THE IMPACT OF DISSOLVED ORGANIC MATTER COMPOSITION ON THE FORMATION OF DISINFECTION BYPRODUCTS IN GROUNDWATER

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PROJECT SUMMARY

Title: The impact of dissolved organic matter composition on the formation of disinfection byproducts in groundwater

Project Number: WR18R003

Investigator: Christina Remucal, Associate Professor, Department of Civil and Environmental Engineering, University of Wisconsin-Madison

Period of Contract: July 1, 2019 through June 30, 2020

Background/Need:
Naturally occurring dissolved organic matter (DOM) poses a risk to human health when it reacts with disinfectants (e.g., chlorine) to form harmful disinfection by-products (DBPs) during drinking water treatment. Past research has shown that the DBP formation potential of DOM in surface waters, such as lakes and rivers, is inherently linked to its molecular composition. In contrast, little is known about the composition of DOM in groundwater or about its reactivity with disinfectants, despite the importance of groundwater as a major source of drinking water. Furthermore, there is no reliable method to predict DBP formation based on the composition of groundwater DOM. Characterizing the susceptibility of DOM in groundwater to forming toxic disinfection by-products is critical for ensuring high quality drinking water and protecting human health.

Objectives:
The three objectives of this project were to (1) characterize the bulk properties and molecular composition of dissolved organic matter (DOM), (2) quantify the formation of disinfection by-products (DBP), and (3) predict DBP formation potential based on DOM composition.

Methods:
We collected water samples from 18 drinking water utilities in Wisconsin (14 groundwater; 4 surface water). At 6 of the sites, we collected initial (pre-treatment) water and water that had undergone all treatment except for disinfection. Water receives minimal treatment at the other 11 sites, so samples were collected immediately before disinfection. All waters were disinfected with free available chlorine in our laboratory. We characterized the composition of DOM before and after reaction with chlorine using bulk measurements (e.g., dissolved organic carbon and UV-visible absorption spectra) and high-resolution mass spectrometry (i.e., Fourier transform-ion cyclotron resonance mass spectrometry). The mass spectrometry technique enabled us to identify thousands of unique molecular formulas in each sample, investigate which molecules are most reactive with chlorine, and identify novel chlorinated DBPs. We used a variety of statistical techniques to relate DOM composition with the formation of known DBPs (i.e., trihalomethanes and haloacetonitriles) at the molecular level.

Results and Discussion:
1. Initial DOM composition. The composition of DOM in initial water samples (i.e., prior to any physical-chemical treatment) ranges widely. We categorized sites into three categories: surface water (n = 4), shallow groundwater (n = 10), and deep groundwater (n = 4). The deep sites penetrate

the underlying bedrock, while the shallow sites do not. The surface water sites have the highest dissolved organic carbon concentrations, followed by shallow groundwater and deep groundwater sites. UV-vis spectroscopy and high-resolution mass spectrometry reveal that the DOM in the surface and deep groundwater sites is relatively low in molecular weight and aromaticity, which is indicative of DOM that is either microbially-derived or highly processed. The DOM in shallow groundwater sites is higher in apparent molecular weight and aromaticity, which is indicative of DOM from terrestrial sources.

2. Disinfection-by product formation. Chlorine reacts with DOM to form known and novel DBPs. The reactivity of DOM with chlorine is first characterized by measuring chlorine demand. Surface water sites has the highest chlorine demand, followed by shallow and deep groundwater. However, deep groundwater has the highest chlorine demand on a carbon-normalized basis. The higher reactivity of deep groundwater DOM with chlorine does not translate into increased formation of the DBPs measured in this study. We find that production of trihalomethanes and haloacetonitriles is similar in all water samples when normalized to the initial organic carbon concentration. Hundreds of novel high molecular weight DBPs are measured in the samples after chlorination. The largest number of novel HMW DBPs are generated from surface waters followed by shallow groundwater and deep groundwater. Although we considered Br in our formula assignments, none of the novel DBPs detected contain bromine.

3. Predicting DBP formation. The formation of trihalomethanes and haloacetonitriles correlates with bulk properties including the dissolved organic carbon concentration, specific UV absorbance, and chlorine demand. DBP formation potential can also be related to parameters derived from high-resolution mass spectrometry. Additionally, the mass spectrometry data show that chlorine reacts preferentially with aromatic lignin- and tannin-like formulas in DOM, regardless of water source. These are the same formulas where we identify novel DBP formation.

