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Formation of Halonitromethanes and Iodo-Trihalomethanes in Drinking Water [Project #4063]

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OBJECTIVES:
The main purpose of this study was to examine the conditions and precursors involved in the formation of two emerging classes of disinfection by-products (DBPs), halonitromethanes (HNMs) and iodo-trihalomethanes (I-THMs), which are not currently regulated but have been observed in some drinking water systems.

BACKGROUND:
Since THMs were first discovered in drinking water in the early 1970s, DBP issues have become a major regulatory driving force in the United States. To date, more than 600 DBPs have been identified in drinking waters; however, only 11 DBPs (4 trihalomethanes [THMs], 5 haloacetic acids [HAAs], bromate and chlorite) are currently regulated. Available toxicological data indicates that regulated DBPs do not produce urinary bladder cancer consistently associated with chlorinated water. Additionally, it has been shown that their potencies are orders of magnitudes too low to account for other associations such as cancer and reproductive/developmental effects.

APPROACH:
Water samples from five drinking water treatment plants and nine municipal wastewater treatment plants were collected and tested for different phases of the project. In addition, NOM fractions isolated from selected drinking water sources were utilized in some experiments.

For HNMs, the approach was to (1) evaluate different disinfection/oxidation processes for HNM formation potential, (2) identify the general characteristics of HNM precursors, and (3) investigate the influences of pH and elevated nitrite and bromide concentrations on HNM formation and speciation.

For I-THMs, the approach was to (1) determine the importance of pH; (2) evaluate the effect of contact time and dose of prechlorination; (3) determine the role of chloramination strategy (chlorine added before ammonia vs. preformed monochloramine [NH_2Cl]), and the role of natural organic matter (NOM) characteristics (a low- vs. high-specific ultraviolet absorbance [$SUVA_{254}=UV_{254}/DOC$] water); and (4) examine the impact of preoxidation with potassium permanganate ($KMnO_4$), chlorine dioxide (ClO_2), and hydrogen peroxide (H_2O_2) on I-THM formation and speciation.

RESULTS/CONCLUSIONS:

Formation Potential of HNMs in Drinking Water

The results from HNM FP tests showed that among the five disinfection processes tested, the order of HNM formation in molar concentrations and yields on a DOC and DON basis was in the order of ozonation-chlorination >> chlorination ≥ ozonation-chloramination >> chloramination. Ozonation/chlorination significantly enhanced HNM formation as compared to chlorine alone, while chloramination (using preformed monochloramine), alone or after ozonation, produced the fewest HNMs.

HNM yields, both on a DOC and DON basis after conventional treatment, were generally higher than the yields observed for the raw water of the same treatment plant. The precursors with higher reactivity toward HNM formation were not well removed during conventional treatment in the plants studied during this project. Therefore, the hydrophilic NOM components remaining in water after conventional treatment contain more reactive precursors for HNM formation than hydrophobic compounds typically removed in conventional treatment. This was also indicated by the results of the NOM fraction experiments. The results also showed that DOC and DON removal alone will not be adequate descriptors to predict the reduction in HNM formation potential. Reasonable correlations were observed between HNM yields and the DOC/DON ratio of a sample. HNM yields decreased with increasing DOC/DON ratio, which indicates that nitrogenous organic compounds play an important role in HNM formation. However, both the type and concentrations of organic precursors (e.g., C/N ratio, the structure of nitrogenous organic compounds) will be important for predicting HNM formation.

Formation Potential of HNMs in Wastewater Effluents

Similar to drinking water treatment, the ranking of HNM formation potential (highest to lowest) in wastewater effluents was ozonation-chlorination >>> ozonation-chloramination >> chlorination > chloramination. In addition, HNM formation was greatly reduced by applying preformed NH_2Cl rather than chlorine (Cl_2), especially after pre-ozonation.

Although a small number of WWTPs were studied in this project, if the influent flow characteristics are also included in the comparison, municipal nitrifying WWTPs exhibited the lowest HNM yields as compared to other WWTPs for ozonation-chlorination and chlorination. Conversely, the impact of biological processes and influent wastewater composition was negligible for HNM formation during chloramination and ozonation-chloramination.

Similar to the drinking waters, the best correlations were that lower DOC/DON ratios and higher DON concentrations resulted in higher HNM yields for ozonation/chlorination and chlorination of municipal nitrifying WWTP effluents.

Comparison of HNM Formations between DWTPs and WWTP Effluents

Treated drinking waters eventually reach wastewater treatment plants after household and industrial uses. Therefore, the HNM FPs of the wastewater effluents in the service area of the Greenville DTWP was compared with those of the drinking water. The results showed that HNM yields from ozonation followed by chlorination were higher in the wastewater effluents than in the treated drinking water. This indicated that there were HNM precursors in the treated wastewater effluents that were more reactive than the hydrophilic NOM components remaining in drinking water after treatment. This suggests that a significant amount of HNM precursors were either produced during biological treatment, or existed in the influent wastewater. This study examined the HNM precursors in the effluents of WWTPs before discharge. The fate and attenuation of HNM precursors in water bodies before reaching DWTPs has not been evaluated.

