Total Organic Carbon:
A Reliable Indicator of TTHM and HAA5 Formation?

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Abstract

In 2002, the Disinfectants/Disinfection Byproducts (D/DBP) Rule affected surface water treatment plants serving at least 10,000 people. The rule required staff at conventional treatment plants to begin monitoring for total organic carbon (TOC). Staff at smaller plants also started monitoring for disinfection byproducts, TOC and other parameters in the first quarter of 2004. Additionally, the D/DBP Rule contains provisions for TOC removal through the conventional treatment processes. Because these monitoring and removal requirements are a vital part of regulations affecting numerous water suppliers across the nation, TOC is now used as the primary surrogate for the determination of precursors to disinfection byproduct formation. These same water suppliers must comply with maximum contaminant levels for total trihalomethanes (TTHM) and haloacetic acids (HAA5), both of which are implicated as having long-term, adverse health consequences. Up until now, few large-scale studies have analyzed the data collected during the first two years of the D/DBP Rule, and fewer still have compared treatment plant TOC data to TTHM and HAA5 data collected from the distribution system.

In Pennsylvania, compliance data for TOC, TTHM and HAA5 is available from 73 surface water systems using a total of 85 conventional filtration plants, covering the first two years of monitoring under the D/DBP Rule. The data was gathered from a regulatory reporting database housed at the Pennsylvania Department of Environmental Protection. This compliance

data was then compiled and analyzed to examine the relationships between TOC concentrations at the plants and TTHM/HAA5 formation in the distribution system. In addition, an analysis was completed on 8 plants with the highest and lowest finished water TOC concentrations out of the 73 systems in Pennsylvania. Finally, three plants in southeastern Pennsylvania were examined more closely to study the effects of enhanced coagulation on the levels of TTHM and HAA5 in the finished water.

When comparing data from the 73 water systems, the authors observed no apparent correlation between either raw or finished water TOC and TTHM concentrations over much of the range of TOC values examined in this study. In addition, they found no apparent correlation between TOC and HAA5 over the entire range of TOC values. Examining data from the 8 plants with the highest and lowest average TOC concentrations in the finished water showed no group relationship with TTHM or HAA5 levels in the distribution system. Of the three treatment plants studied in detail, all were able to improve TOC removal through the plant as a result of enhanced coagulation. Enhanced coagulation processes reduced TTHM levels but not HAA5 levels. Overall, this study found no universal relationship that can be used to predict disinfection byproduct formation in the distribution system based on TOC values in the source water or finished water. While such a relationship may be possible at an individual water system, the relationship would have to be established empirically on a system-by-system basis.

Introduction

The recently enacted Stage 1 Disinfectants/Disinfection Byproducts (D/DBP) Rule and the proposed Stage 2 D/DBP regulations have raised awareness about the potential health effects of disinfection byproducts in drinking water. Likewise, total organic carbon (TOC), used to measure precursors to disinfection byproduct formation, is now a major part of regulations affecting both large and small water suppliers across the United States.

Currently, the D/DBP Rule requires all filtered surface water suppliers to collect samples for total trihalomethane[1] (TTHM) and haloacetic acid[2] (HAA5) analysis. The surface suppliers serving at least 10,000 people—the group analyzed in this study—must collect quarterly TTHM and HAA5 samples at three locations that represent the "average" residence time and at one location that represents the maximum residence time in the distribution system. The U.S. Environmental Protection Agency required this sampling regimen under the D/DBP Rule because long-term exposure to disinfection byproducts could cause cancer. Also, both long- and short-term health effects are currently under scrutiny. Some studies suggest that byproducts such as TTHMs may be associated with spontaneous abortions in humans. TTHMs may also negatively affect reproduction and fetal development in laboratory animals. Recent studies seem to indicate that the volatile nature of TTHM provides greatest exposure through inhalation and dermal absorption (during hot showers) rather than through ingestion. This exposure depends

[1] For the purposes of this report, the total trihalomethanes (TTHM) of interest includes: Chloroform, Bromodichloromethane, Bromoform, and Dibromochloromethane.

[2] For the purposes of this report, the five haloacetic acids (HAA5) of interest include: Dibromoacetic Acid, Dichloroacetic Acid, Monobromoacetic Acid, Monochloroacetic Acid, and Trichloroacetic Acid.

on the concentrations in the water and air as well as the amount of time a person spends in the bathroom after showering. In the future, additional research will improve our understanding of disinfection byproduct exposure and any linkages to adverse health effects.

Another part of the D/DBP Rule involves monitoring for indicators of byproduct formation. Natural organic matter is common in most streams, rivers and lakes, and when combined with chlorine, can form compounds such as TTHM and HAA5. This organic matter is often a precursor to byproduct formation. Even properly designed and well-operated surface water filtration plants that treat water for human consumption are not able to remove all of the organic matter from the source water. As a result, the chlorine that is used to treat for disease-causing microorganisms reacts with the remaining organic matter and forms disinfection byproducts in the filtration plant and throughout the distribution system. Under the D/DBP Rule, the precursors to byproduct formation are difficult and expensive to measure, so TOC is one of two parameters used as a substitute and indicator of precursors (specific ultraviolet absorbance is the other, and it indicates organic matter reactivity). TOC, then, is considered a precursor to disinfection byproducts.

The D/DBP Rule requires the collection of TOC samples of the source water and the finished water at treatment plants using conventional filtration technologies. At these conventional plants, sufficient TOC removal must occur between the raw water sampling point and the finished water monitoring point. The finished water monitoring point is typically located at the combined filter effluent; the source water must be sampled prior to any treatment. The required removal of TOC ranges from a 15 percent reduction to as high as a 50 percent reduction. These percentages depend on the source water TOC and alkalinity levels at the time of sampling. Table 1, also called the "3-by-3 matrix," shows the acceptable TOC removal percentages for these parameters. Under the routine monitoring requirements, the percentage of TOC removal must be calculated monthly. Because source water conditions will change throughout the year, the removal requirements will likely change from month to month.

Source Water TOC (mg/L)	**Source Water Alkalinity (mg/L as $CaCO_3$)**		
	0 to 60	**> 60 to 120**	**> 120**
> 2.0 to 4.0	35.0%	25.0%	15.0%
> 4.0 to 8.0	45.0%	35.0%	25.0%
> 8.0	50.0%	40.0%	30.0%

Table 1. *The 3-by-3 matrix shows required TOC removal percentages depending on source water parameters.*

To use the table, consider this scenario: during July 2004, a conventional filter plant obtains raw water samples from a reservoir with a TOC level of 4.2 mg/L and an alkalinity concentration of 62 mg/L. To determine how much TOC must be removed from the raw water, find the source water TOC level in the ranges on the left and the alkalinity level at the top; the intersection of these two points shows that at least a 35.0 percent removal of raw water TOC must occur. In other words, the finished water TOC sample must be 35.0 percent lower than the raw water TOC sample at this treatment plant in July 2004.

For maximum public health protection, the regulations and research efforts have primarily focused on the reactions between natural organic matter and chemical disinfectants. However, the authors wish to stress that water suppliers should consider enhancing existing treatment for the removal of organic matter for several other reasons as well. These benefits include reduced bacterial regrowth in the distribution system, improved taste and odor, decreased disinfectant demand, residual disinfectant stability, and reduced levels of unknown or unregulated disinfection byproducts.

Compliance with the D/DBP Rule weighs heavily on the 3-by-3 matrix. However, is the *removal* efficiency more important than the actual TOC concentrations in the finished water? In compiling the data for this study, the authors closely examined the ranges of raw and finished water TOC, and then correlated this data with TTHM and HAA5 concentrations in the distribution system. Did any of these parameters show a significant correlation? Were other predictors of byproduct formation determined? To answer these questions, the authors examined the compliance data available from 73 surface water systems using a total of 85 conventional surface water treatment plants. In addition, they also conducted a detailed investigation at three of the treatment plants to examine TOC removal and disinfection byproduct formation at the entry point to the distribution system.

