

Removal of Chloramines by Granular Activated Carbon

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Many retail and wholesale utilities are converting disinfection from free chlorine to chloramines to achieve compliance with the Disinfectants/Disinfection By-Product (D/DBP) Rule. Although this conversion may meet the needs of the primary provider, consecutive systems and customers may have difficulties with the change. Other utilities that subsidize their own systems with wholesale water may be faced with converting portions or all of their systems to chloramines to be compatible. Customers or primary or consecutive utilities, such as beverage manufacturers that have historically provided subsequent treatment to remove chlorine, may now find it necessary to remove ammonia as well.

Pasco County, located on the Gulf Coast of Florida north of the Tampa Bay metropolitan area, provides water to nearly 250,000 residents through a countywide conveyance and distribution system. The county's water supply comes from groundwater pumped through 29 dispersed wells and three

interconnects with Tampa Bay Water, as shown in Figure 1. Tampa Bay Water provides wholesale water to six member governments, including Pasco County.

As of June 2002, Tampa Bay Water was scheduled to convert its entire system from a free chlorine residual to a combined chloramine residual. In order to be compatible, Pasco County was faced with converting major portions of its system to chloramines, which included adding ammonia at potentially 22 sites or converting back to a free chlorine residual at two of the Tampa Bay Water interconnects. Because the use of chloramines by Tampa Bay Water does not remove natural organic matter (NOM), the potential to form disinfection by-products (DBPs) with subsequent chlorine addition still remains, so additional NOM removal may also be necessary to achieve compliance with the D/DBP Rule.

Pilot-plant studies were conducted by Parsons to identify effective treatment methods for removing chloramines, both chlorine and ammonia, while

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reducing NOM from the chloraminated water to be provided by Tampa Bay Water. Although possible technologies exist, including granular activated carbon (GAC), their effectiveness to remove chloramines (i.e., chlorine and ammonia) is not well documented. Essential for converting from chloramines to free chlorine is the removal of ammonia. If ammonia were to remain, chloramines would once again be formed by the addition of chlorine intended to provide a free chlorine residual.

Experimental Design

A GAC pilot plant as shown in Photograph 1 was designed and fabricated for testing. The pilot plant consisted of four five-foot-long columns operated in series. Each column was filled with 2.5 feet of GAC (Calgon FilterSorb 300®), achieving a total 10-foot simulated bed depth. All four columns were mounted on a metal frame (Unistrut®) with one-inch diameter PVC pipe interconnecting between each. The pilot plant was specifically designed to simulate the actual operating conditions of a full-scale plant. Sample taps were installed after each column representing one-fourth of the total bed depth. These were

installed to observe the advancement of the NOM, trihalomethane formation potential (THMFP), and haloacetic acids formation potential (HAAFP) concentration wave fronts. Water flow rate was maintained at 0.44 gal/min achieving an empty bed contact time (EBCT) of 15 minutes. A 15-minute EBCT was selected to enhance NOM removal based on values reported in the literature (AWWA/ASCE, 1998; Fair, Geyer and Okun, 1968).

The pilot plant was installed in the pump room at Tampa Bay Water's Cypress Creek Pumping Station and Groundwater Treatment Facility (Cypress Creek Facility) located in Pasco County. Four different wellfields feed the facility: (1)Cross Bar, (2)Cypress Creek, (3)Cypress Bridge and (4)Morris Bridge. During the study period, nearly 80 percent of the flow was from Cross Bar and Cypress Creek, with the other 20 percent from Cypress Bridge and Morris Bridge. Total organic carbon (TOC) concentrations, which are commonly used as a surrogate measure of NOM, were lowest for Cross Bar and Cypress Bridge wellfields averaging 1.7 and 1.4 mg/L, respectively. These concentrations are in contrast with Cypress

