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THMs and HAAs in Drinking Water: Considering the Factors and Meeting the Requirements

This article discusses how Kansas public water supplies (PWSs) meet the maximum contaminant level (MCL) for trihalomethanes (THMs) and for haloacetic acids (HAAs). Water treatment plant processes, rechlorination in the distribution system, and consecutive systems purchasing water will be addressed.

The U.S. Congress passed the Safe Drinking Water Act. But it is the federal requirements issued by the U.S. Environmental Protection Agency (EPA) that often seem unnecessarily complex, costly, and sometimes difficult to understand. PWSs struggle with these requirements. Concerning THMs and HAAs, the nearby sidebar lists the three sets of regulations and some important provisions of these regulations. Find the article, *Federal Regulations: Taking It To The Next Level* at http://krwa.net/lifeline/1503/018.pdf.

Kansas PWSs add one or two of the following chemicals for disinfection: chlorine, ozone or chlorine dioxide. All Kansas PWSs add chlorine to maintain chlorine residual in the distribution system as required by the Kansas Department of Health and Environment (KDHE).

Most surface water in Kansas and some groundwater in Kansas contain natural organic matter (NOM), mainly decaying vegetation that will react with free chlorine to form THMs and HAAs. Chlorine dioxide also forms THMs and HAAs but to a much lesser extent than chlorine. Ozone does not form THMs and HAAs.

There are many tests that can be used to measure the natural organic matter in the water. The most common test is for the total organic carbon (TOC). TOC is thought to be a significant factor in the

Federal Regulations promulgated by U.S. EPA concerning Trihalomethanes (THMs) and Haloacetic Acids (HAAs)

November 29, 1979: Total Trihalomethanes Rule

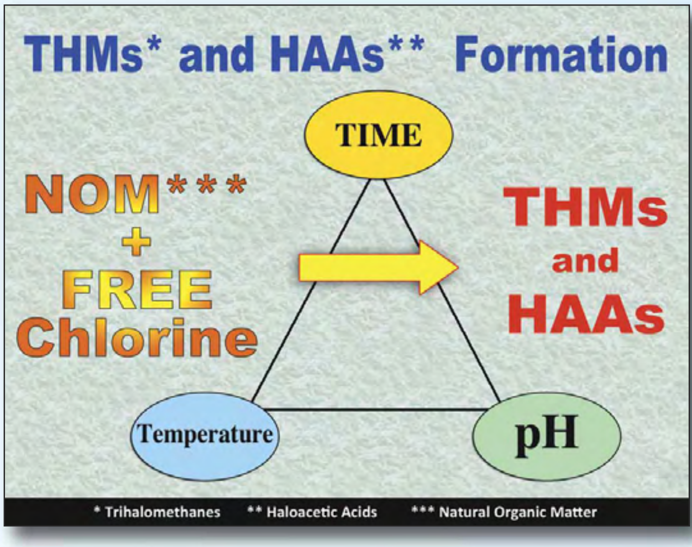
- 44 Federal Register 68624
- 0.10 mg/L MCL for THMs
- Quarterly Compliance Monitoring
- Regulation only applies to systems treating surface or groundwater under the direct influence of surface water; and serve 10,000 persons or more

December 16, 1998: Stage 1 Disinfectants and Disinfection Byproducts Rule

- 44 Federal Register 69390
- 0.080 mg/L MCL for THMs
- 0.060 mg/L MCL for HAAs
- Monitoring schedule determined by source of water, size, and past sampling record
- Monitoring can be quarterly, or yearly, or every three years
- Regulation applies to systems that add a chemical disinfectant to the water

January 4, 2006: Stage 2 Disinfectants and Disinfection Byproducts Rule

- 44 Federal Register 338
- MCLs stay the same
- Monitoring schedule quarterly, or yearly, or every three years
- Regulation applies to all systems including purchasing systems



formation in the levels of THMs and HAAs in drinking water but this is of no practical advantage or significance in Kansas waters.

Treatment factors that determine THMs and HAAs levels

Some or all of the following eight factors are considered in designing, evaluating, and operating treatment systems. Some of these have significant effect on determining THMs and HAAs levels. Others are discussed in theory but have little practical consequence in Kansas PWSs operations.

1. Free chlorine contact/reaction time

In Kansas the free chlorine contact time is the most important factor by far in determining the level of THMs and HAAs in water. This applies to all except one system treating surface water, and to a few systems treating groundwater. If the free chlorine contact time is not properly limited, then the Maximum Contaminant Levels (MCLs) will not be met.