Materials and Methods

Information on available water quality data was retrieved from compliance data housed in the Pennsylvania Drinking Water Information System (PADWIS) database. The data identified the public water system's name, 7-digit identification number, plant ID, population served, treatment facilities, disinfectant used, and concentrations of TOC, TTHM and HAA5. The data encompassed 85 conventional filtration plants representing 73 water systems that use surface water sources in Pennsylvania (Figure 1). All of these systems serve at least 10,000 people. Similar filtration and disinfectant systems were compared to minimize variability.

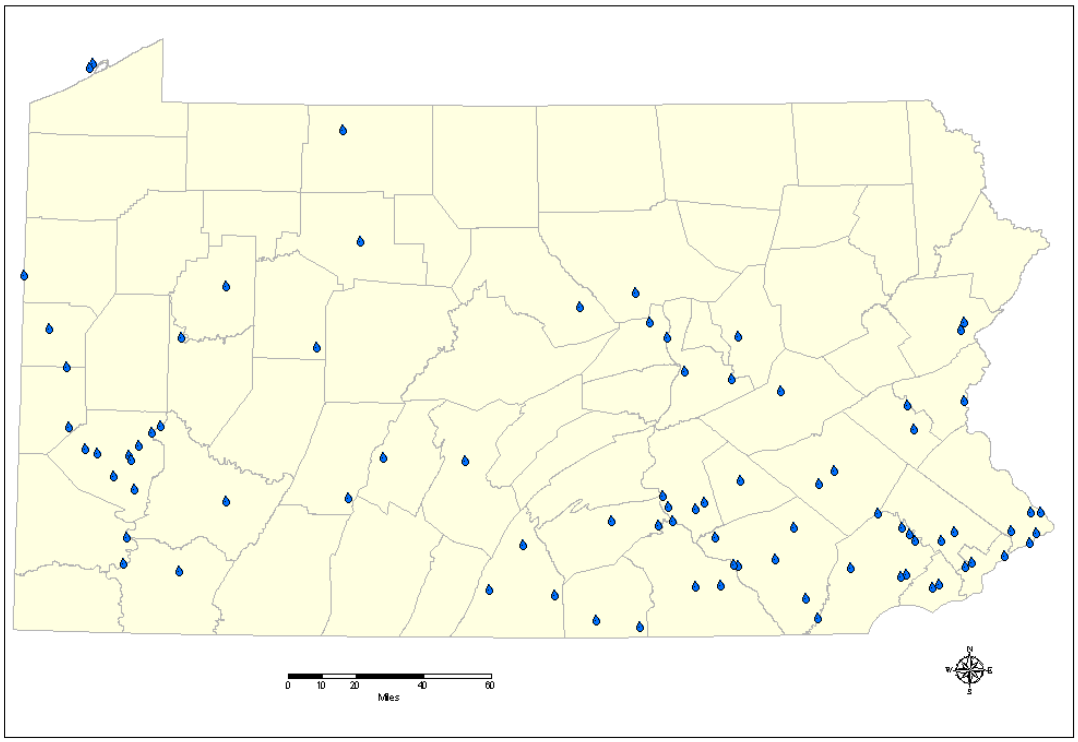


Figure 1. *Locations of conventional surface water treatment plants where data was collected.*

The study encompassed a two-year period from January 1, 2002, to December 31, 2003. This criterion was established because monitoring for large surface water systems serving a population of at least 10,000 people began in January 2002. TOC, TTHM, and HAA5 results were submitted by state-certified laboratories and entered into PADWIS. The TTHM and HAA5 data in this part of the study represents the average of the four D/DBP Rule sample locations in the distribution system. The sample collection and analytical methods followed those prescribed in the federal D/DBP Rule. The study's approach included two perspectives: one examined a global view of the 73 water systems while the other looked at approximately 10 percent (8 plants) in greater detail.

As mentioned in the introduction of this paper, the D/DBP Rule requires water suppliers to collect TOC, TTHM and HAA5 samples at various locations and frequencies. The complexity of the regulations, and the fact that suppliers were faced with new contaminant types and collection methods in 2002, resulted in missing TOC results for some of the treatment plants. Also, TTHM or HAA5 results were unavailable at the maximum residence locations for a few of the facilities. Consequently, the authors encountered some difficulties in gathering a complete data set for comparison purposes.

Summaries of the data are presented in graphical format for this report. They describe the correlation coefficient (r) and coefficient of variation (R^2) between the TOC values for the raw or plant (finished water) samples, and the TTHM or HAA5 values for the distribution

samples. Box-and-whisker plots[3] and line graphs are used to summarize the relationship between TOC and the formation of disinfection byproducts.

Simple regression analysis was computed using Microsoft Excel® to determine whether a linear correlation existed between the TOC values for the raw or plant samples and the TTHM or HAA5 values for the distribution samples. The number of samples analyzed varied from 2 to 253 per water system; therefore, the mean value was calculated for each system and used in the regression analysis. The authors caution that the highly variable number of samples from each water system may have skewed some of the results. Scatter plots were also graphed to visually describe the nature of the relationship between the independent variable (TOC) and the dependent variable (TTHM or HAA5). The regression line and R^2were also depicted on the scatter plots.

The global view provided a general comparison between the presence of TOC and the formation of TTHM and HAA5. In addition, 10 percent (8) of the facilities were selected for a more detailed analysis. The facilities chosen represented both extremes of the finished water TOC range in 2003 i.e., the 4 highest and 4 lowest mean TOC values in Pennsylvania. The disinfection byproduct formation in the distribution system was evaluated relative to the concentration of TOC in the finished water to determine if any relationships existed. The authors speculated that if any correlations were to occur between TOC and byproduct concentrations, such relationships would be evident in either or both of these extremes.

Finally, the authors more closely examined three plants in southeastern Pennsylvania to study the effects of enhanced coagulation—and the new TOC removal goals—on the levels of TTHM and HAA5 in the finished water. Plants A, B, and C are large conventional surface water plants. The treatment schemes consist of pre-sedimentation; ferric chloride as a primary coagulant; sedimentation; filtration with sand- and dual-media filters; potassium permanganate addition for seasonal taste, odor and algae control; pH control with hydrated lime; and sodium hydroxide treatment at Plants A and B and sulfuric acid addition at Plant C. For primary disinfection, gaseous chlorine is used at Plants A and C and sodium hypochlorite is used at Plant B. All three treatment plants rely on chloramines for residual disinfection in the distribution system.

Each of the plants has an extensive database of disinfection byproducts data. In addition to the four quarterly samples in the distribution system for compliance with the D/DBP Rule, weekly TTHM and HAA5 monitoring is conducted at the entry point of each plant. TOC/alkalinity levels of the source water and TOC of the finished water are also monitored weekly at each plant.

An in-depth study of these three treatment plants examined a four-year period from January 2000 through December 2003. *At these plants, this part of the study focused on the source water data and the finished water (entry point) data rather than distribution system data*.

[3] A box-and-whisker display is a graphic representation of five key data points: maximum value, minimum value, median, 25th percentile, and 75th percentile. The upper line represents the top 25 percent of the data. The lower line represents the lower 25 percent of the data. The box represents the middle 50 percent of the data (the data that lies between the 25th and 75th percentile). The line in the box represents the median value.