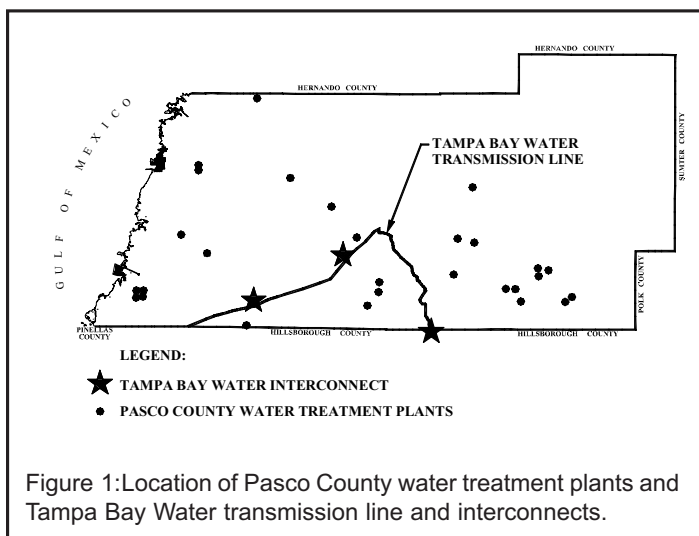
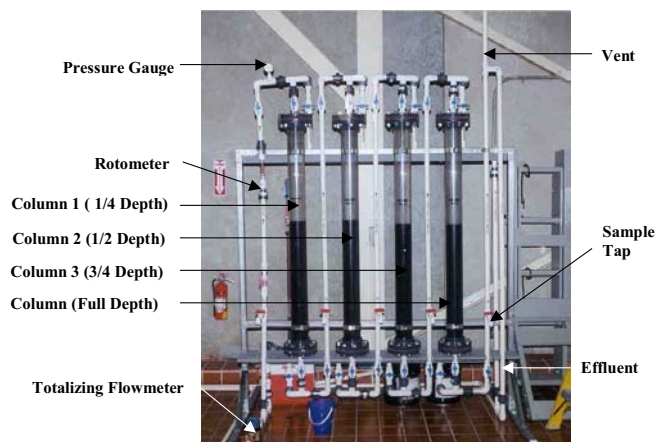


Figure 1: Location of Pasco County water treatment plants and Tampa Bay Water transmission line and interconnects.



Photograph 1: Granular activated carbon (GAC) pilot plant shown installed at Tampa Bay Water's Cypress Creek Facility Pump Room.

Creek and Morris Bridge well-fields with reported averages of 2.4 and 3.0 mg/L, respectively. During the course of pilot testing, the blending of these well-fields contributed on average 2.0 mg/L, varying between 1.4 and 4.0 mg/L as TOC.

Groundwaters entering the Cypress Creek Facility are combined and blended into a 72-inch pipe and prechlorinated with a dose of 4 mg/L as Cl₂, achieving a downstream free residual of 1.5-1.8 mg/L as Cl₂. Prechlorinated groundwater was provided to the pilot plant through a 3/4-inch tie-in connection with an air release valve on the influent line to Cypress Creek. Ammonia in the form of ammonium hydroxide (NH₄OH), also known as aqua ammonia, was metered into the 3/4-inch feed line at a chlorine-to-ammonia ratio ranging between 3:1 and 4:1 Cl₂:NH₃-N to form monochloramines at a concentration of 2.5 to 3.0 mg/L as Cl₂.

The pilot plant was monitored each Monday, Wednesday, and Friday for monochloramines, total chlorine, free chlorine, free ammonia, pH, TOC, and ultraviolet light absorbance at a wavelength of 254 nanometers (UV254). Seven-day trihalomethane formation potentials (THMFP_{7-Day}) and haloacetic acid formation

potentials (HAAFP_{7-Day}) were also monitored once each week.

Pilot-plant studies were conducted over approximately five months. Chlorine in the form of sodium hypochlorite and ammonia in the form of ammonium hydroxide were injected into raw groundwater supplied by Tampa Bay Water to simulate target monochloramine residuals of 2.5-3.0 mg Cl₂/L.

Results

Figures 2 and 3 illustrate the removal of both total chlorine and monochloramine by GAC with time, respectively. As a point of reference, corresponding plots of influent chlorine-to-ammonia ratio were included. Influent total chlorine and monochloramine concentrations, which varied from 0-8.5 and 1-3.4 mg/L as Cl₂, respectively, were reduced to below detection limits.