Conclusions/Implications/ Recommendations:
Both the bulk and FT-ICR MS analyses conducted in this study demonstrate that the composition of groundwater DOM is highly variable and is also distinct from surface water DOM. Despite the variability in DOM composition, chlorine reacts selectively with aromatic, electron-rich DOM. The formation of trihalomethanes and haloacetonitriles correlate well with easily measured bulk properties and this study provides mechanistic evidence to support these relationships. Importantly, the formation of novel DBPs correlates with the targeted DBPs, which indicates that DBPs such as trihalomethanes are good proxies for the DBPs detected by high-resolution mass spectrometry.

Related Publications:
A paper will be submitted for peer review in early 2021.

Key Words:
Groundwater, disinfection by-products, chlorine, dissolved organic matter

INTRODUCTION

Dissolved organic matter (DOM) is comprised of thousands of naturally occurring organic molecules that are derived primarily from plant or microbial residues. This heterogeneous mixture is found in all natural waters in concentrations ranging from 1-3 mg-C/L in groundwater to 5-30 mg-C/L in lakes. Although the composition of DOM in all waters varies with time and space, the composition of groundwater DOM is considered to be much less variable than surface water DOM due to the longer hydraulic residence time in the subsurface.[1] Within groundwater, DOM plays an important role in transporting metals, radionuclides, and organic contaminants.[2] Groundwater DOM is generally considered to be derived from soil and sedimentary organic carbon that has undergone microbial diagenesis, although the source depends on the aquifer. Groundwater DOM is depleted in oxygen, enriched in carbon, lower in aromaticity, and lower in molecular weight compared to surface water (e.g., lakes and rivers),[2-5] which has implications for its reactivity.

Although DOM is not toxic on its own, it reacts with disinfectants during drinking water treatment to produce harmful disinfection by-products. The most commonly used disinfectant in public water systems in the United States is free available chlorine (hypochlorous acid; HOCl), which is effective, inexpensive, and provides residual disinfectant throughout the distribution system. Water disinfection is critical for protecting human health, yet this benefit must be weighed against the formation of potentially carcinogenic DBPs. A subset of DBPs, including four trihalomethanes (THMs) and five haloacetic acids (HAAs), are regulated in drinking water in the United States. The regulated DBPs represent only a fraction of the DBPs that are actually present in treated water and scientists are still not able to identify all of the DBPs produced when water is chlorinated. Unregulated DBPs, including haloacetonitriles (HANs), contribute significantly to the toxicity of chlorinated drinking water.[6-8]

The formation of DBPs depends on the concentration and composition of DOM. Traditional approaches to characterize DOM rely on bulk measurements, such as quantification of the dissolved organic carbon (DOC) concentration, or spectroscopic techniques (e.g., ultraviolet-visible spectroscopy). DOC describes the overall concentration of DOM, but does not provide any information about its composition. Parameters derived from UV-vis spectroscopy provide information about composition. For example, $E_2{:}E_3$ (absorbance at 250 nm / absorbance at 365 nm) is inversely proportional to molecular weight.[9] In addition, specific UV absorbance ($SUVA_{254}$) values correlate with the degree of aromaticity.[10, 11]

Analysis of DOM by high-resolution mass spectrometry is a state-of-the-art technique that provides insight into the molecular composition of DOM. The analysis of DOM by Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) demonstrates that this heterogeneous mixture is comprised of thousands of unique molecular formulas.[11] This data is often presented in van Krevelen diagrams, which are used to assess the general chemical composition of DOM since different regions on the diagram correspond to different compound classes. FT-ICR MS has provided unique insights into the transformation of surface water DOM during drinking water treatment and has been used to identify naturally occurring and novel chlorinated and brominated formulas (i.e., DBPs).[12-15] Interestingly, a recent study found positive correlations between FT-ICR MS formula intensity of highly aromatic formulas and THM yields in surface waters.[16] However, the few studies that analyze groundwater DOM by FT-ICR MS are limited to coastal systems,[17, 18] fulvic acid isolates,[4] or hydrocarbon-contaminated groundwater,[19]