The authors used a database of weekly TOC data and the disinfection byproduct data. In an effort to highlight predicted benefits of improved TOC removals on disinfection byproduct formation, the byproducts were analyzed in both the pre-enhanced coagulation (pre-EC) mode and the post-enhanced coagulation (post-EC) mode. After the initial bench-, pilot-, and full-scale trials, enhanced coagulation went into effect in June 2001 at Plant A, in October 2001 at Plant B, and in March 2003 at Plant C. The pre-EC and post-EC data were thus analyzed separately based on these dates. Overall, the authors examined the pre-EC and post-EC scenarios at these three plants for the following effects on TTHM and HAA5 levels in the finished water:

- Source water TOC and temperature;
- Finished water TOC; and
- TOC removal.

Results and Discussion

Analysis of 73 Water Systems

Figure 2 shows a summary of the raw water TOC concentrations for the 73 water systems for the years 2002 and 2003. The box-and-whisker plots show the median, minimum, maximum and one standard deviation values. The data used to prepare this graph represent the average of all samples collected at each water system during a particular calendar year. The median of these averages was 2.4 mg/L for 2002 and 2.1 mg/L for 2003.

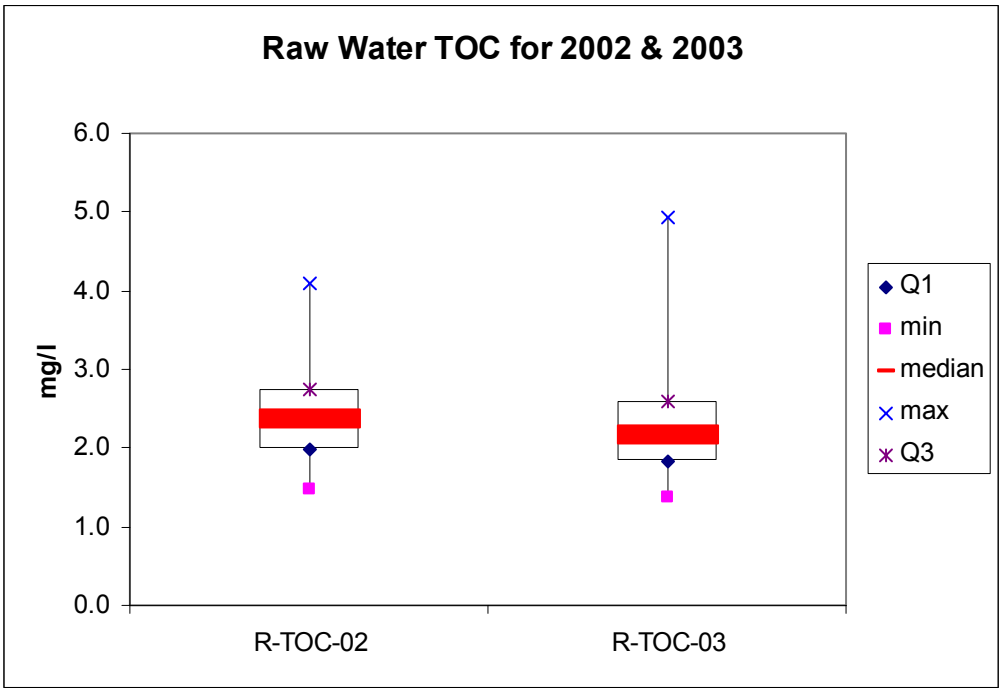


Figure 2. *Box-and-whisker summaries of total organic carbon in the raw water at 73 filtered surface water systems for years 2002 and 2003.*

Figure 3 shows a summary of the finished water TOC concentrations for the 73 systems for 2002 and 2003. The median of these averages was 1.4 mg/L for 2002 and 1.3 mg/L for 2003. A comparison of the raw and finished water median values indicates that the TOC removal was 42 percent for 2002 and 38 percent for 2003.

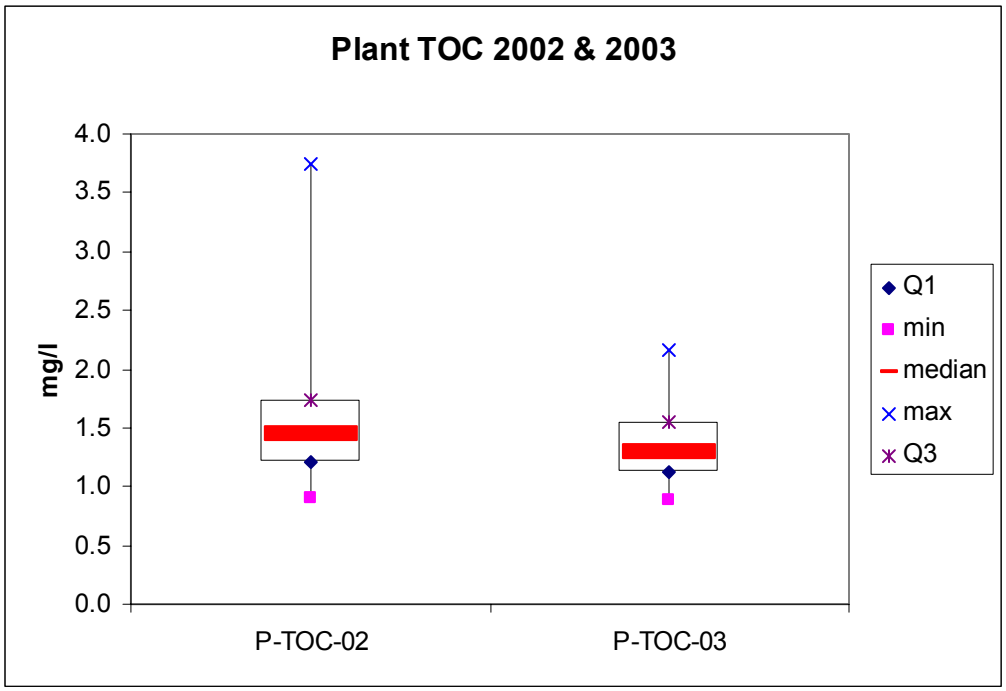


Figure 3. *Box-and-whisker summaries of total organic carbon in the plant (finished water) at 73 filtered surface water systems for years 2002 and 2003.*

Figure 4 reveals a summary of disinfection byproducts in the distribution system for 2002 and 2003. The median TTHM values were 0.038 mg/L and 0.033 mg/L for 2002 and 2003, respectively, while the median HAA5 values were 0.021 mg/L and 0.033 mg/L. These values were obviously well below the compliance values of 0.080 mg/L for TTHM and 0.060 mg/L for HAA5. A review of the data from the individual water systems showed that all of the systems met the TTHM running annual average limit for 2002 and 2003. All of the systems met the limit during 2003 if compliance were based on a calendar year average. The individual system data also shows that 39 systems out of 73 had at least one water sample in excess of 0.080 mg/L in 2002, and in 2003, 28 systems fell into this same category.

