Relative Dominance of HAAs and THMs in Treated Drinking Water
[Project #339]

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PRINCIPAL INVESTIGATORS:
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OBJECTIVES:
The objectives of this project were to investigate the relative occurrence of HAAs and THMs in treated drinking waters and to determine water quality, treatment, and distribution system conditions that influence their relative concentrations.

BACKGROUND:
THM levels have been shown to exceed HAA levels in some water systems, while the reverse is true in others. THM formation has been well-studied, and THMs tend to be stable in water distribution systems. HAAs are less well-studied, and their kinetics of formation and stability are not as well characterized. They appear to be formed faster than THMs, some of the species are thought to decompose at elevated pH values, and some of the species are believed to biodegrade in the absence of a chlorine residual.

HIGHLIGHTS:
The following are highlights from the project:

• pH is the dominant factor controlling the relative distribution of THMs and HAAs in finished drinking water.
• Waters with high hydrophobic organic carbon concentrations and high SUVA values produce more HAAs relative to THMs than waters having low SUVA values and predominantly hydrophilic organic carbon.
• The HAA9/THM4 ratio tends to be highest in the winter months and lowest in the summer months.
• HAAs are biodegradable in the absence of a chlorine residual, thereby impacting the relative distribution of THMs and HAAs.
• HAA5 measurements significantly underestimate overall HAA occurrence. Inclusion of the other non-regulated HAA species contributes significantly to overall HAA occurrence.

APPROACH:
The project consisted of a laboratory phase of controlled investigations to assess the stability of the different HAA species under different solution conditions. A controlled laboratory chlorination study was undertaken in which six waters with differing NOM characteristics from different regions of the United States were chlorinated under different solution conditions. ICR data were analyzed to examine the relative occurrence of HAA and THM concentrations in finished drinking water and factors influencing the relative dominance of these two classes of DBPs. A full-scale plant study assessed the distribution and speciation of THMs and HAAs in a variety of different waters from geographically diverse regions, with differing water quality, treatment, and distribution system characteristics. Lastly two controlled biostability studies with annular reactors and biologically active filters were used to evaluate the biodegradability of different HAA species.

RESULTS/FINDINGS:
The researchers reached the following conclusions as a result of the project:

• HAA9 concentrations decrease with increasing pH whereas THM4 concentrations increase with increasing pH. Among the HAA species, trihalogenated acetic acid formation decreases with increasing pH whereas dihalogenated acetic acid formation is relatively independent of pH.
• Waters with high hydrophobic organic carbon concentrations and high SUVA values tend to produce more HAAs relative to THMs than waters dominated by hydrophilic organic carbon.
• The HAA9/THM4 ratio increases with decreasing temperature and HAAs are favored over THMs in winter months.
• HAA species are biodegradable in the absence of a chlorine residual whereas THM species are not.
• The THMs and the three classes of HAA species (mono-, di-, and trihalogenated species) have different formation mechanisms and, to some degree, different precursors.
• For the over 5000 samples examined from the first 12 months of ICR data, HAA9 concentrations in finished drinking water are approximately equal to total THM concentrations. By comparison, HAA5 concentrations are approximately only 60 percent of the corresponding total THM concentrations.

**IMPACT:**

**Analytical**
All 9 HAAs can be measured by the modified derivatization method developed and validated in this research.

**Treatment**
Formation of trihalogenated HAAs can be reduced by decreasing pH, but formation of dihalogenated HAAs is independent of pH. HAAs are biodegradable in the absence of a chlorine residual, and HAA concentrations can be lowered by biodegradation.

**Regulatory Implications**
HAA5 measurements significantly underestimate overall HAA occurrence. HAA9 concentrations in finished drinking water are approximately equal to total THM concentrations. Temperature, pH, and contact time are important determinants in assessing the relative dominance of THMs and HAAs.

**PARTICIPANTS:**
Four utilities from throughout the United States participated in the project.

**RESEARCH PARTNER:**
M/DBP Council