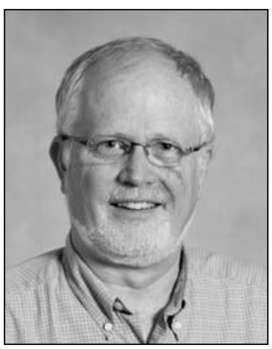
by Pat McCool

The TOC removal requirement: is it necessary?

In the last issue of *The Kansas Lifeline*, KRWA General Manager Elmer Ronnebaum wrote about the compliance costs of Federal and State requirements on public water supplies. No requirement is more frustrating to many operators of surface water treatment plants than the total organic carbon (TOC) percentage removal requirement. Compliance with this requirement is not only uncertain, but the costs of monitoring, reporting, and public notice are substantial. And then there is the public's reaction to the public notice. What makes this most frustrating is that the requirement may be unnecessary.

The TOC percentage removal requirement was promulgated on December 16, 1998 as part of what is known as the Stage 1 Disinfection Byproduct Rule (DBPR). The TOC requirement applies to public water supplies that use surface water or groundwater under the direct influence of surface water as a water source. The TOC requirement essentially requires that the treatment plants remove a certain percentage of TOC in the source water based on the alkalinity of the water source. The table on the next page shows the specific removal requirement.



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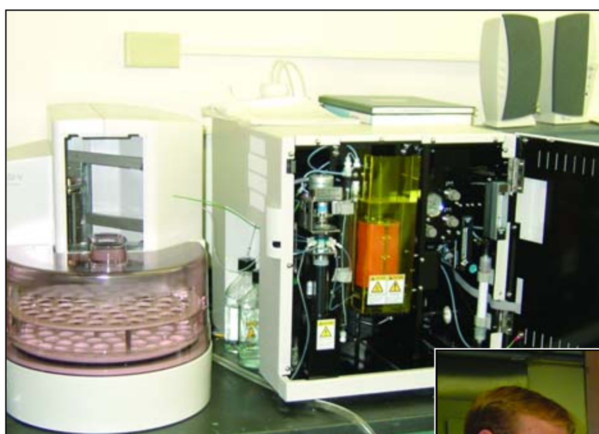
Total organic carbon (TOC) is a direct measurement of the carbon contained in the organics, that is, the organic matter in the water. KDHE's laboratory uses the persulfate-ultraviolet oxidation method for TOC analyses for water from public water supplies. The KDHE laboratory performs approximately 3,500 TOC analyses annually of which approximately 2,000 are for determining water treatment plant compliance.

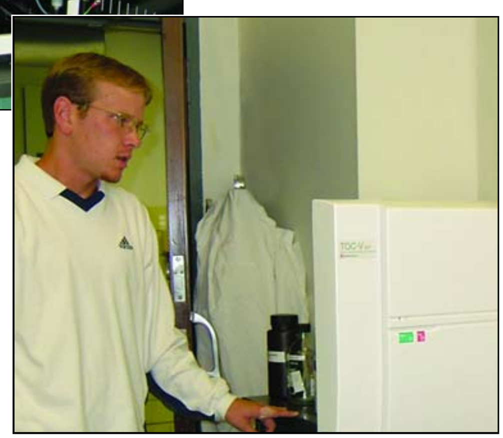
Based on the EPA statements, it seems that the TOC requirement is unnecessary and does not provide any health benefits.

TOC in the water is believed to be mainly from natural, humic substances from plant and plant residues. These substances include humin, humic acid, and fulvic acid. Algae and animal wastes can also be a contributing factor. TOC levels in Kansas surface waters are highly variable and unpredictable. The levels can be as low as 2 – 3 mg/l (milligrams per liter) and as high as 20 mg/l; but the range of 4 – 8 mg/l contains a majority of the values.

The reasoning for the TOC requirement is that (some of) these organics may react with disinfectants to form disinfection byproducts (DBPs). The most extensively used disinfectant in Kansas is free chlorine and its regulated DBPs are trihalomethanes (THMs) and haloacetic acids (HAAs). Chlorine dioxide is also being used as a disinfectant at Kansas water treatment plants and its main, regulated DBP is chlorite; however this byproduct does not contain carbon.

Many requirements of water treatment are based on a maximum





Right: *KDHE laboratory instrument for persulfate-ultraviolet oxidation for TOC analyses.*
Below: *KDHE Chemist Shawn Manos checking the instrument set-up.*

contaminant level (MCL) of a "contaminant" in the water. However, the TOC requirement is what is called a "treatment technique" requirement (in this case, a percentage removal) in that it requires a certain treatment but the level a "contaminant" in the water is not regulated.

A 2001 EPA guidance manual states that the treatment technique (TOC requirement) "…was established because disinfectants can react with disinfection byproduct precursors (DBPPs) to form both regulated and non-regulated DBPs. The treatment technique requirements in the rule are designed to provide public health protection by minimizing the production of all DBPs".

