 Untargeted Screening of Brominated Disinfection By-Products in Drinking Water by DIPIC-Frag Method

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Introduction

• Hundreds of DBPs have been detected in drinking water, but Health Canada only regulates 14.¹
• Cell assays, in vivo animal studies, and epidemiological studies have confirmed that DBPs can increase the risk for cancer.¹³
• Brominated DBPs (Br-DBPs) are consistently demonstrated to be more toxic than their chlorinated analogues. The identification of novel Br-DBPs has been a challenging task due to complicated interferences, the extremely low concentrations at which Br-DBPs exist, and their chemical diversity.¹³

Objectives

1) Perform untargeted screening for Br-DBPs in drinking water by adapting a data-independent precursor isolation and characteristic fragment (DIPIC-Frag) method.⁴⁵ Identify precursor ions and predict chemical formulas.

2) Compare profiles of Br-DBPs at different stages of water treatment.

Methods

• Water samples were collected from the Buffalo Pound Water Treatment Plant (BPWTP) January 19, 2015.
• Extracts were analyzed using a Q Exactive™ Ulitmate™ 3000 UHPLC system. Data were acquired in data-independent acquisition (DIA) mode.
• Analytical conditions were compared:

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<th>Method</th>
<th>SPE</th>
<th>C18</th>
<th>Amide</th>
<th>APCI</th>
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<td>Freeze-dry</td>
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• A novel chemometric strategy which combined chromatographic profiles, isotopic peaks, precursor isolation window information, and intensities was used to identify precursor ions and chemical formulas. A homologous model was further used to reduce the false positive rate.

Results: Untargeted Screening

Precursor ions and formulas were predicted for 752 (80.8%) Br-DBPs detected by ESI and 604 (78.2%) of Br-DBPs detected by APCI. With a peak cut-off of 50,000, a non-redundant library of 1,303 compounds was established.

Future Work

• Use effect-directed analysis to identify the most toxic fractions of chlorinated water, and subsequently predict which novel Br-DBPs are of greatest concern. Genotoxicity will become the endpoint of interest (comet assay).

• New water samples have been collected from BPWTP and the Prince Albert Water Treatment Plant, a plant that does not chlorinate until the final step. Br-DBP profiles will be compared between plants.

Acknowledgements

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References


Conclusions

• Different analytical conditions produced complimentary information on Br-DBP, thus, such methods are necessary for the best coverage of Br-DBPs.

• A library of 1,303 Br-DBPs was established. Many of these Br-DBPs have not been previously reported in actual drinking water.

• Br-DBPs were detected throughout the water treatment process, many even after activated carbon treatment.

• Finished water exhibited a different trend in cytotoxicity compared to raw and post-sedimentation water. Cytotoxicity may not be the most suitable endpoint for identifying Br-DBPs of greatest concern.

Results: Untargeted Screening

Fig 2. Distribution of Br-DBPs along with retention times, m/z values, and number of Br atoms. (A) Distribution of 931 Br-DBPs detected using the ESI source. (B) Distribution of 772 Br-DBPs detected using the APCI source.

Fig 3. Peak abundances of Br-DBPs detected by different analytical conditions. Peak abundances are log-transformed. Each method detected unique Br-DBPs.

Fig 4. Example of a high resolution MS² spectrum used for the prediction of chemical structures. This spectrum corresponds to a novel Br-DBP, a halogenated sulfonic acid.

Fig 5. Peak abundance distribution of Br-DBPs in chlorinated water. The 50 most abundant Br-DBPs contribute to 36.6% of total abundance, and the 100 most abundant account for 47.7%.

Fig 6. Distribution of Br-DBPs at different stages of water treatment. Many Br-DBPs produced by chlorination remain present in the water throughout the treatment process, but some are removed or newly formed in later stages. Finished water was filtered over activated carbon.

Fig 7. CHO-K1 72h cytotoxicity of concentrated water extracts from different stages of water treatment. When the concentration factor was less than 9.375x, the finished water was more toxic than the raw water and water collected post-sedimentation; however, at concentrations greater than 9.375x the finished water was less toxic.