# Stage 2 DBP Considerations: Comparison of DBP Formation and Treatment Efficiencies for Different Source Waters

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With the deadlines for Stage 2 Disinfectants and Disinfection Byproducts Rule (DBPR) compliance monitoring fast approaching, some water suppliers with no violations under the Stage I monitoring requirements are realizing that long detention times in some areas of their distribution systems may result in Stage 2 monitoring violations. To comply with the new monitoring requirements, various options are feasible, including modifications to treatment plant and distribution system operations, changing disinfectant agents and contact times, or adding an additional treatment technology for the removal of total organic carbon (TOC) and DBP precursors. When considering adding a new treatment to an existing process, it is often necessary to perform bench- or pilot-scale treatment studies to determine the effectiveness in reducing DBPs, as the measurement of TOC and DBP formation in a source water sample is not specific enough to determine which treatment technologies are the most efficient.

The results of five different DBP formation potential studies and three bench-scale treatment studies to determine the rate of DBP formation were investigated, as was the efficiency of TOC/DBP precursor removal and the resulting reduction in DBP formation. The DBP formation studies were performed on three different groundwater samples with moderate to relatively high TOC concentrations, and two different surface water samples with low to moderate levels of TOC. In comparing the differences of groundwater and surface water sources with relatively similar TOC levels, important considerations can be revealed that can help in designing cost-effective solutions for maintaining Stage 2 DBP compliance.

## Experimental Design

The bench-scale testing included a DBP formation potential study (DBPFP) for each sourcewater and a treatment technique evaluation (TTE) study for select source waters, which included laboratory testing of activated carbon and ion exchange resins to quantify TOC removal and subsequent reductions in DBP formation. The DBPFP studies involved dosing the water samples with a standard chlorine solution and drawing samples at different contact times to determine the rate of formation. The results of the DBPFP studies for three groundwater sources and two surface water sources were compared. The sources are identified as follows:

- GW#1 – Raw groundwater, no treatment, sampled from 2 different wells
- GW#2 – Lime-softened groundwater that has been recarbonated and filtered
- GW#3 – Raw groundwater, no treatment
- FSW#1 – Surface water that has been conventionally treated and filtered
- FSW#2 – Surface water that has been conventionally treated, ozonated, and filtered

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### DBPF Study

The primary goal of a DBPF study is to evaluate the DBP formation potential at different chlorine contact periods to generate a relationship of DBP formation with contact time. The procedure used for the DBPF study was modeled after the simulated distribution system (SDS) procedure in accordance with Standard Method Procedure 5710-C, simulated distribution system trihalomethanes (SDS-THM). In this procedure, several aliquots of sample are poured into amber glass bottles, and all bottles are dosed with a predetermined chlorine dose. Samples are taken from the amber bottles at denoted contact times, which are immediately dechlorinated and sent to commercial laboratories for DBP analysis. In these studies, attempts are made to preserve field conditions, and the chlorine dosage is intended to simulate the maximum free chlorine residual that would be expected in the distribution system, therefore maximizing the DBP formation potential that could potentially occur at a Stage 2

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DBP monitoring site. The results of the study quantify the formation of DBPs under the stated conditions so that they can be compared to the U.S. Environmental Protection Agency (EPA) Maximum Contaminant Levels (MCLs) for THMs and haloacetic acids (HAAs). It should be noted that contaminants such as ammonia and iron that can affect chlorine oxidation were not removed prior to chlorination. Water samples containing sulfide were unable to be preserved without altering the samples, and some of the sulfide was likely to have volatilized during collection and transport.

### Activated Carbon

Activated carbon has been shown in numerous pilot studies and full-scale operation to remove a wide variety of natural organic matter (assumed to be the primary component of TOC in natural waters) by adsorption. Adsorption is a process by which molecules of a dissolved compound collect on, and adhere to, the surface of an adsorbent solid. Activated carbon adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid. The adsorption capacity of granular activated carbon (GAC) to adsorb a specific organic compound is related to the molecular surface attraction, the total surface area available per unit mass of carbon, and the concentration of the specific organic contaminant in the water stream.