As Figure 4 shows, ammonia concentrations were unaffected for the first 70 days. During this period, effluent concentrations were, for the most part, the same as influent concentrations, so the GAC removed only the chlorine portion of the monochloramines; ammonia remained. Equation 1 describes this reaction (Kim and Snoeyink, 1980). C* and CO* represent the GAC surface



and a surface oxide on the GAC, respectively.

From a project perspective, it was essential to remove ammonia. After a review of the literature (Bauer and Snoeyink, 1973) and subsequent discussions with Dr. Vernon Snoeyink of the University of Illinois, it was determined that only by increasing the chlorine concentration to the breakpoint concentration (i.e., 7.6 Cl₂:NH₃-N) would ammonia be converted to nitrogen gas and removed. Although there is another reaction with GAC as described by Equation 3 (Kim and Snoeyink, 1980) that provides a direct conversion of monochloramines to nitrogen gas without the need to add chlorine, this reaction does not appear to govern based on the results. The influent and effluent ammonia concentrations were approximately the same, suggesting that Equation 1 governs.

To accommodate breakpoint chlorination, an additional chlorine injection point was added immediately upstream of the GAC pilot plant. Chlorine in the form of sodium hypochlorite was injected into

the chloraminated water to raise the chlorine concentration above breakpoint or a chlorine-to-ammonia ratio slightly greater than 7.6 Cl₂:NH₃-N. The pilot plant was also converted to an upflow configuration to allow nitrogen gas to be released from the GAC bed and vented out the top of each column through air release valves.

As shown in Figure 4, increasing the chlorine-to-ammonia ratio to >8Cl₂:NH₃-N effectively reduced effluent ammonia concentrations to below detection limits. Although breakpoint alone could achieve the same result, the GAC helped to catalyze the reaction while reducing effluent total chlorine concentrations to below detection limits, as shown in Figure 1.

As shown in Figure 5, TOC levels were initially reduced from an average of 2 mg/L to 0.6 mg/L by adsorption on the GAC in the effluents of all four columns. As time progressed, the effluent TOC concentrations increased as the GAC became saturated with NOM. These data show the saturation of the first column (1/4-column

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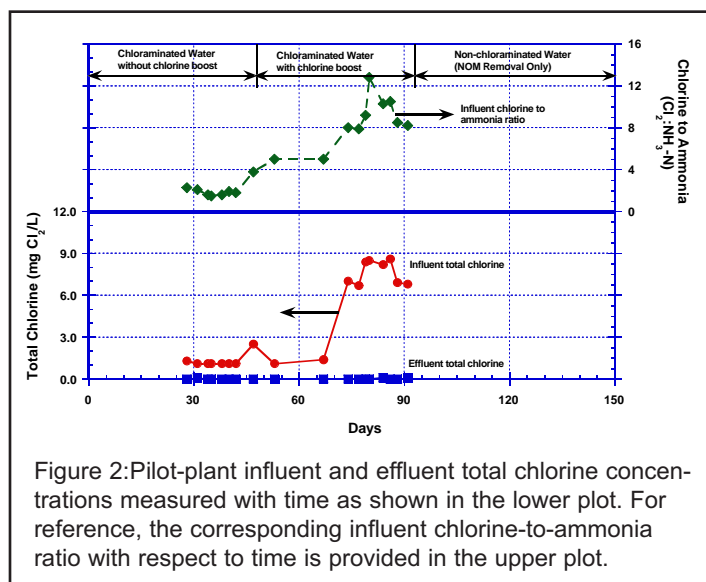


Figure 2: Pilot-plant influent and effluent total chlorine concentrations measured with time as shown in the lower plot. For reference, the corresponding influent chlorine-to-ammonia ratio with respect to time is provided in the upper plot.