which are not representative of the aquifer systems used to supply drinking water in Wisconsin.
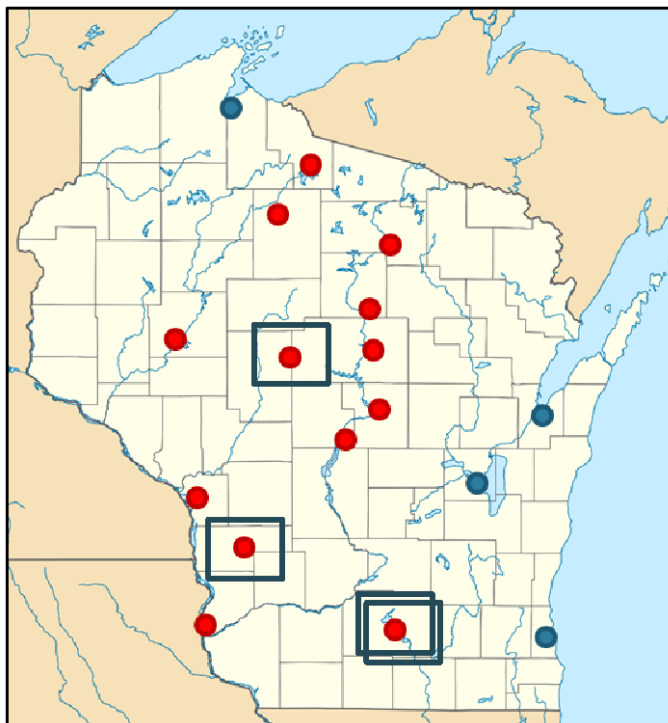
Despite the importance of groundwater as a drinking water source, little is known about DOM composition in groundwater. Groundwater is the major source of drinking water in Wisconsin, supplying 591 of the 610 utilities in the state. The remaining 19 utilities use Lake Winnebago (4), Lake Superior (2), and Lake Michigan (13). More importantly, there has been no previous attempt to systematically link the composition of groundwater DOM with its formation of toxic DBPs, which represents an important human health risk for municipal water treatment systems. A better understanding of the composition of DOM in groundwater is critical for assessing its potential to form DBPs, which is the focus of the proposed research. Thus, the three objectives of this project were to (1) characterize the bulk properties and molecular composition of dissolved organic matter, (2) quantify the formation of disinfection by-products (DBP), and (3) establish an approach to predict DBP formation potential based on DOM composition.

PROCEDURES AND METHODS

Sample collection. All water samples were collected from municipal drinking water utilities prior to disinfection in Wisconsin, USA during December 2018, March 2019, and June 2019. Four samples were collected from utilities that use surface water and 14 were collected from utilities that use groundwater (**Figure 1**). Four of the groundwater samples were collected from wells that make contact with or penetrate the underlying bedrock/confining unit and are grouped together as deep groundwater samples. The remaining 10 groundwater samples do not make contact with the underlying bedrock/confining unit and are grouped together as shallow groundwater samples. Samples were filtered (0.45 μm) and stored at 4 ºC in the absence of light.

Figure 1. Sites of water utilities sampled during this project. Surface water sites are indicated in blue. Groundwater sites are indicated in red. Deep groundwater sites that reach bedrock (>150 feet) are noted with a rectangle.

Chlorination experiments. All water samples were buffered with 1 mM phosphate (pH 7.0) for chlorination experiments. Samples were dosed with appropriate amounts of hypochlorous acid (i.e., chlorine) to yield 1 mg-Cl_2/L chlorine residual after a 24-hour reaction time at room temperature. After a reaction time with chlorine of 24 hours, remaining chlorine was quenched with sodium thiosulfate.

Bulk water chemistry. The pH and alkalinity of each sample were measured using a pH meter and autotitrator, respectively. Dissolved organic carbon concentrations ([DOC]) were measured

using a TOC Analyzer. Ions and metals were measured by ion chromatography and inductively coupled plasma-mass spectrometry, respectively. Ultraviolet-visible (UV-vis) spectra were collected from 200-800 nm. Specific UV absorbance ($SUVA_{254}$) was determined for each sample by dividing absorbance at 254 nm by [DOC]. E_2:E_3 was determined as the ratio of absorbance at 250 nm to the absorbance at 365 nm.

High-resolution mass spectrometry. Organic matter was extracted from samples using solid phase extraction and analyzed using Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) with negative mode electrospray ionization. Exported *m/z* ions were converted to neutral masses and assigned formulas in R.[11,20] Potential formulas considered for matching include $C_{0-80}{}^{13}C_{0-1}H_{0-140}O_{0-80}N_{0-1}S_{0-1}P_{0-1}Cl_{0-1}Br_{0-1}$.