Prior to performing extended pilot-scale studies, it is often helpful to initially examine the effectiveness of carbon treatment through isotherm studies. Isotherm tests were conducted on the samples in fully mixed reactors to determine the maximum amount of TOC/DBP precursors that could be removed from the water samples. Initially, a carbon contact time study was performed to determine the amount of time required for the carbon to reach pseudo-equilibrium concentration with the TOC in solution. The initial tests consisted of adding a small carbon dose to the water samples in a continuously stirred reactor. Samples were drawn from the reactor and filtered to analyze TOC and UV-254 absorbance at various carbon contact times. Samples were drawn until the UV-254 absorbance was nearly constant for three consecutive samples. This was interpreted to be a pseudo-equilibrium organics concentration and was determined to be between 60 and 90 minutes for each water sample.

The bench-scale study incorporated adding powdered activated carbon (PAC) to GW#1 and adding PAC to both FSW samples. Two liters of sample were poured into jar testing vessels and various PAC dosages were added based on the measured TOC concentration. The jar testing machine was programmed to perform a rapid mix phase for a duration that was determined to result in a pseudo-equilibrium of organics for all samples. After the rapid mix phase, the samples were filtered using a standard vacuum filter apparatus with a nominal 0.5 micron glass fiber filter. The samples were then analyzed for water quality, and the remaining sample volumes were chlorinated for and analyzed for DBP formation.

Table 1

| Parameter | GW#1 (Untreated Well #1) | GW#1 (Untreated Well #2) | GW#2 (Lime-Softened/ Recarbonated) | GW#3 (Untreated Well) | FSW#1 (Conventional) | FSW#2 (Conventional with Ozone) |
|---|---|---|---|---|---|---|
| pH | 7.9 | 7.9 | 8.6 | 7.8 | 7.1 | 9.1 |
| Alkalinity (mg/L $CaCO_3$) | 220 | 204 | 48 | 164 | 68 | 15 |
| App. Color (CPU) | 13 | 13 | 5 | 12 | 3 | 2 |
| TOC (mg/L) | 3.7 | 4.3 | 7.9 | 2.5 | 1.5 | 3.8 |
| UV-254 (cm-1) | 0.148 | 0.162 | 0.27 | .103 | 0.03 | 0.12 |
| Conductivity (uS) | 600 | 584 | * | 362 | 210 | 224 mg/L(TDS) |

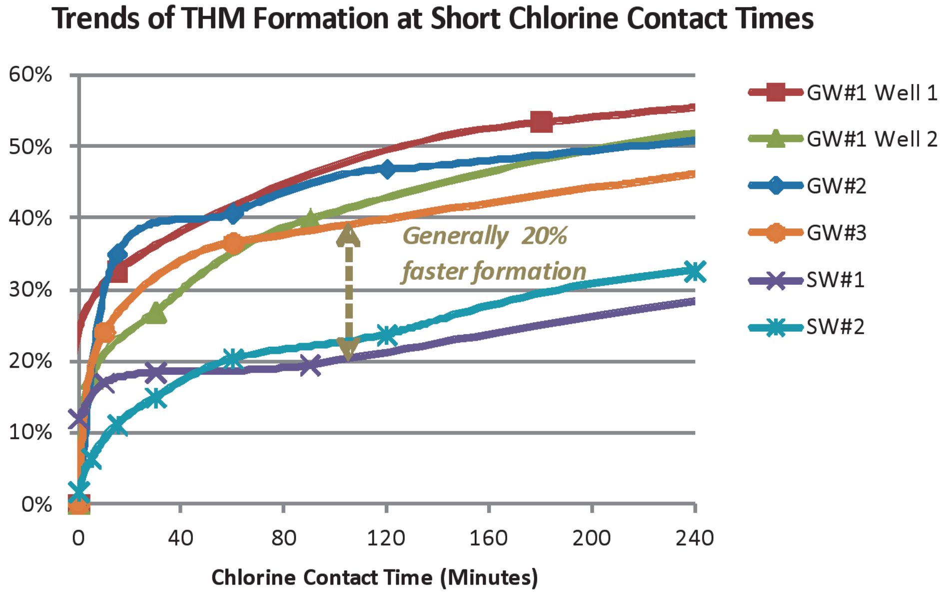

Figure 1

### Ion Exchange

Any TOC in water is generally considered to be composed of fulvic and humic acids, which are negatively charged organic molecules. Anionic exchange resins have been developed with specific affinity for these organic molecules and can be used on raw or treated waters to remove TOC and thereby reduce the DBP formation potential of the treated water. Bench-scale evaluation of this treatment technique was performed in mixed reactors and in small bench-scale fixed-bed columns on GW#1 and both surface water samples.