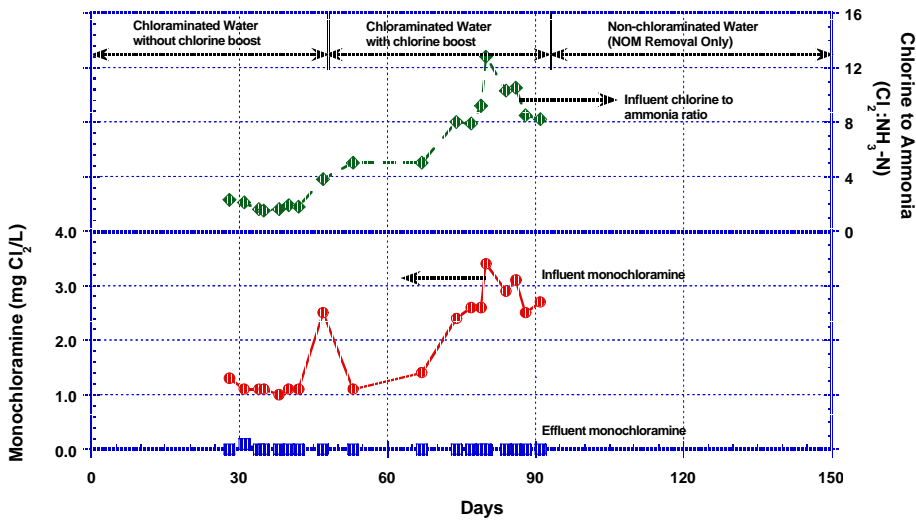


Figure 3: Pilot-plant influent and effluent monochloramine concentrations measured with time as shown in the lower plot. For reference, the corresponding influent chlorine-to-ammonia ratio with respect to time is provided in the upper plot.

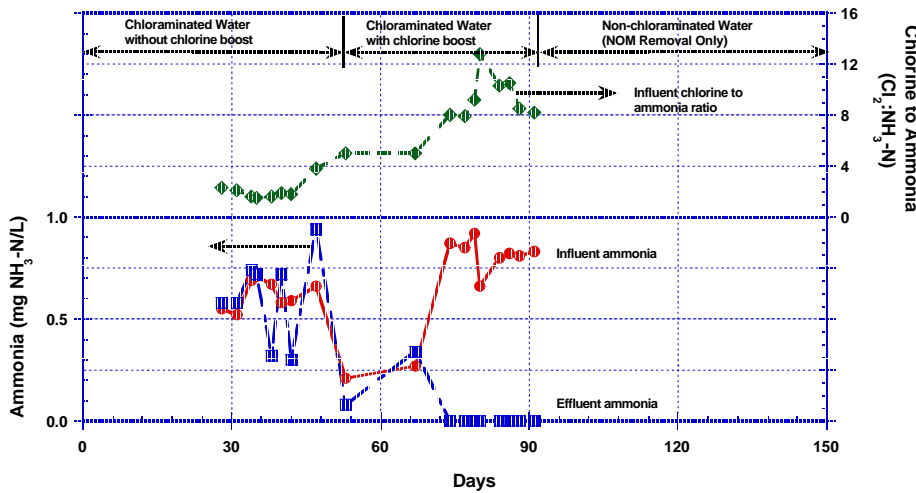


Figure 4: Pilot-plant influent and effluent ammonia concentrations measured with time as shown in the lower plot. For reference, the corresponding influent chlorine-to-ammonia ratio with respect to time is provided in the upper plot.

