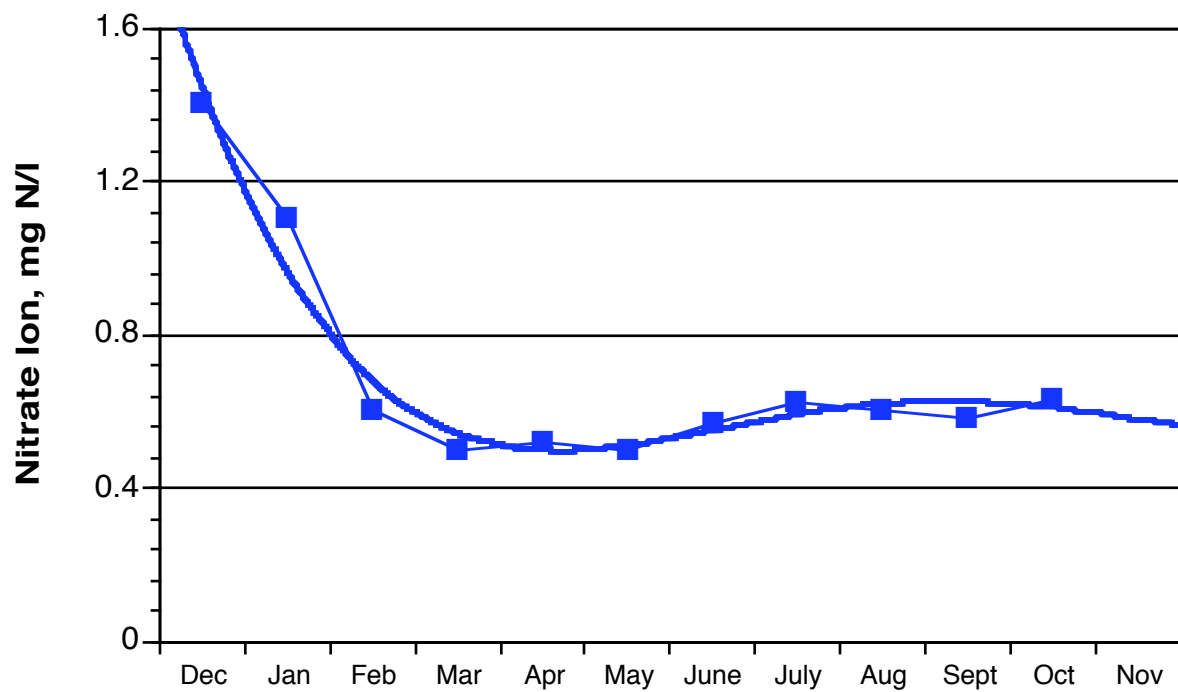


Figure 9. Average Nitrate Ion Concentration after BART

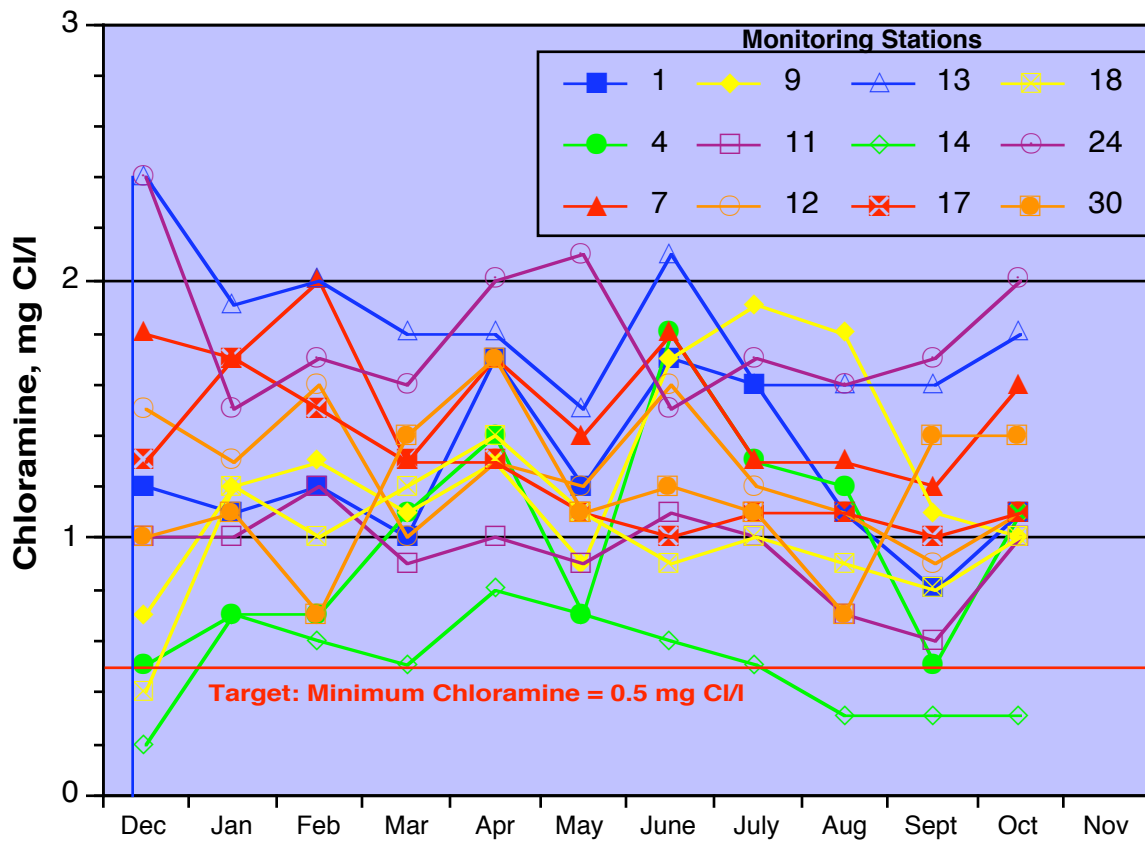


Figure 10. Distribution System Chloramine after BART

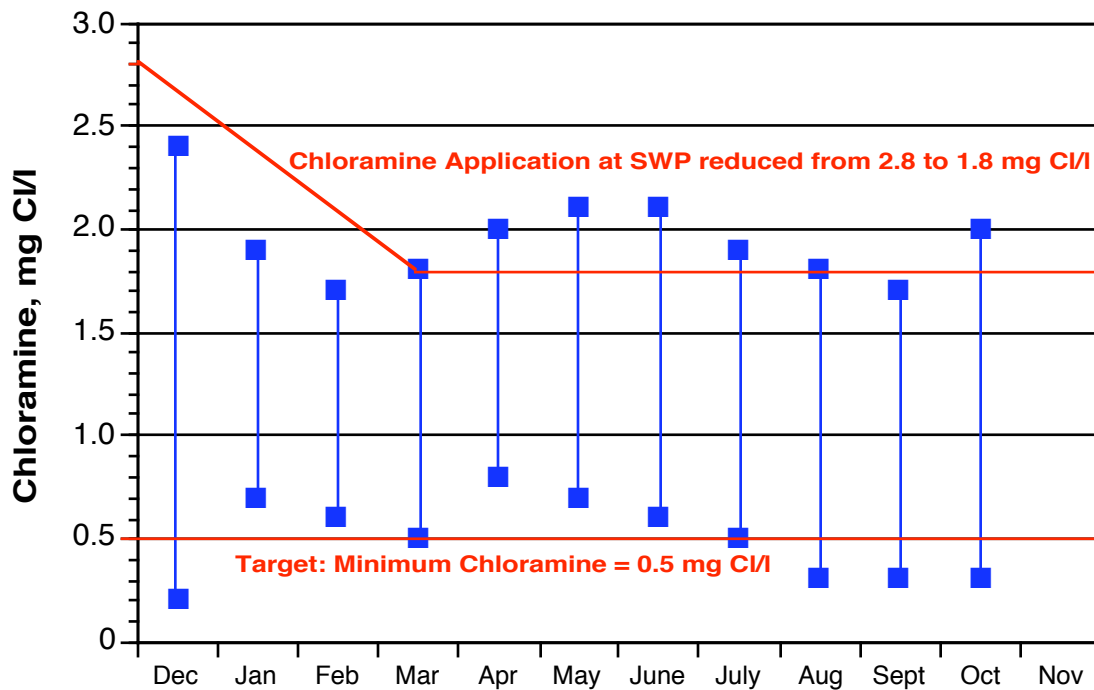


Figure 11. Range of Chloramine Concentrations after BART

Effects of Implementation of BART

Continued operation of the BART and chloramine treatment trains have demonstrated or indicated the potential effectiveness of BART in achieving the following objectives:

- Flexible control over ammonium ion concentrations and nitrification in the distribution system from near-breakpoint reduction of ammonium ion,
- Potential for sustaining chloramine residuals in the distribution system by suppression of nitrite ion formation,
- Avoidance of prolonged contact with free chlorine resulting in the formation of unacceptable levels of trihalomethanes,
- Enhanced manganese removal, exceeding even that obtained using permanganate-regenerated greensand,
- Reduction of true natural color in well water equivalent to color reduction observed using ozone,
- Reduced nitrite and nitrate formation in the distribution system,
- Avoidance of oxygen depletion due to nitrification,
- Potential for control of copper corrosion due to decreased levels of chloramine in household and building plumbing systems.

Continuing distribution system monitoring is planned to observe the long-term impacts of maintaining a stable disinfectant residual on microbial growth and activity leading to nitrification.

Benefits of Control of Nitrification through Implementation of BART

The major benefit of the control of nitrification in the Willmar distribution system through the implementation of breakpoint ammonium reduction treatment (BART) was the reduction in the level of nitrite ion.

Of greatest importance was the significant reduction in any potential for adverse human health effects due to methemoglobinemia in susceptible individuals.

In addition, the reduction in nitrite concentrations benefited regional industry in terms of the prevention of discoloration of meat and poultry products, a staple of the local economy.

Finally, the reduction of nitrite ion has increased the propagation of disinfectant residuals throughout the water distribution system. This both reduces the range of chloramine concentrations in the system and lessens the potential for water contamination due to back siphonage.

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