The mixed reactor study involved adding resin to a continuously stirred reactor for a predetermined time. After the mixing, the resin is allowed to settle and the treated sample is filtered and analyzed for water quality. The remaining sample volumes are then chlorinated and analyzed for DBP formations. Bench-scale columns generally come prepackaged from the manufacturer and are flushed out prior to data collection. After flushing, the column is monitored for organic removal until a noticeable breakthrough occurs or the sample is exhausted. The results from both of these studies are analyzed to determine the maximum potential organics removal that can be achieved to determine if the treatment is effective enough to warrant further pilot-scale studies.

## Results

The raw water quality for the three raw groundwater sources and the two filtered surface water sources are summarized in Table 1 (* indicates that the value was not measured):

It is noted that the GW#1 and the FSW#2 have similar concentrations of TOC, GW#3 has a TOC concentration between the FSW#1 and FSW#2, GW#2 has the highest TOC concentration, and FSW#1 has the lowest TOC concentration. Since the water quality data has no distinct trend with respect to the type of source water, it is reasonable to look for trends in the way DBPs are formed and the way DBP precursors are removed. The main similarity for all samples is that the TOC is primarily dissolved, as over 90 percent of the organic carbon was maintained in each sample after passing through a 0.45 micron filter. The UV absorbance also exhibits a positive correlation with the TOC concentrations and was used as a surrogate measurement of TOC, where instant TOC approximation was warranted. Other inorganic water quality not presented is not suspected to significantly impact DBP formation and has been omitted.

**DBPF Results**

After conducting a DBPF study on all six water samples, the DBP formations at various chlorine contact times were assembled into graphs. The primary observation from the DBPF studies was that the THMs were formed at a faster rate in the GW samples than in the filtered FSW samples. Figure 1 displays the formation of THMs as a percentage of the ultimate THM formation (THM ultimate is THMs formed after at least three days of contact time).

As shown in Figure 1, the THMs in the groundwater samples showed an initial rapid formation period, while the surface water samples showed a more gradual formation over the first few hours. The trend appears to show a difference of 20 percent faster formation in the groundwater, which remains fairly consistent up to chlorine contact times of 24 hours. At a 24-hour contact time, the groundwater samples have generally formed 80 percent of the ultimate formation potential, in contrast to the surface water samples, which have formed generally 60 percent of the ultimate formation potential. This trend was not as apparent in the HAA5 formations; however, data generated from SW #1 showed an unusual formation curve that is likely due to experimental or laboratory error. The HAA5 formations are displayed in Figure 2.

The difference in formation rates between the groundwater and surface water samples is observed for chlorine contact times up to 24 hours, of which, at a 24-hour chlorine contact time, the groundwater samples have generally formed over 80 percent of the ultimate formation potential, in contrast to the surface water samples, which have generally formed approximately 60 percent of the ultimate formation potential.

It is also observed from the graph, that with the exception of HAAs in FSW#2, the initial DBP formation rates are similar for the three groundwater sources, and surface water source THMs formations are also similar, even though the concentrations of TOC are very different for each sample in both source water groups. The GW#2

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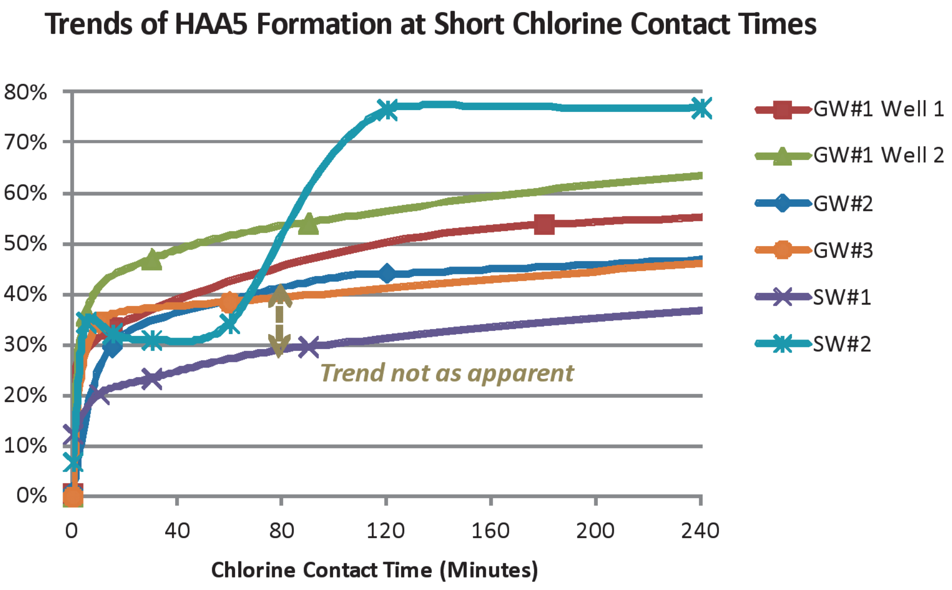

