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INNOVATIONS AND APPLICATIONS 2

Effect of UV treatment on formation of disinfection by-products in chlorinated seawater swimming pools
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Abstract
A laboratory scale study has been conducted to analyse the effect of UV irradiation on the formation of several DBPs in seawater pools. The pool samples were collected from three indoor public seawater pools and exposed to two different UV doses and then chlorinated in dark for 24 h. In this study, effect on the formation of various volatile disinfection by-products e.g. trihalomethanes (THM), haloacetonitriles (HAN) and haloacetic acids (HAA), were observed in laboratory experiments using medium pressure UV treatment after post-UV chlorination. Results showed that post-UV chlorine demand was increased, dose dependently, with UV treatment. Results also indicated that post-UV chlorination induced formation of several DBPs. However, the formation of HAAs were decreased significantly, dose dependently, with post-UV chlorination which could also mean that HAAs decomposition might occur due to heat from UV exposure. Furthermore, the breakage of HAAs molecules into smaller molecules would also mean that they resulted an increase in THMs. Overall, the formation of HAAs were decreased but the formation of THMs and HANs were increased with post-UV chlorination. There is need to standardize the application of UV system in the seawater pool.
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DTU Environment
Department of Environmental Engineering
Disinfection By-Products

**Dissolved matters:** Sweat, Urine, Lotion, Shampoo, Make-up

**Particles:** Hair, Skin cells

Bacteria & virus

**Dissolved Organic Carbon (DOC)** + Chlorine

**Disinfection By-Products (DBPs)**

- e.g. Chloramines
- Trihalomethanes
- Haloacetonitriles
- Haloacetic acids
# Seawater Pools

## Brominated DBPs

**Composition of seawater (mg/L)**

<table>
<thead>
<tr>
<th></th>
<th>Typical Seawater</th>
<th>Eastern Mediterranean</th>
<th>Arabian Gulf at Kuwait</th>
<th>Red Sea at Jeddah</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride (Cl⁻)</td>
<td>18.980</td>
<td>21.200</td>
<td>23.000</td>
<td>22.219</td>
</tr>
<tr>
<td>Sodium (Na⁺)</td>
<td>10.556</td>
<td>11.800</td>
<td>15.850</td>
<td>14.255</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>2.649</td>
<td>2.950</td>
<td>3.200</td>
<td>3.078</td>
</tr>
<tr>
<td>Magnesium (Mg²⁺)</td>
<td>1.262</td>
<td>1.403</td>
<td>1.765</td>
<td>742</td>
</tr>
<tr>
<td>Calcium (Ca²⁺)</td>
<td>400</td>
<td>423</td>
<td>500</td>
<td>225</td>
</tr>
<tr>
<td>Potassium (K⁺)</td>
<td>380</td>
<td>463</td>
<td>460</td>
<td>210</td>
</tr>
<tr>
<td>Bicarbonate(HCO₃⁻)</td>
<td>140</td>
<td>-</td>
<td>142</td>
<td>146</td>
</tr>
<tr>
<td>Strontium (Sr²⁺)</td>
<td>13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bromide (Br⁻)</td>
<td>65</td>
<td>155</td>
<td>80</td>
<td>72</td>
</tr>
<tr>
<td>Borate (BO₃³⁻)</td>
<td>26</td>
<td>72</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total dissolved solids (TDS)</td>
<td>34.483</td>
<td>38.600</td>
<td>45.000</td>
<td>41.000</td>
</tr>
</tbody>
</table>

Source: Water Condition & purification, 2005

**Chemical Reactions**

- HOCl + Br⁻ → HOBr + Cl⁻
- HOBr + DM → Br⁻-DBPs

Seawater pools disinfection resulted in brominated DBPs
Approach
Emerging treatment technologies

