Formal Modeling of Yields and Speciation of Dihaloacetonitriles Formed in Chlorinated Drinking Water at Varying Bromide Concentrations

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Background: Chlorination and DBP formation

Chlorination + Natural Organic Matter (NOM) → Control of microbiological risk

Surface waters

Disinfection by-products (DBPs)

THMs, HAAs, Others (HANs; MX; etc.)

Total Organic halogens (TOX)

>50% unknown (Krasner et al., 1999; 2006)

Many DBPs are toxic and carcinogenic (Richardson et al., 2003; 2007; Plewa et al., 2004)

Regulation for controlling DBPs (Roccaro et al., 2005; 2007)

Rook, 1974
Background: **DBP ICEBERG**
What we know of unknown DBP (Richardson et al., 2002)

Regulated DBPs (e.g. THMs, HAAs, Bromate, Chlorite)

Unregulated known DBPs (>600 species)

Unknown DBPs (70%)

Non-halogenated compounds

Halogenated compounds

Background: **DBPs occurrence**

Unlike other contaminants that may or may not be present in drinking water…

**DBPs are ubiquitous**
The nature of halogen atoms incorporated in DBPs also affects their toxicity which follows an I > Br >> Cl order (Richardson et al., 2007)

Nitrogenous DBPs (e.g. HANs and HNMs) are much more toxic than carbonaceous DBPs (Richardson et al., 2007)
Background: DBPs toxicity per group
(Richardson et al., 2007)

Among unregulated DBPs, several species occur at much lower concentrations (ng/L to sub-μg/L) than those of THMs and HAAs but their toxicity is higher.

Some of the Emerging DBPs include Haloacetonitriles (HANs), Halonitromethanes (HNMs), Haloamides (HAMs), iodo-THMs, iodo-acids, halofuranones (MX), Nitrosamines (e.g. NDMA).

Many species of Emerging DBPs are much more toxic than regulated DBPs.
Background: Concentration and speciation of DBPs

- Content and reactivity of NOM
- pH, temperature
- NOM and Br⁻ removal
- Reaction time and Temperature
- Chlorine dose

Surface water quality

DBPs concentration and speciation (Reckhow et al., 1990; Cowman and Singer, 1996; Krasner, 1999; Crouè et al., 2000)

Background: NOM


Complex entity Site specific Halogenation processes are complexes and not well understood

NOM
- Hydrophilic fractions
- Humic species (humic, fulvic acids)
- Hydrophobic fractions
- DBPs

NOM isolation and fractionation to study its properties and reactivity

- Dissolved organic carbon (DOC).
- Dissolved organic nitrogen (DON).
- UV Absorbance (UV₅₀).
- Specific UV Absorbance (SUVA₅₀).
- Fluorescence.
Several models have been developed in order to understand how water quality parameters affect DBPs formation, to explore the kinetics of DBPs formation or to predict DBPs yields in the field (Nokes et al., 1999; Sadiq et al., 2004; Hong et al., 2007).

Modeling DBPs consists of establishing relationships between DBPs levels in waters, and the parameters of water quality that can be linked to their formation:

- chlorine dose, NOM characteristics (DOC, UVA, SUVA, Fluorescence, arc.), pH, water temperature, bromide, iodine, reaction time, residual chlorine, etc. (Sadiq et al., 2004; Obolensky and Singer, 2008).

Fundamentally, models for DBPs formation have been developed using statistical and limited mechanistic approaches.

- **Statistical models** produce best-fit empirical equations that serve only as predictive tools, without providing any insight into the halogenation mechanisms.

- **Mechanistic modeling** is based on the characterization of the kinetics reactions of chlorination process. For this purpose, these models often incorporate “a priori” kinetics assumptions.
Objective

- Study of DHAN (dichloro-, bromochloro- and dibromoacetonitrile) formation and NOM transformations based on the kinetic analysis of DHAN data and also via differential spectroscopy that quantifies the extent of NOM halogenation.

Materials and methods: Experimental

- Chlorination experiments were carried mostly using Lk. Washington water at pH 7 at widely varying reaction times and bromide concentrations (from background to 2 mg/L). Additional data sets were obtained for water chemistries of North American and Italian provenance.
- UV absorbance were analyzed using a 5 cm quartz cell on a Perkin-Elmer Lambda 18 UV/Vis Spectrophotometer at $\lambda=200-600$nm. All reported spectra were normalized to the cell length of 1 cm. DOC was analyzed using an O.I. Analytical 1010 total organic carbon analyzer.
- Concentrations of THMs, HANs, HAAs were determined using standard analytical procedures (EPA methods 551.1 and 552.2) and a Perkin-Elmer AutoSystem gas chromatograph equipped with an electron capture detector.
Materials and methods: Modeling

- A previously published approach to model mixed chlorination/bromination pathways via apparent dimensionless ratios of bromination/chlorination reaction rates at each halogen incorporation node (Nokes et al., 1999; Cowman and Singer, 1999) was used to study DHAN speciation.
- Relevant theoretical speciation formulas were modified to account for the hypothesis that DHAN species are cleaved from dihalogenated precursors in NOM.
- A genetic algorithm (Pikaia) for function optimization (Charbonneau and Knapp, 1995) was used to find the halogenation reaction rates.