Targeted DBP quantification. Targeted DBPs including trihalomethanes (chloroform, bromoform, bromodichloromethane, dibromochloromethane) and haloacetonitriles (bromochloroacetonitrile, dibromoacetonitrile, dichloroacetonitrile, trichloroacetonitrile were quantified by gas chromatograpy with electron capture detection using modified EPA standard methods 551.1.

RESULTS AND DISCUSSION
1. Initial DOM composition. The composition of DOM in initial water samples (i.e., prior to any physical-chemical treatment) ranges widely. We categorized sites into three categories: surface water (n = 4), shallow groundwater (n = 10), and deep groundwater (n = 4). The deep sites penetrate the bedrock, while the shallow sites do not. The surface water sites have the highest dissolved organic carbon concentrations, followed by shallow groundwater and deep groundwater sites (**Figure 2a**). These concentrations are within the range reported in the literature.

The composition of DOM in the different water samples was first assessed using UV-vis spectroscopy (**Figures 2b** and **2c**). $SUVA_{254}$ and E_2:E_3 values reveal that the DOM in the surface and deep groundwater sites is relatively low in molecular weight and aromaticity, which is indicative of DOM that is either microbially-derived or highly processed. The DOM in shallow groundwater sites is higher in apparent molecular weight and aromaticity, which is indicative of DOM from terrestrial sources.

FT-ICR MS was used to investigate the molecular composition of DOM in the initial water samples. A total of 9,929 unique chemical formulas were assigned in the eighteen pre-chlorination samples. The shallow groundwater samples had the largest number of total formulas (4,179 ± 362), followed by surface water (3,969 ± 338) and deep groundwater (3,653 ± 579). In each sample, 14.8 – 22.8% and 5.3 – 16.0% of the identified formulas contain nitrogen and sulfur, respectively. Analysis of weighted averages derived from FT-ICR MS data provides additional insights into molecular level differences between surface and groundwater DOM. The DOM in deep groundwater samples is more highly saturated and reduced (higher H:C values and lower O:C values) compared to shallow groundwater and surface water (**Figure 3**).

Principal component analysis (PCA) using the assigned chemical formulas and their corresponding signal intensities demonstrates the variability of DOM in the samples. This analysis shows a clear distinction between DOM derived from surface waters and DOM derived from groundwater