It is worth noting that the EPA statement justifies the TOC requirement on the basis of regulated and non-regulated DBPs. The regulated DBPs of THMs and HAAs already have MCLs and the non-regulated DBPs are that, that is, not regulated. Based on EPAs justification, it seems that the TOC requirement is both redundant (regulated DBPs) and not justified (non-regulated DBPs).

Also, the EPA statement says that the requirement is designed to provide public health protection; but the statement does not say that the requirement does, in fact, provide public health protection. Based on the EPA statements, it seems that the TOC requirement is unnecessary and does not provide any health benefits. A review of actual TOC reductions/compliance and the concentrations of THMs and HAAs in the drinking water supports that the TOC requirement provides no significant, regulated DBP reduction and makes no sense.

There are two major factors that control the THMs and HAAs concentrations formed in the water during the treatment process. In Kansas, the two major factors are water temperature and the free chlorine contact time (see page 43 sidebar on controlling/limiting DBPs at Kansas' water treatment plants). The level of precursors, that is organics as measured by TOC, is not a major factor. Thus, the TOC requirement does not accomplish what it pretends to do.

There are treatment plants that meet the THMs and HAAs MCLs but do not meet the TOC percentage reduction requirement. Additionally, there are treatment plants that do not meet these MCLs but do meet the TOC percentage reduction requirement. So, there is no necessary correlation between MCL compliance and meeting the TOC percentage reduction requirement.

Also, there are many situations where a treatment plant will have both a higher TOC concentration and lower THMs and HAAs in the drinking water than another plant.

STEP 1 REQUIRED REMOVAL OF TOC BY ENHANCED COAGULATION AND ENHANCED SOFTENING FOR SUBPART H SYSTEMS USING CONVENTIONAL TREATMENT

Source-water TOC, mg/L	Source-water alkalinity, mg/L as $CaCO_3$ (in precentages)		
	0-60	>60-120	>120
>2.0 - 4.0	35.0	25.0	15.0
>4.0 - 8.0	45.0	35.0	25.0
>8.0	50.0	40.0	30.0

Thus, the level of TOC in the water (and the percentage removal of TOC) has no direct effect on the concentrations of THMs and HAAs as long as there are sufficient TOC in the water with which to form THMs and HAAs.

The fact is that the TOC percentage removal does not relate or significantly affect the THMs and HAAs concentrations in the drinking water. What is important is that certain, unknown, specific organics in the water react with chlorine to form DBPs in the water. The TOC analyses measures the total (all) organic carbon in the water and not just the specific organic carbon that can react. These specific organic carbons are only a small, unknown percentage of the total organics.

For example, a TOC of 3.0 mg/l would equal a total of 3,000 ug/l (micrograms per liter or parts per billion) of organic carbon in the water. If in that same water the total THMs formed were 80 ug/l (which is the MCL), the amount of carbon contained in the THMs would be 8 ug/l or less depending on the distribution of the four types of THMs. It is obvious that an operator can not predicatively control/remove those specific 8 organics and that there wouldn't be another similar 8 to replace them if they were removed.

In this example, the TOC requirement is addressing 3,000 ug/l carbon to regulate the reaction of 8 ug/l. It is a Herculean requirement that does not succeed in doing what it is stated to do. How does the operator/manager know what eight are going to react to form these THMs? No matter how much TOC you remove from Kansas water, there is still a lot of TOC left to react with free chlorine and form THMs.

The TOC percent removal requirement shown in the table on the previous page was based on reasoning that does not include any public health benefits. Explaining the original percentage removal numbers in the earlier, proposed rule, EPA states that the percentages "…which were set with the intent that 90% of affected systems would be able to achieve them, were developed with limited data".

EPA then used additional studies including models and predictive equations to subsequently analyze the percentages that were "operationally feasible". Based on the one-time sampling of 76 water treatment plants, the removal percentages were made law based on the estimation that 90% of the plants being able to comply

Roughly one-quarter of the approximately 90 surface water treatment plants in Kansas are out of compliance with the TOC percentage removal requirement. And many other water suppliers are uncertain about continuing compliance.

Many TOCs are left in the water after coagulation/flocculation/sedimentation.

Factors that affect THMs and HAAs formation at Kansas water treatment plants

There are several factors that affect the types and concentrations of disinfection byproducts (DBPs) in the drinking water from Kansas water treatment plants. These factors include: 1) type, concentration, and contact time of the primary disinfectant used; 2) pH of the water; 3) water temperature; 4) types and concentrations of precursor organics in the water and; 5) the removal of the DBPs after they are formed. Some of the factors can be more readily used in designing and operating treatments plants in order to minimize the production and concentrations of DBPs in the water.

The primary disinfectant most widely used at Kansas surface water treatment plants is free chlorine. Free chlorine reacts with natural organics in the water to form the regulated DBPs of trihalomethanes (THMs) and haloacetic acids (HAAs). The free chlorine contact time is the most used and the most important factor in determining THMs and HAAs concentrations and compliance. The practice of limiting the free chlorine contact time to predetermined ranges results in compliance at most all Kansas treatment plants. Also, reducing the chlorine dosage will give some reduction of THMs and HAAs concentration, but the lower dosage may not provide significant results when considering the need to maintain free chlorine residuals to achieve CT compliance.