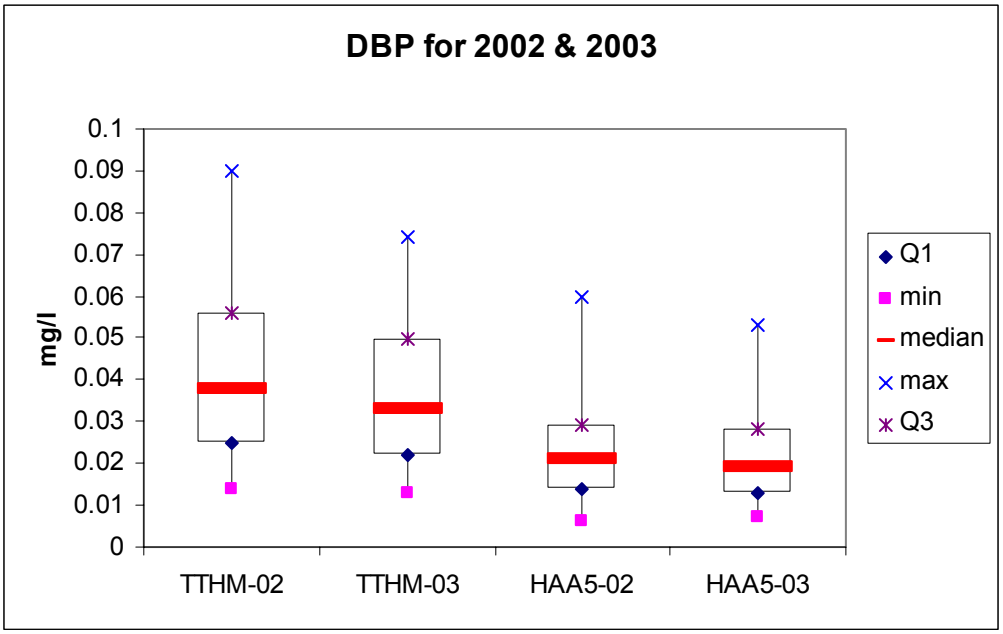
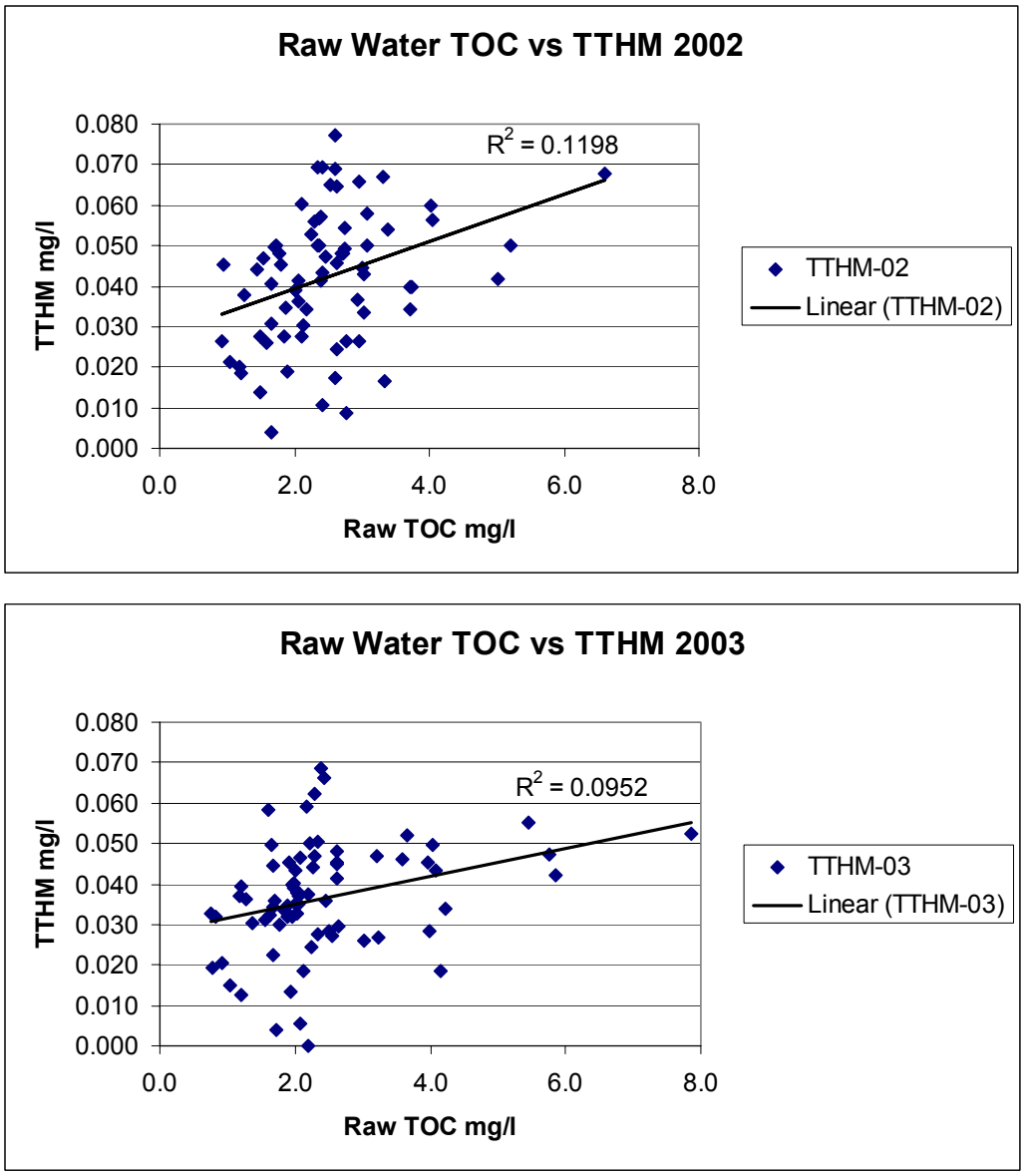


Figure 4. *Box-and-whisker summaries of disinfection byproducts (DBP) in the distribution system for years 2002 and 2003.*

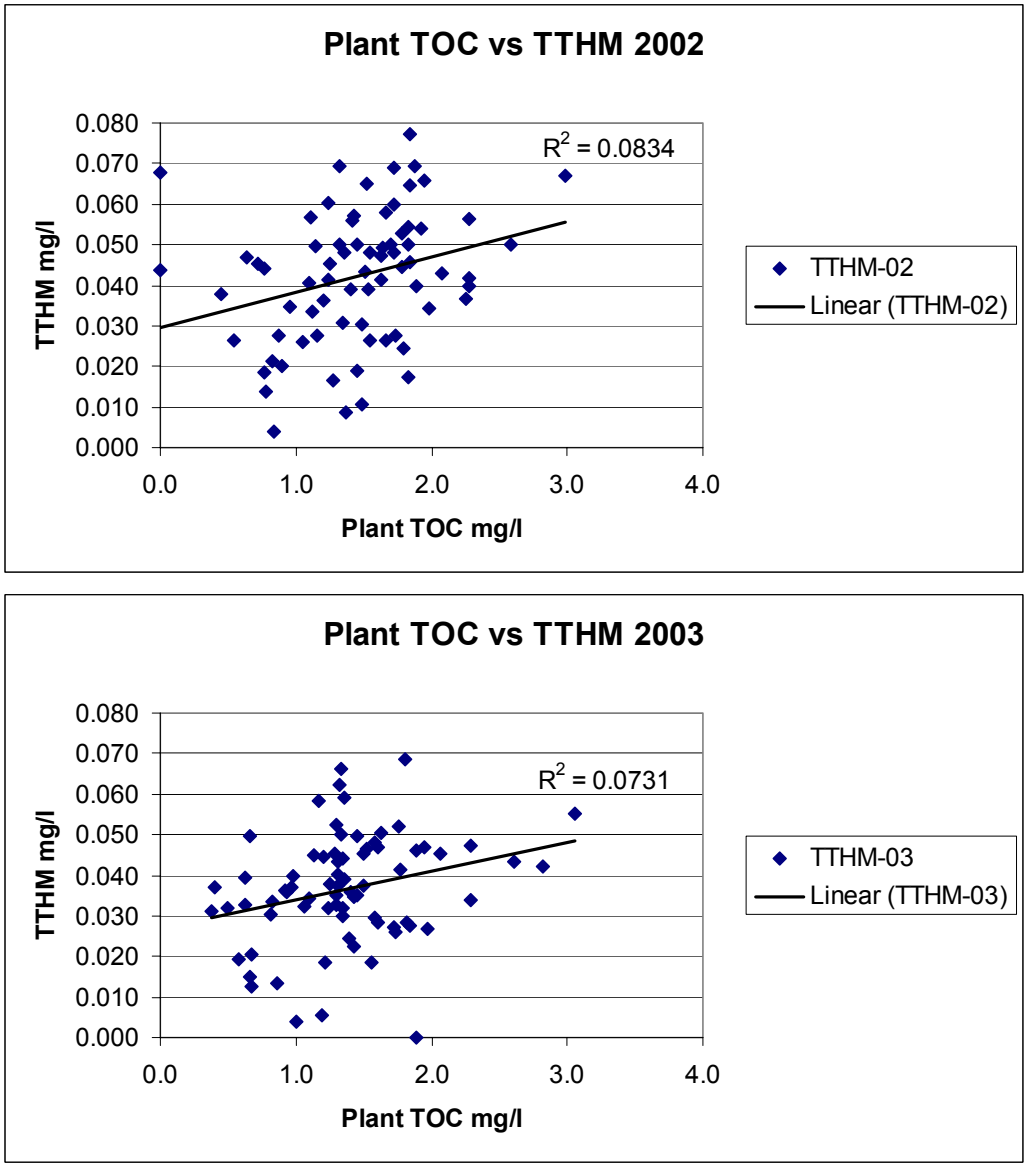
HAA5 values are also shown in Figure 4. The median concentrations were 0.021 mg/L and 0.019 mg/L for 2002 and 2003, respectively, indicating that median values were well below the distribution system compliance level of 0.060 mg/L. A review of the data from the individual water systems shows that only one system did not the meet the running annual average limit for 2002, while all the systems were below the limit based on calendar year 2003. The data also indicates that 21 systems out of 73 had at least one finished water sample in excess of 0.06 mg/L in 2002, and there were 22 systems in 2003 in the same category.