(**Figure 4**). Additionally, groundwater DOM samples cluster together based on the properties of the drinking water wells. Deep samples obtained from wells whose casings penetrate the underlying bedrock formations cluster tightly together and are dissimilar from shallow groundwater samples. Interestingly, the shallow groundwater samples are widely distributed, indicating a wide variety of DOM composition. The variability in composition observed using PCA is similar to the variability in bulk properties, demonstrating that groundwater DOM is even more diverse than DOM in the surface water samples studied here.
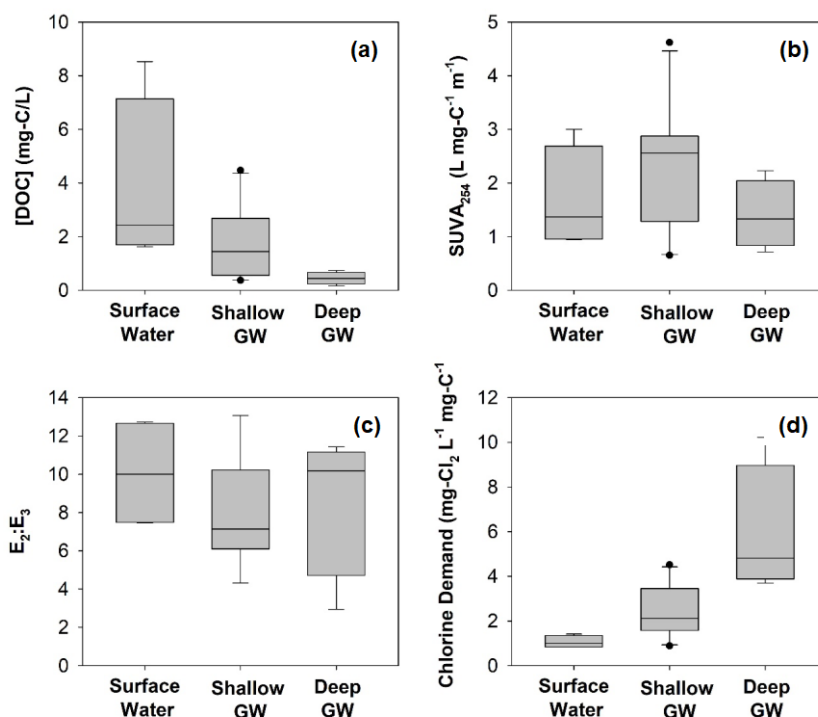
Figure 2. Summary of (a) [DOC], (b) $SUVA_{254}$, (c) E_2:E_3, and (d) chlorine demand normalized to [DOC] in initial water samples collected from surface water, shallow groundwater, and deep groundwater.
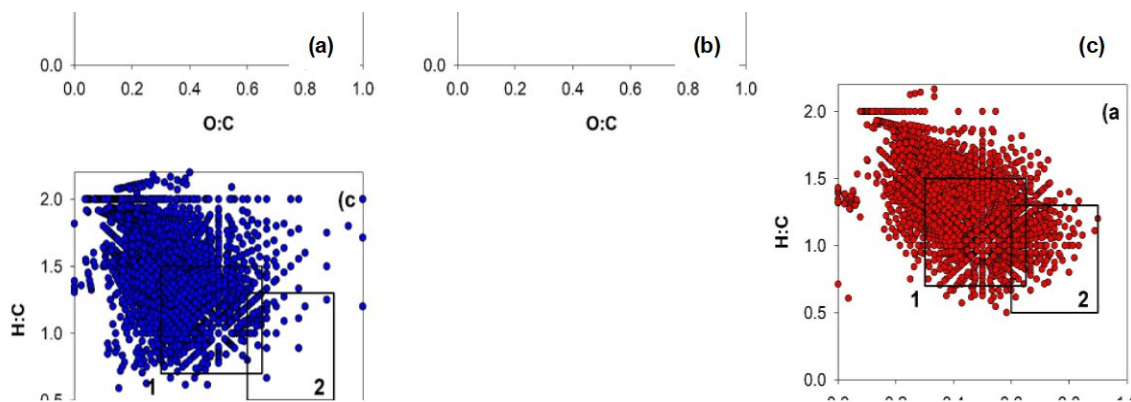
Figure 3. van Krevelen diagrams of matched formulas present in (a) all surface water samples (n = 4), (b) shallow groundwater samples (n = 10), and (c) groundwater samples that penetrate underlying bedrock (n = 4). Points correspond to individual molecular formulas identified by FT-ICR MS. Box 1 indicates lignin-like formulas. Box 2 indicates tannin-like formulas.

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2. Disinfection-by product formation. Chlorine reacts with DOM to form known and novel DBPs. The reactivity of DOM with chlorine is first characterized by measuring chlorine demand. Surface water sites had the highest chlorine demand, followed by shallow and deep groundwater. However, deep groundwater has the highest chlorine demand on a carbon-normalized basis (**Figure 1d**), which means that the organic carbon in deep groundwater is more reactive with chlorine. The higher reactivity of deep groundwater DOM with chlorine does not translate into increased formation of the DBPs measured in this study.
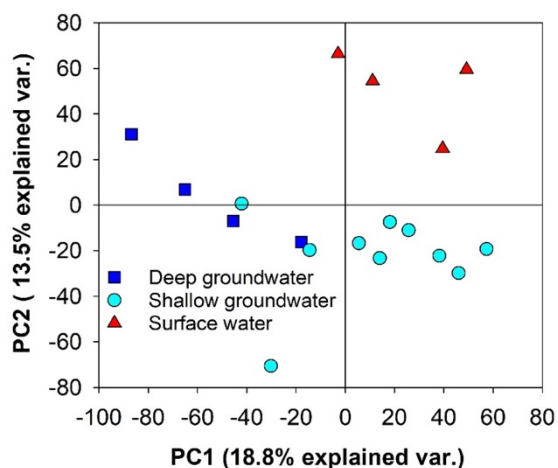
Figure 4. Principal component analysis of the matched formulas for all initial water samples.