Figure 2

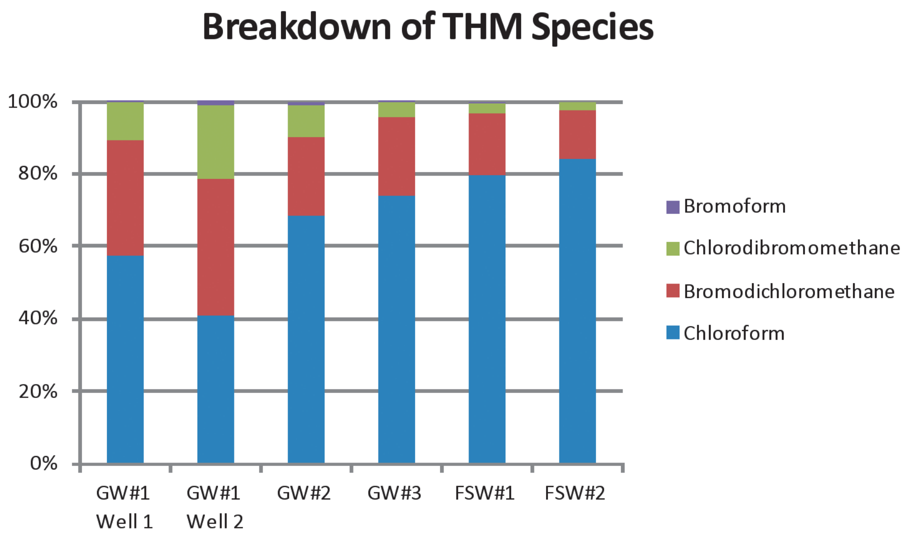

Figure 3

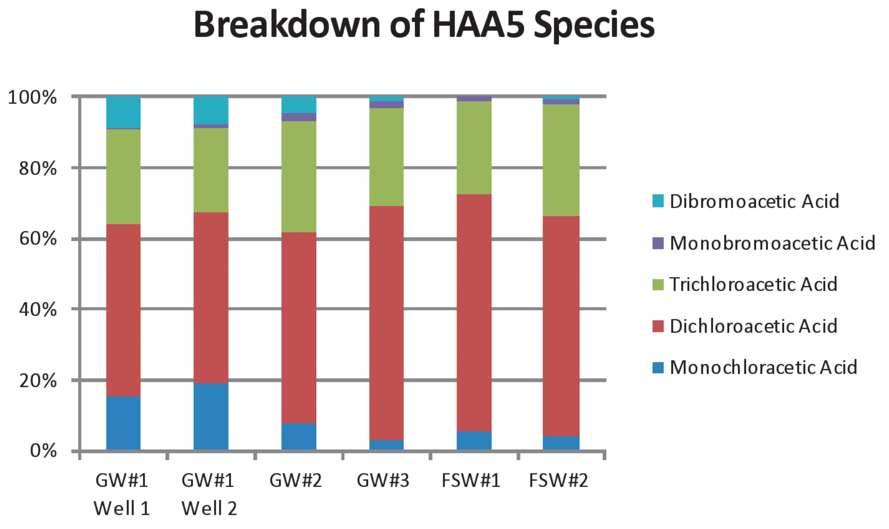

Figure 4

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TOC is almost double the GW#1 TOC, and over triple the GW#3 TOC, but the formation rates are very similar, of which GW#2 has at least twice to three times the DBP formation potential of the other samples. The THM formations in the surface water also had similar formation rates, but again, the FSW#2 formation potential was significantly higher than FSW#1, which is in correlation to the increased TOC concentration.