In Kansas, only one surface water source PWS does not control or limit the free chlorine contact time and meets the MCLs for THMs and HAAs. That one PWS is the exception to the rule as it applies to surface water sources; see sidebar to the right.

In Kansas, PWSs using groundwater sources under the influence of surface water and several PWSs using groundwater that have high bromide levels also have to limit the free chlorine contact time to meet MCLs. The majority of PWSs using groundwater sources do not limit the free chlorine contact time, maintain free chlorine residual in the distribution system, and meet MCLs for THMs and HAAs.

The free chlorine contact time is limited by the addition of ammonia that reacts with the free chlorine to form monochloramine – that is, free chlorine "combined" with ammonia. The combined chlorine, that is monochloramine, does not react with natural organic matter in the water to form THMs and HAAs.

Generally speaking for the treatment of surface water, the free chlorine contact time is 30 minutes or less. The "tradeoff" is that free chlorine contact time should be low enough to meet MCLs for THMs and HAAs and high enough to meet required CT compliance

Meeting MCLs for THMs and HAAs A Rule and the One *Exception*

The Rule:

Surface water treatment plants must control and limit the free chlorine contact time in order to meet MCLs for THMs and HAAs.

The Exception:

The city of Eureka has a water supply lake northwest of town. This lake is not accessible by public road or right-of-way. The lake was constructed many years ago at which time the city ceased using Fall River on the west edge of the city.

The lake's watershed is the natural Bluestem Prairie of the Flint Hills. The watershed has only prairie grass, has maybe some cattle some of the time, and maybe is "burnt off" in some years. The lake water is deep and pristine probably as good as or better than an unpolluted Rocky Mountain stream.

The natural organic matter in the lake water is very low. The TOC of the lake water is around 3 mg/L on an average annual basis. The treated water has an average annual TOC of around 2 mg/L. This is by far the lowest TOCs for any surface water source that any Kansas PWSs uses.

The city operates the treatment plant and the distribution system with free chlorine residual. No ammonia is added. In addtion to having a "top notch" water supply lake, the city treatment plant is very well operated and maintained.

The city sells water to Greenwood Co. RWD #1 and Greenwood Co. RWD #2. Both RWDs also maintain free chlorine residual in their system for many miles from Eureka. Both RWDs are also in compliance with THMs and HAAs.

Over the last 10 years the city sample results for THMS and HAAs have been in compliance with MCLs. The THMs have averaged 40 µg/L with a high of 58 µg/L and a low of 21 µg/L. The numbers for HAAs are also very low. That data is for 19 samples of which 13 samples were taken during the month of July when THMs and HAAs are expected to be the highest.

It is not the low levels of TOC in that lake water that are responsible for the low levels of THMs and HAAs that are formed with long free chlorine contact time. It is the very low levels of a particular type(s) of natural organic matter (NOM) in the lake water that are responsible for the Exception to the Rule. More than 99 percent of the TOC does not react with free chlorine.

The city of Eureka and those two RWDs have one good "Best of Show" water supply.

★ City of Eureka

standards. This is best achieved and optimized by having the highest basin factor where the free chlorine is disinfecting the water. Also, different points of chlorine addition and/or ammonia addition can optimize the process for differing water temperatures and flow rates within the same treatment plant.

The CT compliance standards for treatment plants require in many cases a minimum free chlorine contact time that must be met. In some plants that use ozone or chlorine dioxide for disinfection and CT compliance, the free chlorine contact time can be very short. In some cases the chlorine and ammonia are added at the same location.

If a treatment plant is not meeting MCLs for THMs and HAAs, the most likely reason is that the free chlorine contact time is too long and must be reduced. This reduction can be achieved by only changing the chlorine and/or the ammonia addition locations, or by adding chlorine dioxide or ozone and then changing the chlorine and/or ammonia addition locations.

2. TOC level of the water

Total organic carbon (TOC) is only one of many methods to quantify the natural organic matter of the water; it is the method required in EPA-issued requirements. If and how much TOC determines the level of THMs and HAAs in drinking water. This is one of the most discussed, most misunderstood, and most overrated factors.

In a practical sense, it is "much to do about nothing", really. However, TOC has consequences because PWSs treating surface water are required to meet a certain percentage removal of TOCs and to issue public notification if the percentage removal requirements are not met.