Trihalomethane (THMs) and haloacetonitrile (HANs) formation potential was quantified after reaction with chlorine for 24 hours for all waters using samples collected immediately prior to chlorination. Surface waters formed the highest concentrations of THMs and HANs (40.0 ± 23.7 µg/L and 2.9 ± 2.5 µg/L, respectively), followed by shallow groundwater (30.3 ± 21.9 µg/L, 1.3 ± 0.7 µg/L) and deep groundwater (6.7 ± 3.2 µg/L, 0.5 ± 0.1 µg/L). The production of trihalomethanes and haloacetonitriles is similar in all water samples when normalized to the initial organic carbon concentration.
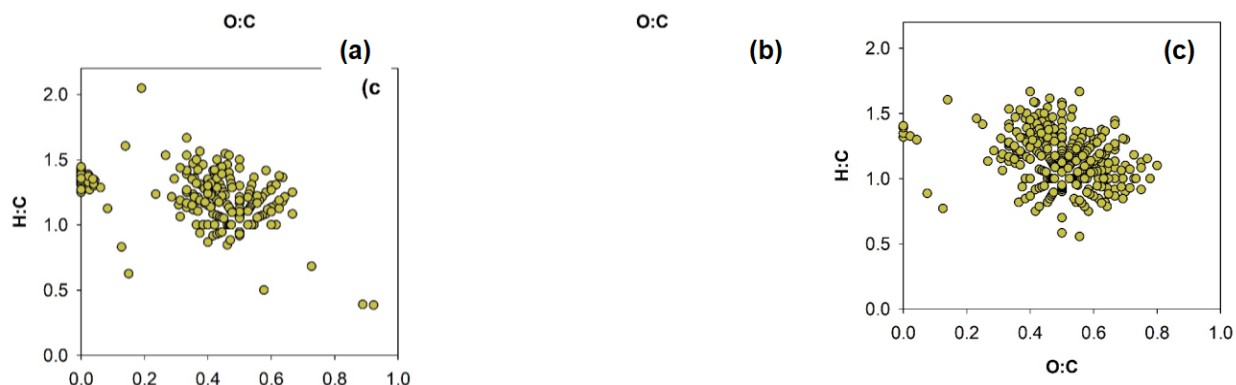
Figure 5. van Krevelen diagrams showing novel chlorinated formulas present in at least half of the (a) surface water, (b) shallow groundwater, and (c) deep groundwater samples.

Novel high molecular weight DBPs are measured in the samples after chlorination (**Figure 5**). The largest number of novel HMW DBPs are generated from surface waters (range: 306 to 773) followed by shallow groundwater (range: 40 to 643) and deep groundwater (range: 0 to 259). Although we considered Br in our formula assignments, none of the novel DBPs detected contain bromine. Despite the wide variety in initial DOM composition and the number of CHOCl formulas produced during chlorination, the composition of chlorinated formulas is similar between samples (i.e., primarily aromatic and oxidized; **Figure 5**).