![Reaction diagram]

\[ \gamma_{HAN}^{k_1} = \frac{k_{HAN}^{k_1}}{k_{HAN}^{k_2}} \]
\[ \gamma_{HAN}^{k_2} = \frac{k_{HAN}^{k_2}}{k_{HAN}^{k_3}} \]
\[ \gamma_{HAN}^{k_3} = \frac{k_{HAN}^{k_3}}{k_{HAN}^{k_4}} \]
\[ \gamma_{HAN}^{k_4} = \frac{k_{HAN}^{k_4}}{k_{HAN}^{k_5}} \]
\[ \gamma_{HAN}^{k_5} = \frac{k_{HAN}^{k_5}}{k_{HAN}^{k_6}} \]
Materials and methods: Modeling

\[
[DCAN] = \frac{TOT_{DBAN}}{\left(1 + \frac{k_2^{HAN}}{k_1^{HAN}} \frac{[HOBr]}{[HOCI]}\right)\left(1 + \frac{k_4^{HAN}}{k_3^{HAN}} \frac{[HOBr]}{[HOCI]}\right)}
\]

\[
[DBAN] = \frac{TOT_{DBAN}}{\left(1 + \frac{k_1^{HAN}}{k_2^{HAN}} \frac{[HOBr]}{[HOCI]}\right)\left(1 + \frac{k_3^{HAN}}{k_4^{HAN}} \frac{[HOBr]}{[HOCI]}\right)}
\]

\[
[BCAN] = \frac{TOT_{DBAN}}{\left(1 + \frac{k_1^{HAN}}{k_2^{HAN}} \frac{[HOBr]}{[HOCI]}\right)\left(1 + \frac{k_3^{HAN}}{k_4^{HAN}} \frac{[HOBr]}{[HOCI]}\right)\left(1 + \frac{k_5^{HAN}}{k_6^{HAN}} \frac{[HOBr]}{[HOCI]}\right)}
\]

• Dimensionless speciation coefficients, designating the molar ratio of HOBr and HOCl as X:

\[
f_{DCAN} = \frac{1}{\left(1 + \gamma_1^{HAN} X\right)\left(1 + \gamma_2^{HAN} X\right)}
\]

\[
f_{DBAN} = \frac{\gamma_1^{HAN} \gamma_3^{HAN} X^2}{\left(1 + \gamma_1^{HAN} X\right)\left(1 + \gamma_3^{HAN} X\right)}
\]

\[
f_{BCAN} = 1 - f_{DCAN} - f_{DBAN} = \frac{\left(\gamma_1^{HAN} + \gamma_2^{HAN}\right)X + \left(\gamma_1^{HAN} \gamma_2^{HAN} + \gamma_2^{HAN} \gamma_3^{HAN}\right)X^2}{\left(1 + \gamma_1^{HAN} X\right)\left(1 + \gamma_2^{HAN} X\right)\left(1 + \gamma_3^{HAN} X\right)}
\]
Absorbance spectra of chlorinated LW water

\[ \Delta A_i(t) = A_{i\text{ (initial)}} - A_i(t) \]

Differential absorbance spectra of chlorinated LW water

Reaction time increases from 5 minutes
DCAN vs. $\Delta A_{272}$ correlation
at varying Br concentrations

![Graph showing DCAN vs. $\Delta A_{272}$ correlation at varying Br concentrations.]

DBAN vs. $\Delta A_{272}$ correlation
at varying Br concentrations

![Graph showing DBAN vs. $\Delta A_{272}$ correlation at varying Br concentrations.]

Effect of bromide on molar concentration of Br-and N-DBPs

DHAN speciation: Experimental and model data

Lake Washington

Ancipa
DHAN speciation: Experimental and model data

\[ \gamma_i = \frac{k_{i-Br}}{k_{i-Cl}} \]

Lake Washington

\[ \chi = 3.0 \]

Ancipa

\[ \chi = 3.0 \]

DHAN speciation - LW: differential absorbance slopes and DHAN speciation coefficients
DHN speciation - LW: Correlation between differential absorbance slopes and DHAN speciation coefficients

\[ R^2 = 0.83 \]

Conclusions

- Total molar yields of DHANs increase more than two-fold at higher bromide concentrations.
- Interpretation of both kinetic and differential absorbance data confirmed the applicability of the formal DHAN speciation model and showed the existence of varying preferences towards bromination pathway at different reaction nodes.
- The results indicate that speciation of several classes or bromine-containing DBPs can be interpreted and modeled based on a consistent and transparent approach.
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