Figures 5 and 6 show plots of TTHM concentrations versus raw water TOC concentrations for 2002 and 2003, respectively. The plots show a high degree of scatter, particularly in the middle concentration range. Above TOC values of 3.5 mg/L, a more apparent correlation exists between TTHM and TOC. Only at TOC values below about 1.5 mg/l does the range in TTHM values drop off. This would indicate that raw water TOC concentrations are not a good predictor of TTHMs, particularly for TOC values above 1.5 mg/l and below about 3.5 mg/L.



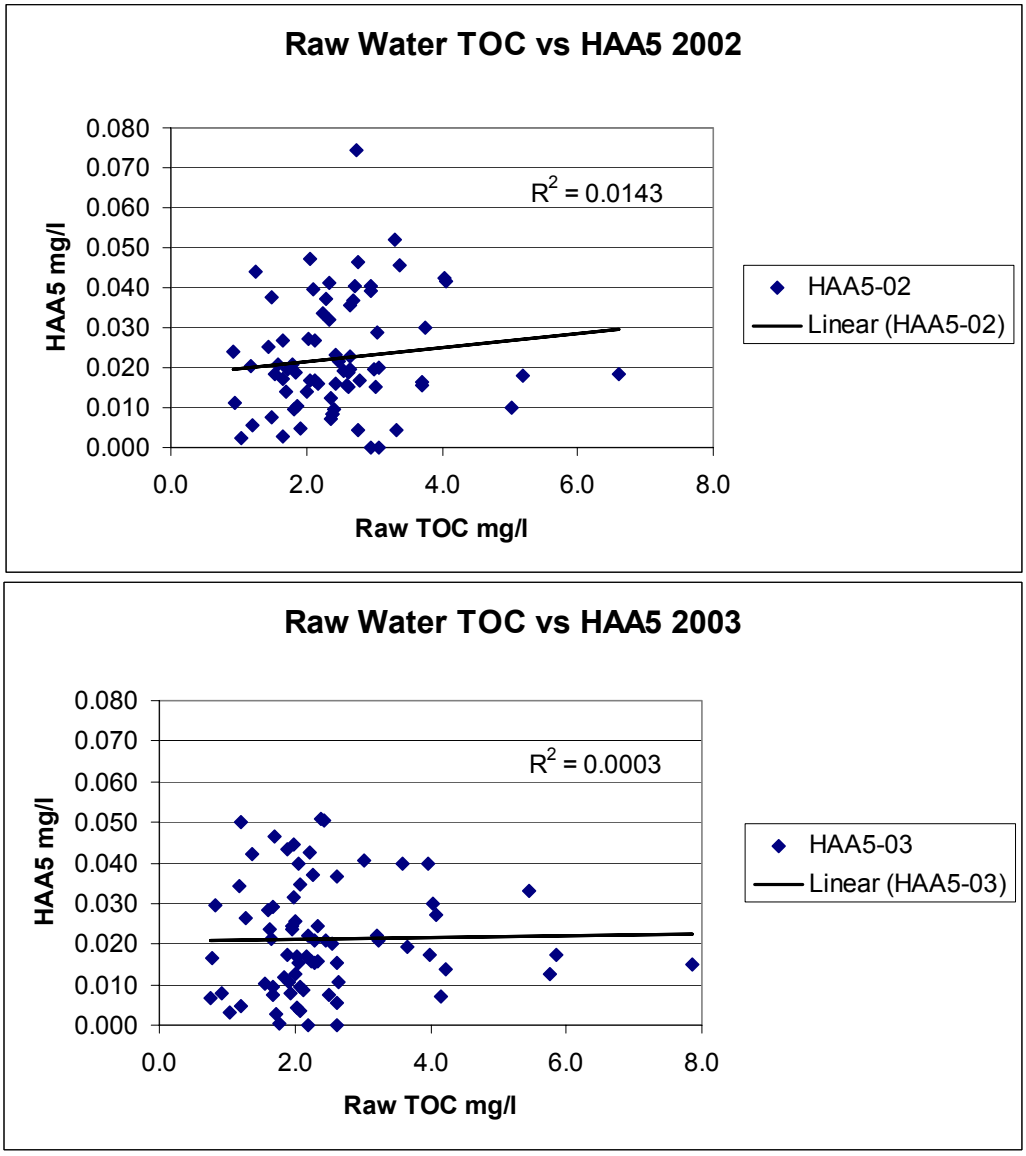
Figures 5 and 6. *Scatter plots showing the relationship between the raw water total organic carbon and total trihalomethanes in the distribution system for 2002 and 2003.*

Figures 7 and 8 show plots of TTHM concentrations versus finished water TOC concentrations for 2002 and 2003, respectively. The results are similar to those for raw water TOC i.e., there is little correlation between TTHM and finished water TOC, especially at lower values.



Figures 7and 8. *Scatter plots showing the relationship between the plant (finished water) total organic carbon and total trihalomethanes in the distribution system for 2002 and 2003.*

Figures 9 and 10 show plots of HAA5 concentrations versus raw water TOC concentrations for 2002 and 2003, respectively. The plots show an even greater degree of scatter than those for TTHMs. There is no evidence of a correlation between the two variables even at relatively high and low TOC concentrations. This is in contrast to TTHMs, which tend to be proportional to TOC at relatively high and low TOC concentrations.