3. Predicting DBP formation. The diversity of DOM composition in the samples included in this study allows us to investigate connections between DOM composition and DBP formation. Significant positive correlations (95% CI) are observed between THM or HAN formation and [DOC], $SUVA_{254}$, chlorine demand, $O:C_w$, double bond equivalents (DBE), and carbon normalized double bond equivalents (DBE/C; **Figure 6**). A significant negative correlation is observed in the relationship between THM or HAN formation and $H:C_w$. The correlations between targeted DBP formation and easily measured bulk parameters (i.e., [DOC], $SUVA_{254}$, and chlorine demand) agree with previous observations. The correlations between DBP formation and high-resolution mass spectrometry measurements (i.e., $O:C_w$, DBE, DBE/C, and $H:C_w$) have not been previously reported in a diverse data set.
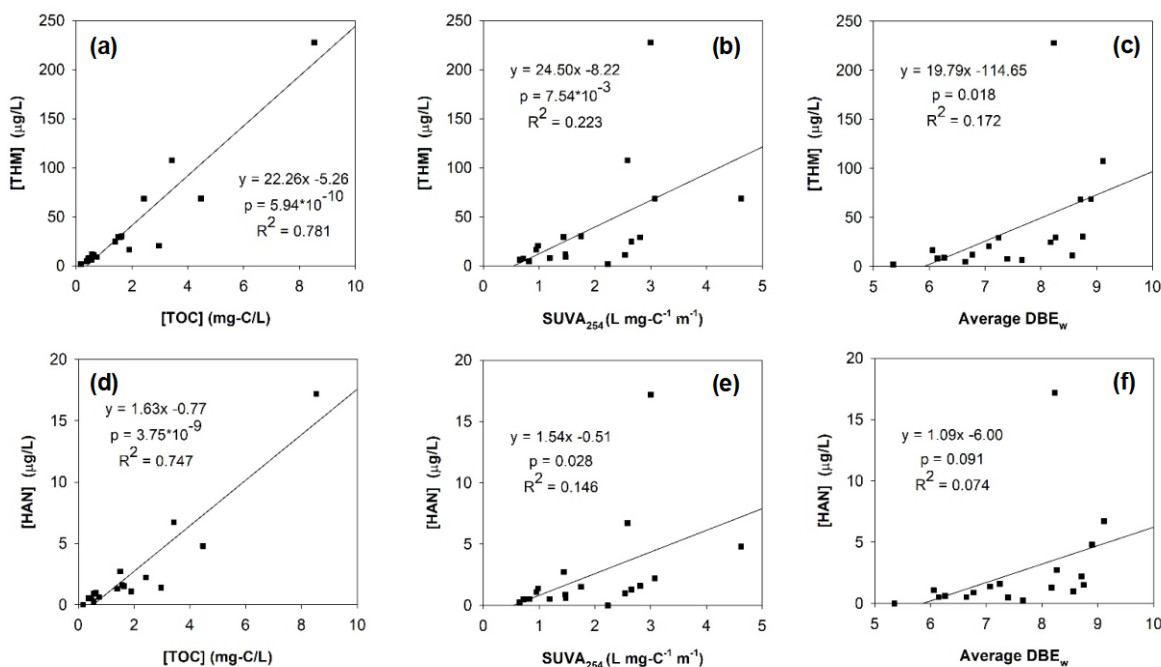
Figure 6. Correlations between THM formation potential and (a) [DOC], (b) $SUVA_{254}$, and (c) double-bond equivalents derived from FT-ICR MS data. Correlations between HAN formation potential and (d) [DOC], (e) $SUVA_{254}$, and (f) double-bond equivalents.

The formulas positively correlated with THM formation and chlorine demand are highly similar to the formulas positively correlated with $SUVA_{254}$ and are primarily located in the lignin- and tannin-like region of the van Krevelen diagram (**Figure 7**). In contrast, the formulas associated with HAN formation are not concentrated to any specific population of DOM, but are widely distributed throughout several different populations that include the same highly aromatic formulas associated with THM formation. The strong positive correlations observed between a tight cluster of aromatic formulas and the bulk properties (i.e., $SUVA_{254}$, THM formation, and chlorine demand) supports the idea that chlorine reacts preferentially with and forms DBPs from electron-rich aromatic compounds. Furthermore, the overlap in formulas associated with both DBP classes indicates that HANs and THMs share some similar precursor compounds, but the additional strong positive correlations between HANs and more aliphatic formulas indicate that these DBPs may have additional precursors.

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A strong positive correlation is observed between both THM and HAN formation and the production of chlorinated formulas detected by high-resolution mass spectrometry. This correlation shows the similarity between the formation of targeted DBPs and novel DBPs and reveals the usefulness of targeted DBPs as proxies for the formation of novel DBPs. In other words, waters that form high concentrations of THMs or HANs are highly likely to form novel DBPs that are detected by FT-ICR MS. While more work is needed to understand the toxicity implications of these novel DBPs, this result suggests that THM formation potential is a useful proxy for these unidentified DBPs.
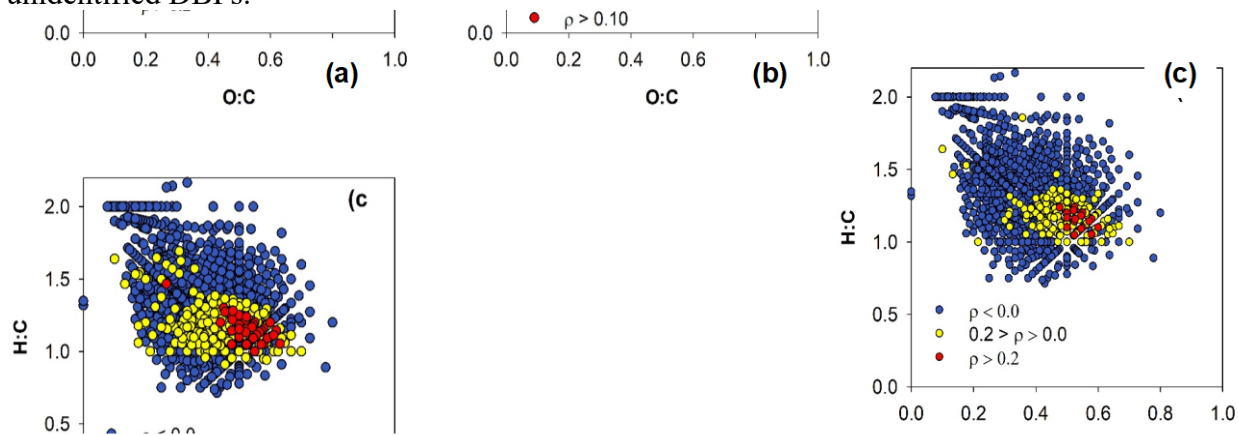
Figure 7. Spearman rank analysis relating formula intensity with (a) SUVA$_{254}$, (b) THM formation potential, and (c) HAN formation potential. Red indicates a strong positive correlation. Yellow indicates a weak positive correlation. Blue indicates all formulas with no correlation or negative correlation. Heat maps show matched formulas that were present in all water samples.