When comparing the GW#1 and FSW#2 DBP formations, which had similar TOC concentrations, the DBPs formed in the FSW#2 are considerably higher than the DBPs formed in GW#1, but the GW#1 DBPs formed at a faster rate.

The initial trend of increased DBP formation rates in groundwater versus surface water led to an investigation of the individual species of DBPs for each source water. For each sample, the 24-hour THM and HAA formations were compiled, and the speciation of THMs and HAA5s for each sample are shown in Figures 3 and 4, respectively. The graph generally shows that some of the groundwater samples had a larger percentage of brominated forms than the surface water samples, with the exception of the GW#3 THM speciations, which appear to be very similar to the surface water samples. Overall, the HAA5 speciation showed a general lack of brominated formations; however, a small percentage of brominated HAA5s were observed in GW#1 and GW#2.

None of the measured typical water quality parameters that are generally accepted to have an influence on DBP formation (pH, chlorine residual, temperature, bromine) show a positive correlation to the vast difference in THM formation rates for groundwater and surface water sources as shown in Figure 1. Combined, the data seem to support that the different speciations of organic matter that comprise TOC in groundwater and surface water sources are generally different but relatively similar for each type of source water, since the treatment employed at each facility is different. The most important trend noticed in the analysis is that the groundwater TOC appears to be more "ready" to form DBPs (particularly THMs) immediately after chlorination.

