Identification of Novel Brominated Disinfection By-Products of Concern in Drinking Water by Use of DIPIC-Frag Untargeted Screening

Tena Watts
November 9, 2016

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Outline

• Introduction

• Research Goals
  • Comparing methods for extraction of Br-DBPs
  • Identification of novel Br-DBPs

• DIPIC-Frag Method

• Results

• Conclusion & Future Work
**Introduction**

*Water disinfection:* process of deactivating or removing pathogens from drinking water by use of physical or chemical technologies

\[ \text{Natural Organic Matter} + \text{Inorganic Precursors} + \text{Disinfectant} = \text{Disinfection By-Products (DBPs)} \]
Disinfection By-Products (DBPs)

Trihalomethanes 0.1 mg/L

Haloacetic Acids 0.08 mg/L

- Genotoxic, bladder cancer and adverse pregnancy outcomes (Jeong et al., 2012)
- > 600 compounds have been identified in drinking water
- Only 50% of total organic halide can be accounted for by known DBPs (Richardson et al., 2012)
- Many unregulated compounds have enhanced toxicities

Brominated > chlorinated analogues
Research Questions

• What brominated compounds are yet to be identified in drinking water and how can we screen for them?
  • DIPIC-Frag method – Q Exactive UHRMS
    • Optimize conditions
    • Identify novel Br-DBPs
  • Can we produce a semi-quantitative method that is reproducible for the analysis of real drinking water extracts?
Buffalo Pound Water Treatment Plant (BPWTP)

- Located northeast of Moose Jaw, SK
- 250,000 customers (Regina and Moose Jaw)
- Water sourced from Buffalo Pound Lake, which is known to contain a high concentration of Br⁻, and it is quite eutrophic
Data Independent Precursor Isolation and Characteristic Fragment Method (DIPIC-Frag)

(a) DIA scanning

(b) Br fragment chromatogram

(c) Isotope profiles of Br

(d) Elution profiles

(e) Isotope peaks

(f) Formula calculation

(g) MS/MS for chemical structures
Data Independent Precursor Isolation and Characteristic Fragment Method (DIPIC-Frag)

A) 
- pH 7
- pH 2
- HLB
- C18
- WAX
- C18 Amide
- ESI(-)
- APCI(-)

B) 
- Relative Abundance
- 78.9172
- m/z
- Precursor ion region
- m/z 171.9466

C) 
- UHRMS
- bromine fragment

D) 
- $M_{error} = \exp\left(-0.5 \times \frac{M_{act} - M_{pred}}{\delta}\right)$
- $Isotope = 1 - \sum |r_{act,i} - r_{pred,i}|$
- $r_i = \frac{I_{M+i}}{I_M}$
- Homologue = \begin{cases} 
0, & no \\
1, & yes 
\end{cases}

E) 
<table>
<thead>
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<th>Compounds</th>
<th>m/z</th>
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<td>C5O3SBr</td>
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<td>2.1e6</td>
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Comparison of Ionization Source and Column

- Amide column, with 0.1% NH$_4$OH in water as mobile phase
- ESI
Profile of Br-DBPs in Chlorinated Drinking Water

- SPE, Amide Column, ESI
Profile of Br-DBPs in Chlorinated Water Compared by SPE Cartridge and pH
Precision of the Method: (SD/mean)

- HLB – Less variability in precision
  - 10-15%
Profiles of Br-DBPs Compared by Time Point, Stage of Treatment, and SPE Cartridge

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Results

- Halo-acetic acids (HAAs) found to be among the most abundant Br-DBPs, but some novel Br-DBPs were also detected with similar or even greater abundance.

- The top 50 Br-DBPs contributed to 35.6% of total abundance (mass of OBr’s).
Results

• Predicted structures for 41/50 most abundant Br-DBPs

• Of these 41 Br-DBPs, 18 were found to be aromatic acids or phenols

• 7 high-abundance heteroatomic Br-DBPs containing nitrogen or sulfur were detected
Sulfonic Acids

Ethyl methanesulfonate

![Chemical structures and mass spectra](slide_image)
Conclusions

1) Established a library of ~700 Br-DBPs; most of these Br-DBPs have not been previously reported in drinking water

2) The method showed good precision on actual drinking water samples, by use of HLB-pH 2

3) Novel heteroatomic DBPs showed unexpectedly high abundance
Future Work

• Compare profiles of Br-DBPs at each stage of treatment

• Effects-directed analysis to identify most toxic fractions
  • Fractionate chlorinated and source water extracts
  • Cytotoxicity and comet assay
  • MS analysis

• Extend method to a water treatment plant that employs a different treatment process (Prince Albert, SK)
Thank you

- Dr. Hui Peng
- Dr. Paul D. Jones
- Dr. John P. Giesy
- Les Dickson
- Dr. Lynn Weber
References