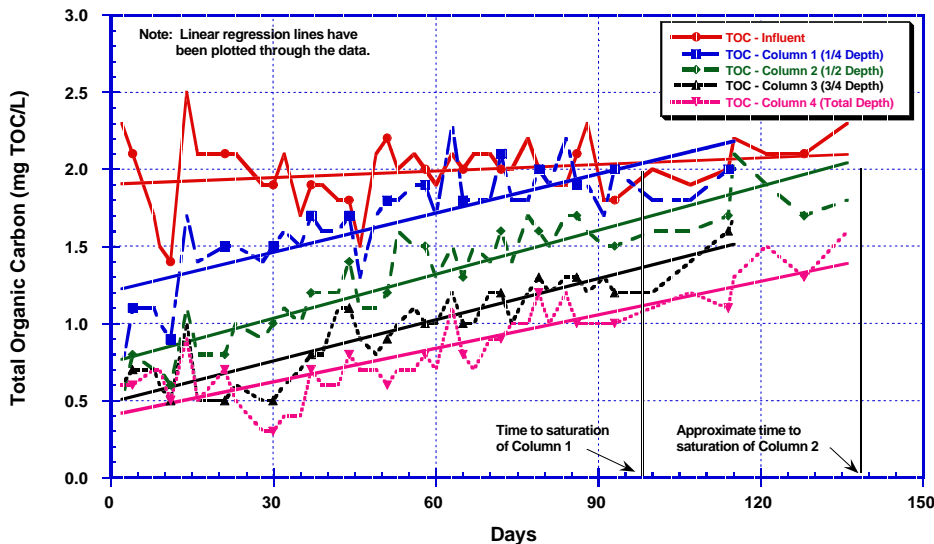


Figure 5: Pilot-plant influent and column effluent total organic carbon concentrations measured with time. A linear regression analysis was performed to identify the approximate time required to saturate each column as shown plotted.

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depth) occurring at approximately 98 days and the apparent saturation of the second column (1/2-column depth) approaching 138 days. Based on a linear regression through each set of data as shown by trend lines added to Figure 5, saturation of NOM at the 1/4-column, 1/2-column, 3/4-column, and total-column depths were estimated at 99, 143, 189, and 258 days, respectively.

Figure 6 shows that during the study period, influent THMFP_{7-Day} data exceeded current limits of 100 µg/L most of the time and exceeded Stage 1 D/DBP limits of 80 µg/L all the time. Column effluent data showed sporadic removals at the 1/4 depth, but also at times exceeded current as well as Stage I limits. Data collected at the total-column depth were more consistent and achieved both current and Stage I limits throughout the five months of testing.

Based on a linear regression analysis through the total-column depth, the expected life of the GAC bed before exceeding Stage I D/DBP limits for THMFP_{7-Day} was 252 days. This period is slightly less than the projected NOM saturation time for the total column, estimated at 258 days.

These trends were also apparent for the HAAFP data, as shown in Figure 7. For most of the data collected, influent HAAFP_{7-Day} data exceeded Stage I D/DBP limits. Column effluent data was again sporadic at the 1/4 depth, but was more consistent at the total-column depth and achieved Stage I limits throughout the five months of testing. Based on a linear regression analysis through the total column depth, the expected life of the GAC bed before exceeding Stage I D/DBP limits for HAAFP_{7-Day} was 236 days. Compared with the THMFP_{7-Day} estimate of 252 days, HAAFP_{7-Day} obviously governs the life of the GAC bed.

A second GAC pilot plant provided by Calgon Chemical Corporation (Calgon) was also set up and operated for a short period of time to evaluate chloramine removal by Centaur®, a catalytic GAC manufactured by Calgon. Centaur® was reported to remove chloramines (Spotts, 1994 and Spotts and McClure, 1995). Although chlorine was effectively removed during the one month of testing, ammonia was not. Later it was learned from Calgon that ammonia had been removed in a previous study in Pittsburgh (the only data available), but not until after eight months of operation. The removal mechanisms are unknown but are suspected to include a biological process,

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based on the eight-month acclimation period reported by Calgon.

Conclusions

GAC is an effective technology for removing chlorine and NOM. It is also effective for removing chloramines, but only because chlorine is removed. Ammonia, the other component used in forming chloramines, still remains. It is only when the chlorine concentration is increased to a chlorine-to-ammonia ratio of greater than 7.6:1 Cl₂:NH₃-N (the break-point chlorination ratio) that ammonia is effectively removed.