CONCLUSIONS AND RECOMMENDATIONS

We analyzed the composition and reactivity of DOM in drinking water sources collected throughout Wisconsin. While we hypothesized that the composition of groundwater DOM would be similar due to the long residence times in this environment, both the bulk and FT-ICR MS analyses conducted in this study demonstrate that the composition of groundwater DOM is highly variable and is also different than surface water DOM. These results demonstrate that it is not possible to generalize about DOM composition in groundwater and that site-specific information is needed to predict DBP formation.

Despite the variability in DOM composition, chlorine reacts selectively with aromatic, electron-rich DOM. The formation of trihalomethanes and haloacetonitriles correlate well with easily measured bulk properties and this study provides mechanistic evidence to support these relationships. Importantly, the formation of novel DBPs correlates with the targeted DBPs, which indicates that DBPs such as trihalomethanes are good proxies for the DBPs detected by high-resolution mass spectrometry.

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APPENDIX A: Awards, Publications, Reports, Patents, Presentations, Students, Impact –

<u>*Publications:*</u>
A paper will be submitted for peer review in early 2021.

<u>*Presentations:*</u>
Remucal C.K. and Milstead R. | *Formation of novel disinfection by-products in drinking water in Wisconsin* | Wisconsin American Water Works Association Conference | Madison, WI | September 17, 2020. Attendees: ~40.

Remucal C.K. and Milstead R. | *The impact of dissolved organic matter composition on the formation of disinfection by-products in groundwater* | International Humic Substances Society Conference | Estes Park, CO | August 18, 2020.[‡]

Milstead R. and **Remucal C.K.** | *Impact of dissolved organic matter composition on the formation of regulated and novel disinfection byproducts during chlorination* | American Chemical Society National Meeting | Philadelphia, PA | March 25, 2020.[‡]

Milstead R. and **Remucal C.K.** | *Identifying disinfection byproducts in groundwater using ultrahigh-resolution mass spectrometry* | North American Mass Spectrometry Summer School | Madison, WI | July 23, 2019. Attendees: ~30.

Trainer E.L., Manley D.M., Balgooyen S., Berg S.M., Milstead R.P., White A.M., and **Remucal C.K.** | *Degradation of organic contaminants in natural and engineered aquatic systems* | AEESP Emerging Contaminants Short Course | Milwaukee, WI | October 23, 2018. Attendees: ~30.

[‡] denotes conferences/meetings that were canceled due to COVID-19

<u>*Awards:*</u>
None to report.

<u>*Funded Students:*</u>
This project supported Reid Milstead for the first two years of his PhD in Environmental Chemistry and Technology at the University of Wisconsin-Madison.

<u>*Impact:*</u>
Naturally occurring dissolved organic matter (**DOM**) poses a risk to human health when it reacts with disinfectants (e.g., chlorine) to form harmful disinfection by-products (**DBPs**) during drinking water treatment. Past research has shown that the DBP formation potential of DOM in surface waters, such as lakes and rivers, is inherently linked to its molecular composition. In contrast, little is known about the composition of DOM in groundwater or about its reactivity with disinfectants, despite the importance of groundwater as a major source of drinking water. Furthermore, there is no reliable method to predict DBP formation based on the composition of groundwater DOM. Characterizing the susceptibility of DOM in groundwater to forming toxic disinfection by-products is critical for ensuring high quality drinking water and protecting human health.