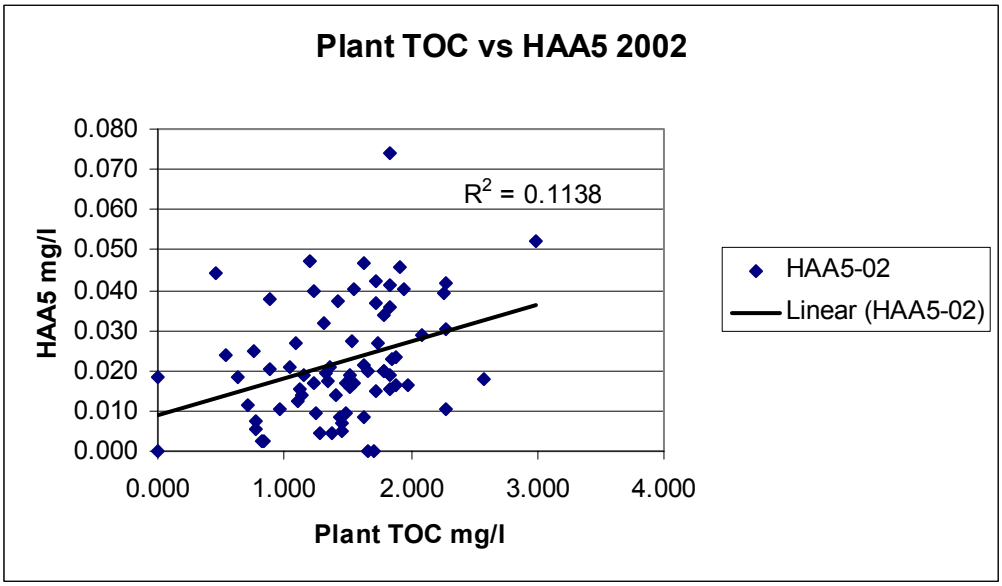


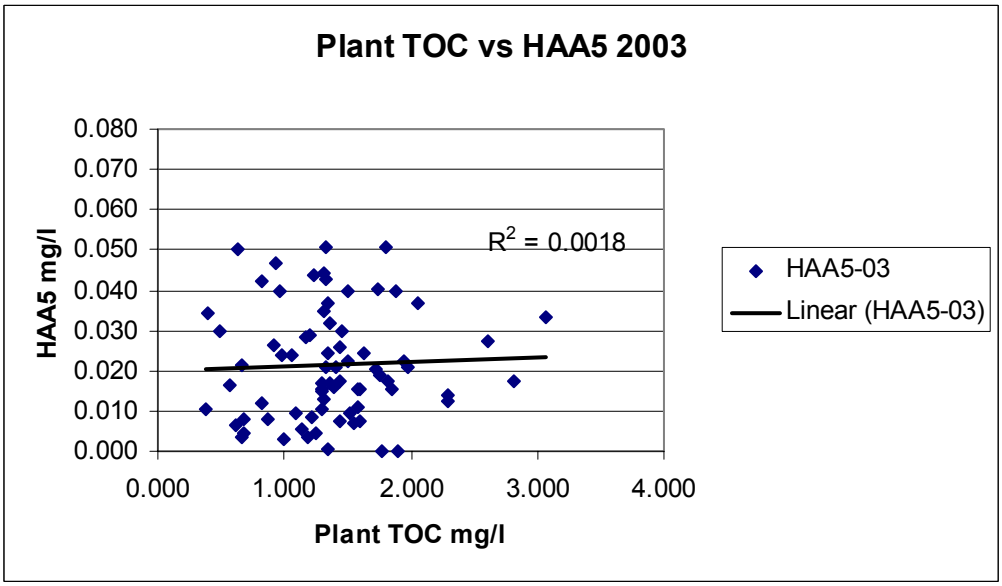
Figures 9 and 10. *Scatter plots showing the relationship between the raw water total organic carbon and haloacetic acids in the distribution system for 2002 and 2003.*

Figures 11 and 12 show plots of HAA5 versus finished water TOC concentrations for 2002 and 2003, respectively. Once again, there is little correlation between HAA5 and filtered water TOC, even at higher TOC values.

A number of possible reasons may explain the lack of an apparent correlation between TOC and disinfection byproducts, including:

- TOC is a gross indicator of the organic compounds in the water. Not all of these compounds necessarily result in the formation of disinfection byproducts. More specifically, TOC is an indicator of mass organic substance and does not differentiate between the various chemical compounds that make up the precursor compounds.





Figures 11 and 12. *Scatter plots showing the relationship between the plant (finished water) total organic carbon and haloacetic acids in the distribution system for 2002 and 2003.*

- For staff at most water systems, the data represent their first experience with D/DBP Rule monitoring and compliance. Staff started collecting data in 2002, but Rule compliance is not determined until 4 quarters of data is calculated. Thus, the running annual averages for the 0.080/0.060 mg/L limits began in the first quarter of 2003. Staff may have delayed treatment modifications needed to comply with the new maximum contaminant levels.

- A wide variety of water quality and treatment conditions can affect byproduct formation. Some conditions that can affect the relationship between TOC and disinfection byproducts are as follows:
    - *Distribution system residence time*. Systems with longer residence times will likely have higher disinfection byproducts than those with lower residence times at equal TOC concentrations.
    - *Disinfectant type*. Some of the systems in the survey used chloramines to maintain a distribution system chlorine residual. Chloramines will form less regulated disinfection byproducts than free chlorine.
    - *Disinfectant concentration*. All things being equal, a lower disinfectant residual will result in lower disinfection byproduct concentrations.
    - *TOC removal*. The data compare raw water TOC with disinfection byproducts without consideration of the degree of TOC removal that occurs in the treatment plant. There is likely a lot of variation in the TOC removal between the various plants, which obviously impacts byproduct formation. In addition, if the source water contains more particulate organic matter than dissolved matter, sedimentation and filtration can be expected to remove a significant fraction of the organic matter.
    - *Alkalinity*. Water systems with high alkalinity concentrations have lower TOC removal requirements under the 3-by-3 matrix. Thus, two systems with identical raw water TOC concentrations but large differences in alkalinity may have a considerable difference in TOC removed. This could affect disinfection byproduct concentrations.
    - *Chlorine application points*. All things being equal, if chlorine is applied prior to coagulation, the water system would likely have higher byproducts than a similar system where chlorine is applied later in the treatment process.
    - *Temperature*. Because of the strong effect of temperature on disinfection byproduct formation, there can be a strong seasonal variation in the relationship between TOC and byproduct formation. Thus, the warm water byproduct levels can be much greater than those for cold water at a constant TOC concentration.

The lack of a linear correlation between average annual TOC and disinfection byproducts in the "global" data set does not mean that quarterly samples collected at individual water systems lack any kind of relationship. In general, a wide range of R^2 values occurred at the 4 plants with higher finished water TOC levels and the 4 plants with the lower finished water TOC levels (Tables 2a and 2b). A few plants in both groups exhibited a moderate to high correlation with the disinfection byproducts, while others exhibited extremely low R^2 values. The authors caution that a small sample size and high degree of variability within the data set used in this study make it difficult to infer that strong relationships exit.

Overall, it is safe to conclude that when comparing data from many systems, there is no apparent correlation between TOC and TTHM over much of the range of TOC values examined in this study. Also, there is no apparent correlation between TOC and HAA5 over the entire range of TOC values. Thus, there is no universal relationship that can predict disinfection byproducts based on TOC values. While such a relationship may be possible at an individual water system, the relationship would have to be established empirically on a system-by-system basis.

