Aeration to remove THMs from drinking water

Ron Hofmann
Susan Andrews
Arash Zamyadi
Hong Zhang
DBPs: a distribution system issue (too!)

- Distribution system strategies to minimize DBPs
  - Chlorine → chloramines
  - Minimize chlorine residual (boost vs. large initial dose)
  - Reduce chlorine demand (e.g. ozone+BAC)
  - Reservoir aeration

DBPs: a bit of history

- THMs discovered in 1970s in tap water
  - Chloroform
  - Bromodichloromethane (BDCM)
  - Dibromochloromethane
  - Bromoform

- 1970s research: THMs → cancer in rats and mice
  = THM regulations

- Recent work: higher bladder cancer rates in communities with higher THMs (epidemiological studies)
But...

• Early rat/mice studies administered THMs in corn oil: subsequent tests administering chloroform in water showed lower/no cancers in rats/mice.

• U.S. EPA now says that chloroform is not carcinogenic at drinking water concentrations
  ▫ The other 3 THMs may still be suspect (e.g. BDCM)

But what about those epidemiological studies? (correlation vs. causation)
DBPs

- Over 500 DBPs have been identified (Plewa 2004)
  - Trihalomethanes
  - Haloacetic acids
  - Haloacetonitriles
  - Haloacetamides
  - Halonitromethanes
  - Iodoacids
  - Aldehydes
  - MX compounds
  - Etc....
DBP formation

organic molecule + Cl₂ →

Cl₂ + bromide/iodide →
DBPs:

Chlorine + organics = hundreds of types of small organics containing N, and Cl, Br, I
Coming back to the epidemiological studies...

• Hrudey (2008) and Nieuwuwenhuijsen (2010)
  ▫ Reviewed previous epidemiological studies, and conducted large European study
  ▫ Urinary bladder, colon, rectum cancers are the only (weakly) correlated illnesses to DBPs
    • Hrudey (2008), Bull (2012): THMs do not have sufficient potency to cause such illnesses

• Counterpoint: High dermal absorption (i.e. showers) of BDCM (a THM) (Leavens, 2007)
The different classes of DBPs

1. DBPs containing N = more toxic (Plewa 2008)
2. Toxicity: I > Br > Cl (Plewa 2008)

(See graphs)
Toxicity based on Chinese hamster ovary cells (cytotoxicity and genotoxicity)

Figure 7. Cytotoxicity and genotoxicity indices for carbonaceous-DBPs (C-DBPs) versus nitrogen-containing DBPs (N-DBPs).

Figure 8. Cytotoxicity and genotoxicity indices of mono-, di- and trihalogenated DBPs from the CHO cell database (6 DBPs in each group).

Plewa et al., 2008. Comparative mammalian cell toxicity of N-DBPs and C-DBPs. ACS.
The different classes of DBPs

1. DBPs containing N = more toxic (Plewa 2008)
2. Toxicity: I > Br > Cl (Plewa 2008)

Interesting Thought of the Day

Chloramines can promote incorporation of I into DBPs (chlorine converts I to iodate, which is inert)
Summary of DBP toxicity

• Epidemiological studies show evidence of DBP-related illnesses

• THM toxicity studies
  ▫ don’t support a link to the types of illnesses in the epidemiological studies
  ▫ show “low” toxicity relative to other DBPs

• More plausible that other DBPs are causing illness
  ▫ N, I, Br-containing DBPs
A note about THM regulations

If THMs probably don’t affect public health, should we eliminate the regulation?

