Health Risk Estimation for Unregulated DBPs in Chloraminated Drinking Water

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Background

Disinfection by-products (DBPs) are formed when natural organic matter (NOM) reacts with chemical oxidants in the water disinfection process. Halogenated DBPs are both cytotoxic and genotoxic, which have the potential to cause adverse health effects [1]. Currently, 4 species of trihalomethanes (THM_4) and 5 species of haloacetic acids (HAA_5) are regulated by USEPA [2]. Although the toxicity of unregulated DBPs can be many orders of magnitude higher than that of regulated DBPs [3], it is difficult to measure these unregulated DBPs because they are generally present at very low concentration levels in drinking water.

Since 1976, more than 600 DBPs have been reported, but only a few of them have been quantitatively assessed for their occurrence and health effects. Since there are so many DBP species present in drinking water, and they have various toxicological pathways, it is even harder for researchers to assess the health risks for DBP mixtures as a whole.

The US EPA has evaluated the chemistry and toxicology of a DBP mixture that represents the compound distribution in a typical chlorinated drinking water in the 2002 four-lab study[4]. But, as of yet, there hasn't been an evaluation for chloraminated water samples.

Objectives

1. Measure targeted unregulated DBPs concentrations in reverse osmosis (RO) concentrates for three chloramination treatment options.
2. Estimate developmental and reproductive health risks associated with the treated RO concentrates by using the US EPA Relative Potency Factor (RPF) approach.

Methods

Sample	Chloramination Options
Batch A	Preformed chloramine is added to water
Batch B	Short free chlorine contact time (3 min) before ammonia added
Batch C	Long free chlorine contact time (20 min) before ammonia added

Table 2: UW Chemical Analysis Methods

Targeted DBPs	Analysis Method
9 haloacetamides (HAM9)	LLE/GC-ECD[6,7]
12 haloacetic acids (HAA12)	LLE/GC-ECD[8]
10 trihalomethanes (THM10)	
12 haloketones (HK12)	
4 haloacetonitriles (HAN4)	SPE/GC-MS[9]
1 halonitromethane (chloropicrin)	
1 haloaldehyde (chloral hydrate)	

RPF method for health risk estimation[5]

First, no-observed-adverse-effect-levels (NOAELs) of DBPs were gathered from a literature review (Table 3). DBP dosages were determined from measured concentrations in RO concentrates and assumed daily water consumption rates for rats (0.1 g drinking water/g body weight). Then bromodichloromethane was selected as the index chemical to standardize the common toxicity of each chemical, and the chemical's dose-response curve (Eqn 1) was developed via EPA benchmark dose software. RPFs for each chemical were calculated according to Eqn 2. The final step was to normalize each chemical's dosage and determine the overall toxicity based on dose response curves of the index chemical via Eqn 3.

$$P(effect) = 1/[1+\exp(11.7 - 2.5\times\ln(dosage))] \quad \textbf{Equation 1}$$

$$RPF_i = \frac{NOAEL(bromodichloromethane)}{NOAEL(otherchemical)} \quad \textbf{Equation 2}$$

$$R_{mixture} = f_1 \cdot \sum_{i=1}^{n} (RPF_i * D_i) \quad \textbf{Equation 3}$$

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Chemical Analysis Results

THM_4 concentration was highest in Batch C (5.4 ppm or 5400 ppb), which was 11 and 0.4 times higher than concentration in Batches A and B. Similarly, HAA_9 concentration was also highest in Batch C (3.1 ppm), which was almost as high as 3.5 times and twice as concentrations in Batch A and B, respectively.

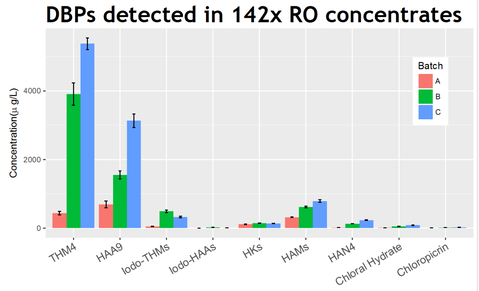

Figure 1: Summary of DBP compound classes detected in 142X RO concentrates (N=3) [10]

As seen with THM_4 and HAA_9, Batches B and C have much higher formation of all unregulated DBPs than in Batch A. Many unregulated DBPs that were below detection limits in Batch A were able to be evaluated in Batches B and C. The trend was more obvious for brominated and iodinated species.