The November 2005 issue of *The Kansas Lifeline* magazine has an article discussing the TOC requirements, and how and why the percentage removal requirements were set. Among other reasons, the TOC in the water has no known adverse health effects; the TOC removal percentage is not a major factor in determining THMs and HAAs in drinking water and its cost of monitoring, reporting, and public notice accomplish nothing. How Kansas water treatment plants meet MCLs for THMs and HAAs has no correlation with TOC removal percentage. Find the article, *The TOC Removal Requirement: Is It Necessary?* at http://krwa.net/lifeline/currentissue/0511toc.pdf.

3. A high pH of the water

A high pH of the water during free chlorine contact time at a treatment plant has a significant effect on increasing the level of THMs and HAAs produced. The pH is not a significant factor in surface water clarification plants. However, in softening plants any free chlorine contact time must be before softening or after the pH is lowered in the recarbonation process. As with clarification plants, groundwater systems also have comparatively lower pH than the softening process and thus pH is not a problem.

4. Temperature of the water

The warmer the water, the faster the chemical reactions in water occur. In general, higher THMs and HAAs occur in the summer than in the winter. There are exceptions to higher summer values but these exceptions are uncommon and are influenced by other factors than temperature.

The temperature of the water is uncontrollable except in certain situations. In Kansas there are surface water treatment plants that also blend in groundwater. In these situations the temperature of the blended, treated water is comparatively lower during the summer, and thus the THMs and HAAs are lower than they would have been in treating surface water only.

In addition to lowering the water temperature in the summer time, blending has another advantage. The blending of groundwater also dilutes/reduces the THMs and HAAs as groundwater generally produces lower THMs and HAAs due to the absence of natural organic matter.

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5. Free chlorine dosage and free chlorine residual

Differing amounts of free chlorine dosage/residual may have an effect on the level of THMs and HAAs produced but only if the dosages/residuals are significantly different and if the lower amount is very low, perhaps 0.4 mg/L or less.

For instance, a 3.6 mg/L free chlorine dosage/residual will not produce nine times the levels of THMs and HAAs produced from a dosage/residual of 0.4 mg/L. The difference in levels can only be determined by controlled laboratory tests or in actual operating conditions.

Either way, CT compliance must be met and the required free chlorine contact time for 0.4 mg/L is much, much longer than for 3.6 mg/L. What one gains (in reduced levels of THMs and HAAs) in reduced free chlorine dosage/residual is more than lost in increased free chlorine contact time to meet CT requirements for the lower residual.

Many plants in Kansas operate with free chlorine dosages/residuals in the range of 2.5 to 3.5 mg/L. These plants meet the MCLs and CT requirements by limiting the free chlorine contact time only. It is much more "operational friendly" or more "operational forgiving" if a plant is operated at the higher free chlorine dosage/residual.

> **Generally speaking, for most all PWSs bromide levels do not adversely affect THMs and HAAs levels in the drinking.**

6. Bromide in the source water

Not much is known in Kansas about the levels of bromide levels in the source water. The Kansas Department of Health and Environment very seldom, if ever, tests for bromide. Probably the levels of bromide are always less than 2 mg/L but even lower levels do cause problems.

Generally speaking, for most PWSs bromide levels do not adversely affect THMs and HAAs levels in the drinking water. But for a few surface water source PWSs and a few groundwater source PWSs, bromide levels in the source water are high enough to increase the THMs to more than they would have otherwise been – even to above the MCLs.

At present, even if the bromide levels are "high" it appears that the MCLs for THMs can still be met by limiting the free chlorine contact time. But these situations are being monitored and addressed, as the bromide is a "wild card" in determining what the THMs are and should be. Present data shows that bromide does not adversely increase HAAs.

7. Ozone and chlorine dioxide addition

There are surface water treatment plants in Kansas that add ozone or chlorine dioxide to meet CT disinfection requirements and MCLs for THMs and HAAs. The THMs and HAAs in ozone plants are characteristically very low, usually below 10 µg/L for either. Also, the THMs and HAAs in chlorine dioxide plants are well below MCLs.

Plants using either ozone or chlorine dioxide also limit the free chlorine contact time to obtain these low levels of THM and HAAs. In these cases the chlorine and ammonia can be added at the same location or a very short time apart because free chlorine contact time is not needed to meet CT disinfection requirements since ozone and chlorine dioxide meet the CT disinfection requirements.