Formation and Speciation of HNMs and THMs in DWTPs—Effects of pH, Br^{-}, and NO_2

HNM formation was at appreciable levels for certain conditions under UFC conditions (e.g., up to 25 µg/L for Br^-/DOC ratio of 100 µg /L and pH=8). The results indicated that the major precursors of THMs and HNMs were not likely identical, as the treated water of DWTPs exhibited significantly lower THM formation than raw water, while HNM concentrations formed in the raw and treated waters were comparable at ambient conditions. However, some similarities were noted regarding the formation of these two classes of DBPs. For both THMs and HNMs, formation increased with pH (6 to 8), and treated waters had higher amounts of brominated THM and HNM species as compared to the raw waters due to the removal of DOC, but not bromide, during conventional treatment. Overall, trihalogenated HNMs (THNMs) were the major HNM species formed, and dihalogenated HNM (DHNM) peaks were also detected, but were always below the minimum reporting levels (MRLs) of the measurements, except for one case.

Tests at elevated Br^- levels showed that HNM formation increased and more brominated HNM species were observed. THNMs were still the major HNM species formed. Bromine was usually incorporated more readily into HNMs than THMs. Additionally, higher brominated HNM formation in the treated water was attributed to the higher reactivity of hydrophilic NOM components for bromine incorporation. Experiments with ozone alone (without post chlorination) did not produce brominated HNMs in waters with elevated bromide.

The presence of nitrite (2 mg/L NO_2^-) increased HNM formation during chlorination and ozonation-chlorination. Although this level of nitrite would not normally be found in drinking waters and was spiked in order to see an effect, it seems that NO_2^- can serve as a precursor to form HNMs from chlorination without preozonation. It was determined that HNM formation was higher in the raw water supplemented with NO_2^- than the treated water. It appears that there are some hydrophobic NOM components in the raw water that are removed during conventional treatment that can form HNMs in the presence of NO_2^- during chlorination.

For ozonation followed by chloramination, HNM formation was minimal (< 1 µg/L) even in the presence of bromide and nitrite.

I-THM Formation From Preformed NH_2C1

I-THM formation and speciation from preformed NH_2Cl depended on a combination of Br^-/I^- ratio and concentrations, NOM characteristics, and I^-/DOC ratios. Generally, I-THM formation decreased as pH increased for a Br^-/I^- mass ratio of approximately 10. However, when the concentrations of Br^- and I^- were elevated (e.g., 800 and 80 µg/L), there was significant I-THM formation at higher pH due to iodoform formation. The formation of iodoform was rarely observed at lower and more typical Br^- and I^- levels. The most important species were dichloroiodomethane (DCIM) and bromochloroiodomethane (BCIM).

I^-/DOC ratio was an important contributor to increases in iodine incorporation and iodoform formation. In addition, the results suggested that there is a NOM effect for iodoform formation. A higher I^-/DOC ratio was necessary in a high-SUVA water than a low-SUVA water for significant I-THM formation to occur. I-THM yields did not depend on the NH_2Cl/I^- ratio, as increasing NH_2Cl concentrations from the UFC dose of approximately 2.4 mg/L to 5.0 mg/L (as Cl_2) did not have an appreciable effect on I-THM yields.

Prechlorination Versus Preformed NH_2C1 for I-THM and THM Formation

Prechlorination (HOCl contact time) prior to ammonia addition did not always result in lower I-THM concentrations as compared to preformed monochloramine. Prechlorination sometimes increased I-THM formation as compared to preformed monochloramine under some circumstances. For prechlorination, the Cl_2/DOC ratio and/or the Cl_2/I^- ratio were critical to control both the extent of THM and I-THM formation as well as the ratio of THM to I-THM in a water sample. However, the critical Cl_2/DOC ratio to control both the concentrations of THM and I-THM in a water sample appears to be water specific.

Iodine incorporation (η_I) dominated over bromine (η_{Br}) incorporation for preformed NH_2Cl, while the reverse trend was observed for prechlorination followed by ammonia addition. Low-$SUVA_{254}$ water was more reactive in incorporating I^- during preformed chloramination, while for a high-$SUVA_{254}$ water, it was necessary to exceed an I^-/DOC threshold before iodine incorporation into I-THMs became significant.