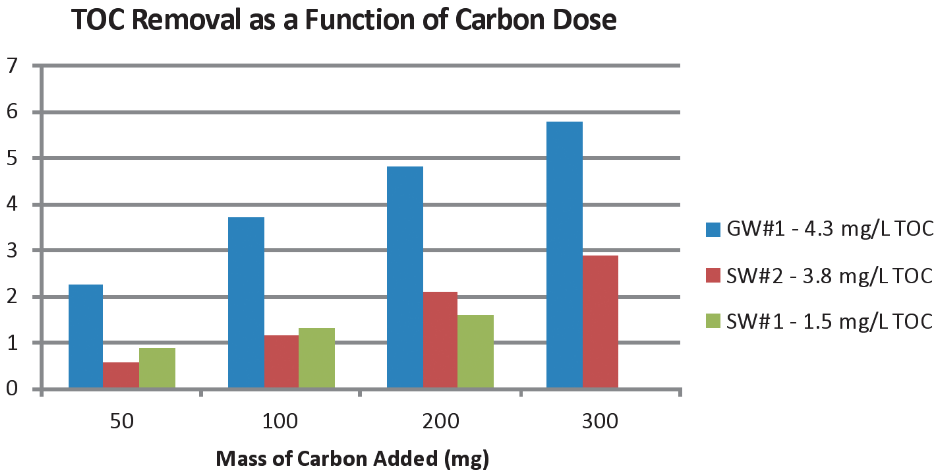

Figure 5

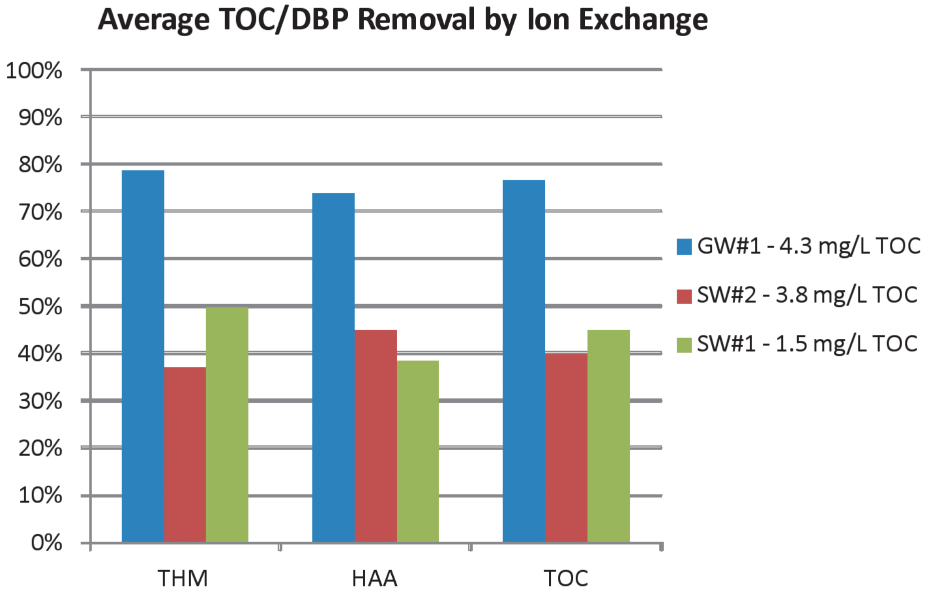

Figure 6

### Activated Carbon Results

The results of the carbon isotherm studies were also investigated to see if trends emerged between the two different source waters. Common practice is to compile the organics removal data and the carbon dosages to fit well-known isotherm expressions to determine which has the best fit. However, the results can also be simplified as mass TOC removal per unit of carbon dosed to gauge the relative efficiency and carbon loading capacity. Figure 5 displays the mass of TOC removed from each water sample at different carbon dosages. The results show that the removal of organics from the groundwater sample was significantly more efficient than the organics removal in the surface water samples. This reduction in carbon adsorption capacity is theorized to be because of the removal of highly adsorbable organics by the coagulation/flocculation/sedimentation process. This is further verified by the reduction in the conventional treatment process TOC removal efficiency, as increasing carbon is dosed prior to coagulant addition. In addition, given that the vast majority of the TOC in groundwater is dissolved, the possibility of higher removal efficiencies due to higher molecular weight organics is unlikely. The TOC removal by carbon in FSW#1 samples achieved decent efficiency at low carbon dosages, but quickly became less efficient as the initial concentration of TOC in the FSW#1 was relatively low, which exhibited decreasing rate of efficiency at higher carbon dosages. The carbon was less efficient in FSW#2, however, the diminishing returns effect was not observed until carbon dosages greater than 300 mg were added.

### Ion Exchange Results

Similar to the activated carbon studies, the ion exchange removal efficiencies were also investigated. The results for the fixed-bed column and the mixed reactor studies were relatively similar to the activated carbon studies, in that the TOC removal efficiency was significantly greater in the groundwater than in the surface water samples. Figure 6 displays these trends, which show high TOC removal efficiencies and a significant correlation to resulting DBP formations after chlorination. The general trends for the fixed-bed and reactor studies were very similar, which allowed the averaging of the results while maintaining the same general trends. Since the removal of negatively charged organics is likely occurring in the coagulation process, the ion exchange resin efficiency is expectedly reduced from the conventional treatment process.

## Summary and Considerations

The observations from the DBPF studies appear to support that THM, and possibly HAA5 formations, are more rapid in groundwaters than in filtered surface waters. These trends in differing formation rates between groundwater and surface water samples were significant for up to 24 hours of chlorine contact time. Although the reason for this trend is not immediately clear from the water quality, the data seem to support that the different speciations of organic matter that comprise TOC in groundwater and surface water sources are generally different, but are relatively similar for each type of sourcewater. The main practical implication from this study could be that the Stage 2 DBP guidelines could be more impactful to surface water plants than to groundwater treatment plants. If surface water DBPs tend to form at a slower rate, then the inclusion of maximum hydraulic residence times (HRT) in distribution sampling could theoretically have a bigger impact on the locational running averages used in calculating compliance with the Stage 2 DBP rule. Consequently, groundwater sources could theoretically see more rapid formation of DBPs, which are more likely to be observed at the average HRT sampling locations already established under the Stage I rule.

The observations from the bench-scale treatment studies appear to support that the TOC removal and subsequent reduction in DBP formation, of common treatment technologies, is not as efficient on conventionally treated filtered surface water as it is on groundwater. This is theorized to be due to the removal of negatively charged TOC in the coagulation process and the removal of readily adsorbable TOC in the flocculation/sedimentation process, removing some of the organics that would be removed by carbon and ion exchange at high efficiencies. As with any treatment process operating in series, the second-stage treatment will usually see less mass of contaminant removal and decreased efficiency than the first stage treatment.

The significant efficiency difference in precursor removal in this study for common DBP treatment between conventionally treated surface water and groundwater sources may lead to a substantial increase in capital or operational cost per unit of water treated. This may motivate water suppliers using surface water sources into looking at different DBP management alternatives for existing conventional treatment facilities that cannot provide the level of organics removal needed for Stage 2 compliance. ◆