> The TOC is a measure of all the organic carbon of which only a very small percentage of it will react with free chlorine to form THMs and HAAs.

Some plants use chlorine dioxide as a primary disinfectant to achieve CT compliance. Using chlorine dioxide alone does not achieve THMs and HAAs compliance other than it allows the subsequent contact time between the free chlorine and the natural organics to be significantly reduced so that compliance is achieved. However, chlorite and chlorate are byproducts of the chlorine dioxide addition and the levels of chlorite must be monitored and must meet required MCLs.

Some plants use ozone as a primary disinfectant to achieve CT compliance. Ozone oxidizes the organics in the water to smaller-sized organics that still can form THMs if there is sufficient free chlorine contact time. These small organics can also contribute to biofilm growths in the distribution system. Most plants using ozone use the treatment plant filter media as a biological filter bed of bacteria to eliminate/reduce the organics in the water. Like chlorine dioxide, after adding ozone, the contact time between the free chlorine and natural organics can be significantly reduced so that THMs and HAAs compliance is achieved. However, the levels of bromate in the water must be monitored and must meet the required MCLs.

Most Kansas water treatment plants that consistently meet DBPs requirements do so by adding ammonia to the water after a predetermined, free chlorine contact time. The ammonia reacts with the free chlorine to eliminate the free chlorine and to form chloramines in the water. Thus, with chloramines the formation of THMs and HAAs ceases. Most Kansas treatment plants meet the THMs and HAAs MCL requirements without the use of chlorine dioxide or ozone.

THMs are produced very rapidly at higher pH levels. The practice of using free chlorine at higher pHs should be avoided. The pHs for clarification plants should be kept below the 8.0 – 8.2 range. The much higher pHs at softening plants are a particular situation to avoid.

THMs and HAAs are produced at much higher rates with increasing water temperatures. The highest concentrations usually occur in the summer and the lower concentrations usually occur in the winter. This factor cannot be controlled unless cooler well water can be added to lower the overall temperature of the water being treated.

The types and concentrations of precursors can theoretically affect the THMs and HAAs concentrations formed. However, this theoretical factor cannot be controlled easily by design and cannot be controlled by plant operations. The types and amounts of specific organics reacting with the free chlorine are not known. The operator cannot predetermine how to remove a known, significant amount. The TOC is a measure of all the organic carbon of which only a very small percentage of it will react with free chlorine to form THMs and HAAs. Even if 50% of the TOC is removed from Kansas waters, there is still a large amount left in the water to react to form THMs and HAAs.

Granular activated carbon (GAC) can be used to remove either organic precursors or THMs and HAAs from the water. GAC can be used in separate vessels called columns or in rapid sand filter beds. GAC has much more capacity to adsorb these compounds than powder activated carbon and can be controlled better. The capital and operating costs of GAC columns are prohibitively high. However, the use of GAC in filter beds is considerably less expensive. Pilot plant testing of the GAC is needed to predict what removals can be expected.

Some plants in Kansas now use microfiltration instead of rapid sand filtration. Microfiltration produces low turbidity, high quality water. However, microfiltration does not significantly remove organics, so here it is still important to use chlorine dioxide or ozone and/or limit the free chlorine contact time.

It is KRWA's experience and the experience at most all Kansas surface water treatment plants that the operation of a treatment plant to meet the required concentrations of THMs and HAAs is best, and most economically, accomplished by limiting the free chlorine reaction time with the organics. How much the contact time is limited is determined by reviewing plant disinfection to ensure CT requirements are met, by evaluating the particular treatment plant's process flow and unit processes, and by considering the possible/actual use of additional disinfectants such as chlorine dioxide and ozone.

without "unreasonable" coagulant dosages.

The final removal percentages in the table were only changed from the original proposal for the category of the low source water

Many TOCs are also left in the water after filtration.

TOC range of 2.0-4.0 mg/l – and those removal percentages were lowered 5% for each of the three alkalinity concentrations.

Thus, the EPA mandated removal percentages were based on limited data and so-called predictive models that would result (possibly) in 90% of the treatment plants being able to achieve the TOC removal percentages. The TOC requirement was not based on human health effects or the resultant amount of TOC in the drinking water.

It is worth noting that U.S. Senator James M. Inhofe of Oklahoma, who is the Chairman of the United States Senate Committee on Environment of Public Works, wrote a September 7, 2005 letter to U.S. Environmental Protection Agency Administrator Stephen Johnson, questioning the legality of EPA to regulate TOC as an indicator of regulated disinfection byproducts. Senator Inhofe also states EPA should have acted to regulate TOC as an indicator of non-regulated byproducts, that is, make the determination that the non-regulated byproducts have adverse health effects. Maybe this is the beginning of something that will have a good ending.

Roughly one-quarter of the approximately 90 surface water treatment plants in Kansas are out of compliance with the TOC percentage removal requirement. And many other water suppliers are uncertain about continuing compliance. These water suppliers are incurring compliance costs and many may have to provide additional capital and operating costs to meet a requirement that has no known direct benefit. Does this make sense? Is it really a necessary requirement?