For preformed NH_2Cl, when the Br^-/I^- level was increased to 800/80, I-THM speciation shifted towards iodoform formation. However, for more typical Br^-/I^- levels, the dominant I-THM species were DCIM and BCIM. For prechlorination, increasing contact time from 5 to 20 minutes generally resulted in a shift towards more brominated I-THM and THMs. This was attributed to the faster formation of brominated than chlorinated species and reduction in iodinated species. For I-THMs, BCIM and dibromoiodomethane (DBIM) were the dominant I-THM species, while bromodiiodomethane (BDIM) was mainly detected for shorter contact times or lower chlorine doses. With increasing Br^- and I^- concentrations, DBIM became the dominant I-THM species, while bromoform became the dominant THM species. The formation of iodoform was almost completely suppressed during prechlorination. This indicates that one consequence of the addition of Cl_2 prior to NH_3 addition will be to almost completely eliminate iodoform formation in practice.

Alternative Oxidants

Fortunately, the preoxidants ($KMnO_4$, ClO_2, or H_2O_2) tested as alternatives to prechorination did not form high concentrations of regulated THMs like chlorine. However, neither did they provide a viable alternative to prechlorination for minimizing I-THM formation. In some cases, small increases in I-THM formation were observed for preoxidation. This was attributed to reactions of alternative oxidants with Br^-, I^-, and NOM.

APPLICATIONS/RECOMMENDATIONS:

For HNMs

HNM formation is likely to be higher at ozonation plants. These utilities should consider monitoring HNM concentrations in their systems. Measuring all nine HNM species, not only TCNM, is important to assess overall HNM formation and speciation in water. Like THMs, the formation of HNMs will increase with increasing pH and bromide level. Chloramination (i.e., using monochloramine) alone or after ozonation will reduce HNMs in addition to reducing regulated THMs and HAAs. However, it is important to note that chloramination results were obtained with preformed monochloramine in this study. At full scale operations, preformed chloramines are not used. Instead, chlorine and ammonia are added in separate streams to form monochloramine. Proper mixing conditions of chlorine and ammonia are critical in monochloramine formation. Sometimes, chlorine is added to water before ammonia addition to gain disinfection credit and/or to inactivate bacteria that slough off of a biofilter. Therefore, the optimization of chloramination practices should consider consistency and compliance with a wide range of operational and regulatory requirements, as well as reducing HNM formation.

Limited results in the literature suggest that one possible approach to remove HNM precursors is to use biofiltration after ozonation. Considering the difficulty of solving several treatment challenges and goals in a single process, biofiltration offers a number of other benefits including removal of assimilable or biodegradable organic carbon, removal of taste and odor causing compounds (geosmin and MIB), removal of selected biodegradable trace pharmaceutical compounds/endocrine disruptors, and a reduction in the probability of biological growth.

The DOC/DON ratio, despite some limitations, can be a simple parameter for water utilities to assess the formation potential of HNMs in their source waters. It is expected that with lower DOC/DON ratios, HNM yields will be greater.

For I-THMs

When I^- concentrations are less than 20 µg/L and/or if the source water is high DOC and high-$SUVA_{254}$, adding HOCl and NH_3 at the same point in plants with good mixing conditions is expected to form minimal levels of I-THMs. Adding HOCl earlier in the plant before NH_3 (prechlorination) will decrease I-THM formation in most cases when iodide concentrations are higher (e.g., >80 µg/L).

Even though alternative preoxidants ($KMnO_4$, ClO_2, or H_2O_2) do not generate as high a level of THMs as chlorine, they will not be a viable alternative to prechlorination for minimizing iodinated THM formation. In some cases, they may even increase I-THM formation.

For HNMs, I-THMs, and the Other DBPs

Overall, the results obtained in this study show that ozonation followed by chloramination or chloramination alone may be a reasonable treatment to control the formation of HNMs, I-THMs, and THMs simultaneously. Because chloramines are a weaker disinfectant/oxidant, DWTPs usually need a pre-oxidant/disinfectant. The use of certain pre-oxidants in an optimized way may help utilities to control and minimize formation of both regulated and unregulated DBPs (e.g., I-THM and NDMA). Although nitrification may be observed in some distribution systems as a result of chloramination, many systems have managed to control this problem. While switching to chloramines has been linked to lead problems in some systems, there are many more systems that have had no lead issues.

Although the use of different oxidants has been linked to various DBP problems (e.g., ozone producing bromate and forming more HNMs; chloramines producing NDMA, iodine- containing DBPs; etc.), they also result in large reductions in total organic halogen (TOX) or under most conditions significantly lower amounts of HNMs or iodine-containing DBPs. Some of these DBPs are an order of magnitude or higher in toxicity, but they are also an order of magnitude or lower in concentration. Nonetheless, it is still an important goal to try to find cost-effective means of minimizing both regulated and emerging DBPs of health concern.