Abstract

Natural organic matter (NOM) is found in soil and water. When chlorine is used to disinfect water it reacts with dissolved NOM to form potentially harmful disinfection byproducts (DBPs). Because NOM is so varied the ways that DBPs form are poorly understood. To better understand the reactions Suwanee River fulvic acid (SRFA), a portion of NOM, was separated by polarity into 100 fractions (FRCs) using high performance liquid chromatography (HPLC). Selected fractions were then analyzed using liquid chromatography mass spectrometry (LCMS) before and after chlorination to observe changes in polarity and mass distribution. Fifteen acids with similar polarity to the fractions (Standards) were also analyzed to compare the results. The analysis showed that early eluting, high polarity samples appeared to fragment and lose material as volatile DBPs, whereas non-polar material reacted by incorporating chlorine. Loss of material resulted in a weaker signal for early eluting samples, whereas later samples increased in signal strength regardless, indicating a higher ionization potential. Evidence for different reactions occurring according to polarity agrees with previous literature indicating NOM follows multiple reaction pathways simultaneously. The HPLC column is currently being exchanged for a preparative column to collect less abundant FRCs for analysis.

Objectives

This experiment aims to use LCMS to reveal the dominant reaction pathways in different portions of SRFA. Because different methods of water flocculation remove different portions of NOM, understanding how the polarity of FA affects the DBPs produced can be used to inform the method selected.

Methods

Fractionation:
SRFA was dissolved in water and fractionated using HPLC with a Water’s Corporation X-Bridge phenyl column (3.5mm, 4.6mm x 150mm). The mobile phase consisted of deionized water (18.2 MΩ) with 0.1% formic acid (Optima LC/MS) with a step gradient of increasing acetonitrile (Optima LC/MS) and 0.1% formic acid concentration. FRCs were dried using a Labconco Centrivap Cold Trap at 80 °C.

Chlorination:
FRCs were dissolved in deionized water and total organic carbon (TOC) concentration was determined using a Shimadzu TOC-L CPH/CPN and chlorinated with 5.65-6.00% NaOCl stock (Laboratory Grade) to a ratio of 1.6 mg Cl to 1.0 mg TOC. Samples were allowed to sit undisturbed in a dark cabinet at room temp (~22 °C) for three days and then frozen at -80 °C until analysis.

LCMS:
Because samples could not be de-chlorinatated prior to LCMS analysis without dowing the parent signal, the samples were thawed and analyzed in small batches. By spending less time thawed the discrepancy in how long each sample could chlorinate was minimized. LCMS analysis was carried out using an LTQ Velos ion-trap mass spectrometer (Thermo Scientific, USA) in negative ion mode using the same liquid chromatography method and material as fractionation.

Results

All samples showed a drastic change in mass spectrum after chlorination. Highly polar FRCs experienced a large loss of higher mass signals, with remaining signals being concentrated toward a lower mass range. Less polar FRCs showed a much stronger signal at high mass ranges than before chlorination. Standards confirmed this trend, with polar Standards losing parent mass signal and non-polar Standards gaining peaks strongly indicative of incorporating one or more chlorine atoms.

Conclusions

• Different portions of SRFA react with chlorine along different reaction pathways, resulting in a large variety of DBPs.
• Polarity can be used as an effective indicator of SRFA’s most likely reaction path.
• Highly polar FRCs experienced the most mass loss, indicating the production of more volatile DBPs.
• Less polar FRCs showed a much higher tendency to result in high mass DBPs by incorporating chlorine into existing compounds, perhaps by adding ClOH to double bonds.

Future Directions

• The HPLC column is currently being exchanged for a preparative column to aid in collecting less abundant FRCs for analysis.
• A method of fractionating Suwannee River humic acid, another portion of Suwannee River NOM, is being explored.
• Samples of chlorinated FRCs are being shared with collaborators for bioassay using cancer cells and potentially shrimp, to discover which type of DBP is most hazardous to living organisms.

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Literature Cited