Plants with the Highest Mean TOC Values in 2003					
Treatment Plant Name	**Finished Water TOC (mg/L)**	**Distribution TTHM (mg/L)**	**TTHM (R^2)**	**Distribution HAA5 (mg/L)**	**HAA5 (R^2)**
Plant 1	3.1	0.053	0.4610	0.032	0.4401
Plant 2	2.6	0.047	0.7738	0.035	0.9994
Plant 3	2.3	0.034	0.5202	0.014	0.1214
Plant 4	2.3	0.044	0.3091	0.011	0.2421

Table2a. *Four plants with the highest mean finished water TOC values in Pennsylvania and their coefficient of variation (R^2) between TOC and the mean TTHM and HAA5 values in the distribution system.*

Plants with the Lowest Mean TOC Values in 2003					
Treatment Plant Name	**Finished Water TOC (mg/L)**	**Distribution TTHM (mg/L)**	**TTHM (R^2)**	**Distribution HAA5 (mg/L)**	**HAA5 (R^2)**
Plant 5	0.8	0.027	0.7348	0.041	0.7430
Plant 6	0.8	0.031	0.5538	0.011	0.4038
Plant 7	0.7	0.041	0.2120	0.045	0.368
Plant 8	0.6	0.031	0.6634	0.005	0.8272

Table2b. *Four plants with the lowest mean finished water TOC values in Pennsylvania and their coefficient of variation (R^2) between TOC and the mean TTHM and HAA5 values in the distribution system.*

Analysis of Three Conventional Treatment Plants

Table 3 shows source water characteristics for three conventional treatment plants in southeastern Pennsylvania that were selected for a more detailed study. Plants A, B and C have relatively low source water TOC levels. The water temperatures range from 32°F (0°C) in the winter to 88°F (31°C) in the summer. Using the available source water TOC and alkalinity data, Plant A fell into the ">35%" category for required removal, and Plants B and C fell into the ">25%" removal category.

Source Water Characteristics	**PLANT A**	**PLANT B**	**PLANT C**
Mean Source Water Temperature, °F (ranges)	58.0 (32.0 - 84.0)	60.0 (32.0 – 88.0)	60.0 (32.0 - 85.0)
Mean Source Water TOC, mg/L (ranges)	2.91 (1.96 - 5.52)	3.17 (1.79 - 6.76)	2.94 (1.45 - 6.66)
Source Water Alkalinity, mg/L as CaCO3	<60	>60	>60
TOC % removal requirement (as detailed in the 3-by- 3 matrix)	35%	25%	25%

Table 3. *Source water characteristics for three plants in southeastern Pennsylvania that were selected for a more detailed study of data from the years 2000 through 2003.*

Seasonal temperature changes appear to be a major factor contributing to disinfection byproduct formation at the entry point to the distribution system. As shown in Figure 13, the three plants show a strong relationship between higher temperatures (as indicated by the months of the year) and higher TTHM values. The same relationship is apparent for HAA5, although it is not as pronounced.

Source water TOC at the three treatment plants was analyzed to examine the impact on TTHM and HAA5 formation in the finished water (at the entry point to the distribution system). Results of this analysis (Figure 14) showed that raw water TOC concentrations have limited value as an indicator of resultant TTHM and HAA5 levels. Overall, HAA5 had a slightly better correlation than TTHM.

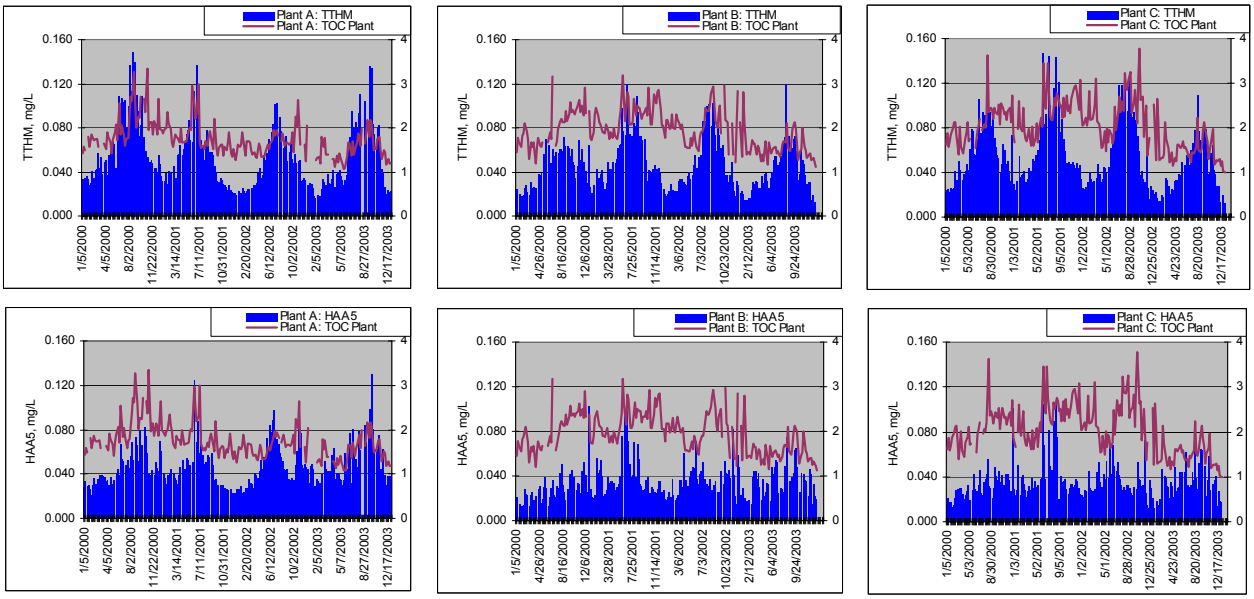


Figure 13. *Seasonal temperature changes appear to be a major factor contributing to disinfection byproduct formation at the entry point to the distribution system at Plants A, B and C.*

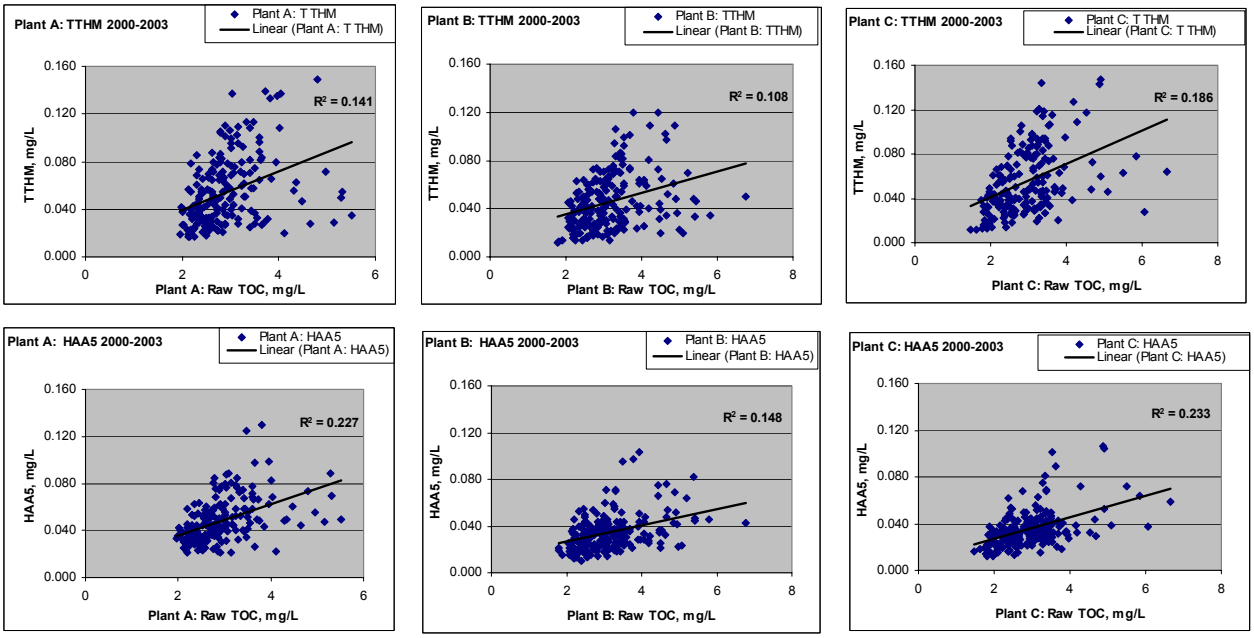


Figure 14. *Source water TOC had limited value as an indicator of TTHM and HAA5 formation at the entry point to the distribution system for Plants A, B and C during 2000 through 2003.*

Table 4 shows the mean source water TOC values for samples where the TTHM levels were either greater than or equal to 0.060 mg/L or less than 0.060 mg/L. The table also shows where HAA5 levels were either greater than or equal to 0.045 mg/L or less than 0.045 mg/L. The values of 0.060 and 0.045 were chosen because these appeared to be levels above which TOC correlated with higher TTHM and HAA5 levels, respectively.