- THMs often correlated to other DBPs
- THMs are easy/cheap to measure

*THMs: maybe a decent indicator of all DBPs*
Aeration for THM removal

In this research, spray aeration achieved trihalomethane (THM) reductions of 20 to > 99.5%, depending on droplet Sauter mean diameter, droplet travel distance, water temperature, and THM species. Some storage systems may require nothing more than a redesign of water tank influent piping and addition of a spray nozzle, similar to what is shown in this illustration, system in order to realize significant THM reductions.

e.g. Opflow, 37:11 (2011)
Project at University of Toronto

- Objective: to determine if aeration significantly reduces overall “toxicity”

- Modelling DBP volatility vs. toxicity
  - Using toxicity data from Plewa et al. (2002-2008)
CHO cell cytotoxicity as %C/3 values - Log Molar Concentration

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**Cytotoxicity**

- Henry’s Law constant

**CHO cytotoxicity.** Plewa et al. (2002, 2004a, 2004b, 2008a, 2008b)
CHO genotoxicity. Plewa et al. (2002, 2004a, 2004b, 2008a, 2008b)

- Henry’s Law constant
<table>
<thead>
<tr>
<th></th>
<th>Approx. “Toxicity”</th>
</tr>
</thead>
<tbody>
<tr>
<td>THMs</td>
<td>1</td>
</tr>
<tr>
<td>Haloacetic acids (HAAs)</td>
<td>10</td>
</tr>
<tr>
<td>Haloacetonitriles</td>
<td>1000</td>
</tr>
<tr>
<td>Haloamides</td>
<td>1000</td>
</tr>
</tbody>
</table>
Predicted % removals during aeration

<table>
<thead>
<tr>
<th>DBP</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>THMs</strong></td>
<td>-</td>
</tr>
<tr>
<td>Chloroform</td>
<td>99</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>28</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>13</td>
</tr>
<tr>
<td>Bromoform</td>
<td>2</td>
</tr>
<tr>
<td><strong>HAAs</strong></td>
<td>-</td>
</tr>
<tr>
<td>MCAA</td>
<td>6</td>
</tr>
<tr>
<td>MBAA</td>
<td>5</td>
</tr>
<tr>
<td>DCAA</td>
<td>40</td>
</tr>
<tr>
<td>TCAA</td>
<td>32</td>
</tr>
<tr>
<td>DBAA</td>
<td>3</td>
</tr>
</tbody>
</table>

### Haloacetonitriles

0.2-12

### Aldehydes

3-16

### Haloacetamides

0.5-5.6

### Halonitromethanes

0.3-3

### Trichloronitromethane

16

### Iodo acids

0.7-11

### MX

0.3

### Iodo THMs

0.7-11
“If we remove 50% THMs (and X% other DBPs), can we quantify overall reduction in toxicity (e.g. CHO cytotox.)?”

No. DBP concentration vs. toxicity model is not completed.

- Work to be completed at U of T
Aeration for THMs: a good idea?

• Does it solve a regulatory problem?  
  Yes!
• Does it improve the safety of the water?  
  Most probably yes!
• By a lot?  
  Probably not.

Should aeration be implemented instead of a different DBP minimization method?
If not aeration, then what?

- Remove organic precursors prior to chlorination or chloramination
  - Avoid prechlorination
  - Enhanced coagulation
  - Optimized coagulation
  - Ozone + BAC
  - MIEX, activated carbon
  - Other technologies...
Questions?
DBPs: a distribution system issue (too!)

- Distribution system strategies to minimize DBPs
  - Chlorine → chloramines
  - Minimize chlorine residual

Derivation of Health Canada chloroform limit:

1979 study: liver cysts in dogs observed at lowest dose of 177 mg/L
\[\div 10\] introspecies variation (= 17.7 mg/L)
\[\div 10\] interspecies variation (= 1.7 mg/L)
\[\div 7\] lifetime vs. short-term exposure (=0.25 mg/L)
\[\div 3\] for LOAEL vs. NOAEL (=0.084 mg/L)
0.084 mg/L rounded to 0.080 mg/L (80 µg/L)
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If you’re in a hurry...

- THMs ≈ 25% of all DBPs
  - volatile
  - minimal toxicity

- Other DBPs
  - may include much more toxic DBPs
  - generally not very volatile