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8. Granular Activated Carbon (GAC) or Powdered Activated Carbon (PAC)

Natural organic matter, THMs and HAAs, and chlorine residual can all be adsorbed and removed by GAC process or PAC process. The GAC process is not used because it is very, very expensive. The PAC process is used in Kansas for taste and odor control. But PAC is not used extensively as better, less expensive operational controls are used in lowering THMs and HAAs by other methods, mainly limiting the free chlorine contact time.

Rechlorination in distribution systems

Many PWSs are rechlorinating in the distribution system to achieve required minimum chlorine residuals. That requirement is 1.0 mg/L combined chlorine residual or 0.2 mg/L free chlorine residual, whichever applies.

Rechlorination is mainly needed and practiced in the warmer water temperature months for those PWSs that have combined chlorine residual. Combined chlorine residual decreases in those systems due to nitrifying bacteria. The November 2012 issue of this magazine has an article discussing maintaining residual in these systems. Here is a link to that article: *Combined Chlorine: Maintaining Residual in Distribution Systems,* http://krwa.net/lifeline/1211/54.pdf.

At rechlorination dosages, rechlorination does not increase the THMs or HAAs in the water. Only if the dosages are very high, achieving breakpoint and providing free chlorine residual, do the levels of THMs and HAAs increase. And those dosages are very high in the range of 10 to 30 mg/L or more. Thus, from the most common and most practiced situation, rechlorination does not increase THMs and HAAs.

Consecutive systems

For PWSs consecutive systems that purchase water, compliance with THMs and HAAs should occur if the PWSs seller is meeting MCLs. If this does not occur, there is one likely reason and one unlikely reason.

First, PWSs sometimes perform free chlorine "burnout" during the warmer water temperature months. The burnout is where the system goes from combined chlorine residual to free chlorine residual to destroy the nitrifying bacteria that are causing the loss of combined residual in the distribution system.

During the free chlorine burnout, the THMs and HAAs are much higher (150 µg/L to 350 µg/L) than the MCLs

because the free chlorine time is much more extensive; it is days or weeks. The most important and a necessary step for a successful burnout is that all storage tanks must achieve free chlorine residual throughout the tanks. Not achieving this is the most common error made in burnout sometimes necessitating a second burnout in the same year.

The most important and a necessary step for a successful burnout is that all storage tanks must achieve free chlorine residual throughout the tanks.

Burnouts usually last from four to six weeks. THMs and HAAs compliance samples must not be taken during the burnout period and for sometime afterwards. Burnout water can still be in the storage tanks and waterlines for several weeks that are a considerable distance from the water source.

The PWSs seller and PWSs purchasers must have good communication so that samples are not collected of burnout water. Also, burnout must be scheduled so that compliance samples can be collected during the sampling quarter and avoid the burnout.

In addition to notifying PWSs purchasing water, it is also most important that PWSs selling water notify KDHE before the burnout begins and the dates of the burnout. Compliance sample scheduling and sampling are most important during the burnout or soon afterward to avoid unrepresentative, out-of- compliance water and its possible public notice. The March 2015 issue of this magazine has an article where good communication did not occur and its consequence to the consecutive system. Here is a link to that article: *Federal Regulations: Taking It To The Next Level* http://krwa.net/lifeline/1503/018.pdf.

An unlikely reason for high MCLs may be rechlorination was too high. There has been no occurrence of this in Kansas; it is unlikely as previously mentioned. The chance of such happening is very, very low.

In conclusion

Overall, Kansas PWSs have had a very good record meeting the MCLs for THMs and HAAs. In the case where this did not occur, one of the eight items mentioned above was the cause.

Again, there are two main causes for not meeting MCLs. First, not limiting the free chlorine contact time in the treatment process is the major cause. This can be corrected by changing the chlorine and/or the ammonia feed locations. Also, choosing ozone or chlorine dioxide as the primary disinfectant is another, more expensive way to correct the situation.

Second, good communication between PWSs sellers and the PWSs buyers is needed to ensure that compliance samples are not collected during free chlorine burnouts or soon thereafter. This is a management issue that falls mostly on the supplying system (seller) that knows when burnouts are to occur.

I encourage any reader to contact KRWA for assistance in addressing the matter of THMs and HAAs or other water supply issues. I can be reached directly by emailing to me at pat@krwa.net. Also, I encourage readers to take advantage of various training sessions where water supply operations and compliance with drinking water regulations will be discussed. KRWA's training calendar is readily available on Association's Web site at www.krwa.net. Also, I hope that readers will mark their calendars for March 29 - 31 for the KRWA Annual Conference & Exhibition. That conference is among the best in the nation and certainly the largest in Mid-America; attending will be a good investment.

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