In general, unregulated DBPs concentrations in Batch C were significantly higher than concentrations in Batch B, such as HAMs, HAN4, chloropicrin and chloral hydrate. HK concentrations in Batch B and C were at a similar range. But iodinated THMs and HAAs had much higher formation in Batch B, revealing iodide oxidation and iodine incorporation during Batch B's chloramination.

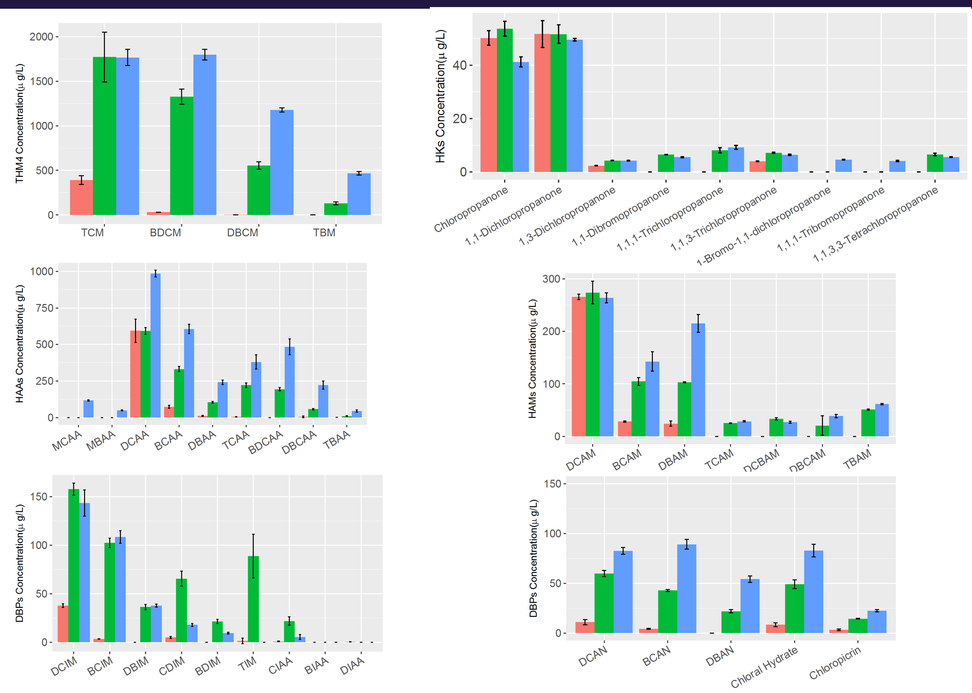

Figure 2: DBP speciation in 142X RO concentrates (N=3) [10]

Health Risk Estimation

Table 3 lists the 17 DBPs with available NOAELs for reproductive and developmental effects that were selected for health risk estimation. BDCM was selected as the index chemical, and probability of an effect was calculated based on BDCM's dose response curve (Eqn 1) and BDCM equivalent dose.

As shown in Table 4, Batch C RO concentrates had a highest probability of effect at 4.65×10^{-6} for rats. It suggested that disinfection with preformed chloramine was associated with the least negative health impacts. Chloraminated RO concentrates with long free chlorine contact time could produce significant health risks compared to ones with short contact time.

The health risk estimation has a few limitations. It only took 17 DBPs into consideration, while the effects resulting from other measured or unidentified DBP fractions were unknown. RPF method could exclude possible interaction effects among components. RPF method also assumes that all other DBPs have similar mode of action and dose-response curve to the index chemical. These assumptions were uncertain before evaluation.

Table 3: Parameters for Risk Estimation[4]

Chemical	NOAEL (mg/kg/d)	RPF
Chloroform	50	0.5
Bromoform	100	0.3
Bromodichloromethane	25	1.0
Chlorodibromomethane	40	0.6
Monochloracetic acid	70	0.4
Dichloroacetic acid	14	1.8
Trichloroacetic acid	33	0.8
Monobromoacetic acid	50	0.5
Dibromoacetic acid	13	1.9
Bromochloroacetic acid	20	1.3
Tribromoacetic acid	39	0.6
Dibromochloroacetic acid	89[11]	0.3
Dichloroacetonitrile	55	0.5
Bromochloroacetonitrile	5.5	4.5
Trichloroacetonitrile	1	25
Dibromoacetonitrile	5	5.0
1,1,3,3-tetrachloropropanone	4.8[12]	5.2

Table 4: Comparison of health risk estimates based on DBP levels in 142X RO concentrates

Sample	P(effect)
Batch A	7.33×10^{-8}
Batch B	1.48×10^{-6}
Batch C	4.65×10^{-6}

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