	PLANT A Mean Source TOC (mg/L)	PLANT B Mean Source TOC (mg/L)	PLANT C Mean Source TOC (mg/L)
TTHM ≥0.060 mg/L **HAA5 ≥0.045 mg/L**	3.14 3.29	3.49 3.72	3.34 3.65
TTHM <0.060 mg/L **HAA5 <0.045 mg/L**	2.75 2.59	3.05 3.06	2.70 2.80

Table 4. *Mean source water TOC values above 3.1 mg/L corresponded well to elevated TTHM and HAA5 formation at the entry point to the distribution system at Plants A, B and C.*

Table 5 shows the mean finished water characteristics for the three selected plants before and after the start of enhanced coagulation (EC) processes. All samples were collected from the entry point to the distribution system. The table also shows the TOC removal goals in the "percent required removal" line.

Finished Water Characteristics	**PLANT A**	**PLANT B**	**PLANT C**
TOC, mg/L: Pre-EC (ranges)	2.0 (1.4 - 3.4)	2.1 (1.2 - 3.2)	2.2 (1.3 - 3.8)
TOC, mg/L: Post-EC (ranges)	1.6 (1.1 - 3.0)	1.9 (1.1 - 3.0)	1.5 (1.0 - 2.2)
TOC percent removal: Pre-EC (ranges)	29 (0 - 55)	31 (0 - 63)	26 (0 - 66)
TOC percent removal: Post-EC (ranges)	43 (5 - 71)	41 (0 - 71)	40 (26 - 71)
Percent required removal	>35	>25	>25
TTHM, mg/L: Pre-EC (ranges)	0.061 (0.028 - 0.149)	0.050 (0.016 - 0.120)	0.056 (0.013 - 0.147)
TTHM, mg/L: Post-EC (ranges)	0.049 (0.016 - 0.137)	0.043 (0.012 - 0.120)	0.046 (0.012 - 0.109)
HAA5, mg/L: Pre-EC (ranges)	0.045 (0.021 - 0.125)	0.035 (0.011 - 0.103)	0.035 (0.012 - 0.106)
HAA5, mg/L: Post-EC (ranges)	0.048 (0.021 - 0.130)	0.034 (0.010 - 0.082)	0.037 (0.014 - 0.072)

Table 5. *Mean finished water characteristics for Plants A, B and C before and after the start of enhanced coagulation (EC) processes. Samples were collected at the entry point to the distribution system.*

As a result of new enhanced coagulation practices, the mean finished water TOC levels dropped below 2.0 mg/L. This reduction brought noticeable changes to TTHM levels at the entry point to the distribution system (Figure 15). Overall, the mean TTHM levels were reduced at each plant in the study group, ranging from 10 to 32 percent reductions. By contrast, the relationship with HAA5 was not as straightforward.

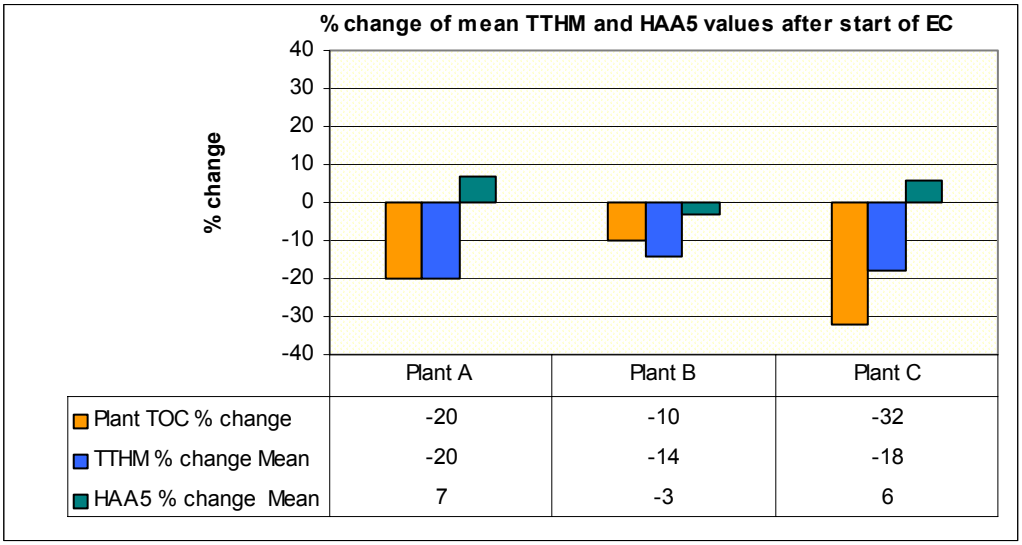


Figure 15. *As a result of new enhanced coagulation (EC) practices, the finished water TOC levels dropped below 2.0 mg/L at Plants A, B and C. This reduction brought noticeable changes to TTHM levels—but not HAA5 levels—at the entry point to the distribution system.*

Comments and Conclusions

In Pennsylvania, compliance data for TOC, TTHM and HAA5 were available from 73 surface water systems using a total of 85 conventional filtration plants, covering the first two years of monitoring under the Disinfectants/Disinfection Byproducts Rule. The data was gathered from a regulatory reporting database housed at the Pennsylvania Department of Environmental Protection. The compliance data was compiled and analyzed to examine the relationships between TOC concentrations at the treatment plants and TTHM/HAA5 formation in the distribution system. In addition, a detailed analysis was completed on data gathered from 8 plants out of the 85 conventional treatment plants in Pennsylvania. Furthermore, the authors studied three treatment plants in southeastern Pennsylvania to provide a more detailed analysis of TOC, TTHM and HAA5 at the plants.

When comparing data from 73 water systems, the authors observed no apparent linear correlation between either raw or finished water TOC and TTHMs over much of the range of TOC values examined in this study. In addition, they found no apparent linear correlation between TOC and HAA5 over the entire range of TOC values. Thus, there is no universal relationship that can be used to predict disinfection byproduct formation in the distribution

system based on TOC values in the source water or finished water. While such a relationship may be possible at an individual water system, the relationship would have to be established empirically on a system-by-system basis.

Because the Disinfectants/Disinfection Byproducts Rule places great emphasis on TOC removal, as specified in the 3-by-3 matrix, data from three plants was further analyzed to determine the effect of improved TOC removal on the levels of TTHM and HAA5. A simple analysis of TTHM and HAA5 data in connection to TOC values also did not provide a clear picture. The benefits of simply having low finished water TOC concentrations, as measured by disinfection byproduct levels at the entry point to the distribution system, were not apparent. All three facilities, however, were able to achieve greater reduction of TOC through the treatment process as a result of enhanced coagulation. While it was evident that *removing* TOC decreased TTHM values, TOC removal did not relate well to HAA5 levels.

Other factors influencing TTHM and HAA5 formation need further exploration, especially in combination with TOC levels. More specifically, TOC is an indicator of mass organic substance and does not differentiate between the various chemical compounds that make up the precursor compounds. The reactivity of chemical bonds and functional groups could be a significant factor in explaining why different water sources with similar TOC concentrations will form different DBP concentrations under identical disinfections conditions. Further investigation might better describe the exact nature of disinfection byproduct precursors and their relationship to disinfection practices and byproduct formation.

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