Although it was shown that chloramines and NOM could be effectively removed, based on the water quality from other sources Pasco County has decided to initially convert most of its system to chloramines in order to achieve compliance with the D/DBP Rule and to be compatible with water supplied by Tampa Bay Water. To limit the number of locations where chloramines will be added, the county is considering consolidating and/or closing certain groundwater supplies and wells. Until this is completed, Pasco will isolate a portion of its system to accommodate the chloraminated water that will soon be provided by Tampa Bay Water.

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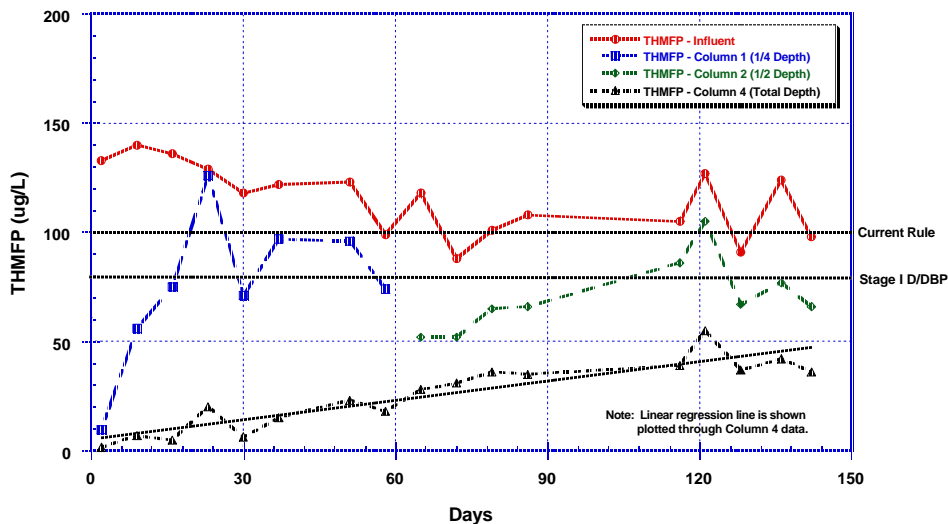


Figure 6: Pilot-plant influent and column effluent seven-day trihalomethane formation potentials (THMFP) measured with time. A linear regression analysis was performed to identify the approximate time to exceed Stage 1 D/DBP Rule from Column 4 as shown plotted.

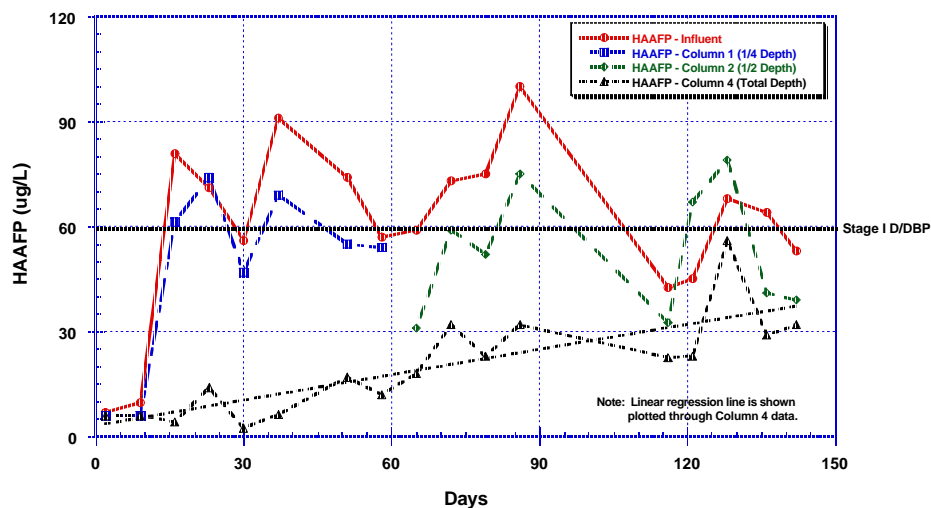


Figure 7: Pilot-plant influent and column effluent seven-day haloacetic acid formation potentials (HAAFP) measured with time. A linear regression analysis was performed to identify the approximate time to exceed Stage 1 D/DBP Rule from Column 4 as shown plotted.

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