Can UV treatment be effective to remove the DBPs?
## Approach

### DBPs

<table>
<thead>
<tr>
<th>Group</th>
<th>Compound</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>THMs</td>
<td>Chloroform</td>
<td>TCM</td>
</tr>
<tr>
<td></td>
<td>Bromodichloromethane</td>
<td>BDCM</td>
</tr>
<tr>
<td></td>
<td>Dibromochloromethane</td>
<td>DBC</td>
</tr>
<tr>
<td></td>
<td>Bromoform</td>
<td>TBM</td>
</tr>
<tr>
<td>HANs</td>
<td>Dichloroacetonitrile</td>
<td>DCAN</td>
</tr>
<tr>
<td></td>
<td>Bromochloroacetanotile</td>
<td>BCAN</td>
</tr>
<tr>
<td>Misc. DBPs</td>
<td>Trichloronitromethane</td>
<td>TCnitro</td>
</tr>
<tr>
<td></td>
<td>Dichloropropanone</td>
<td>DCprop</td>
</tr>
<tr>
<td></td>
<td>Trichloropropanone</td>
<td>TCprop</td>
</tr>
<tr>
<td>HAAs</td>
<td>Bromochloroacetic acid</td>
<td>BCAA</td>
</tr>
<tr>
<td></td>
<td>Dibromoacetic acid</td>
<td>DBAA</td>
</tr>
<tr>
<td></td>
<td>Tribromoacetic acid</td>
<td>TBAA</td>
</tr>
<tr>
<td></td>
<td>Dibromochloroacetic acid</td>
<td>DBCAA</td>
</tr>
</tbody>
</table>
Approach
Toxicity estimation

• Calculated for water samples by:

\[ \text{Toxicity} = \sum \frac{C_i}{EC_{50,i}} \]

\( EC_{50} \) taken from Plewa et al. 2008

• The toxicity of the different groups

  Haloacetonitriles (HANs) > Haloacetic acids (HAAs) > Trihalomethanes (THMs)
UV light

- UV light is short waved, high energy electromagnetic irradiation

Drinking water
- Low pressure UV is used for bacteria control

Swimming pools
- Medium pressure UV is used for combined chlorine control
UV photolysis
Freshwater pools

Total Trihalomethane

% Br-THM | Br-THM
---|---
1st cycle | 2nd cycle | 3rd cycle
2.5% | 2.7% | 2.9%
2.5% | 2.9% | 3.0%
3.1% | 3.3% | 3.5%

UV treatment followed by Cl₂ → increased Br-THM
UV treatment → decreased Br-THM

UV photolysis

Hansen et al., (2013)

- Increased bromine substitution → increasing UV photolysis

Chloroform
Bromodichloromethane
Dibromochloromethane
Bromoform

EED (kWh/m³)
Time (min)
Br-Cl-DBP Formation Theory

**Reaction I**

\[
\begin{align*}
\text{OH} &\quad \text{CH}_2 \quad \text{Cl} \\
\text{Br-CH-CH-C-COOH} &\quad \text{CH}_3 \\
\text{Cl} &\quad \text{Br-C-CH}_2-\text{CH}_2-C-\text{CH}-\text{CH}-\text{COOH} \\
\text{CH}_2-\text{Br} &\quad \text{O} \quad \text{OH} \quad \text{Cl}
\end{align*}
\]

**UV Irradiation**

**Reaction II**

\[
\begin{align*}
\text{Cl}^{-} &\quad \text{Cl} \\
\text{Br} &\quad \text{CH}_3-\text{CH}-\text{COOH} \\
\cdot\text{OH} &\quad \text{CH}_3 \\
\text{Br} &\quad \text{CH}_3-\text{CH}-\text{COOH} \\
\cdot\text{OH} &\quad \text{Cl}
\end{align*}
\]

**Reaction III**

\[
\begin{align*}
\text{Br-CH-Br} &\quad \cdot\text{OH} \\
\text{Cl} &\quad \text{CH}_3-\text{CH}-\text{COOH} \\
\text{OH} &\quad \text{CH}_3 \\
\text{Br-CH} &\quad \text{Cl} \\
\text{Cl} &\quad \text{CH}_3-\text{CH}-\text{COOH} \\
\text{OH} &\quad \text{CH}_3 \\
\text{HOBr} &\quad \text{CH}_3-\text{CH}-\text{COOH} \\
\cdot\text{OH} &\quad \text{CH}_3 \\
\text{HOBr} &\quad \text{CH}_2-\text{CH}_3 \\
\text{HOBr} &\quad \text{CH}_2-\text{CH}_3
\end{align*}
\]

Further reaction

Spiliotopoulou et al., (2015)
Experimental setup

**Sampling**
Seawater Pool

**Treatment**
Medium pressure batch reactor

**Analysis**
LLE – GC-ECD

Residual Chlorine
3±0.3 mg/L

24 hr 25 °C
UV in seawater pools

Results

- UV treatment followed by Cl₂ → increased total THM
- UV treatment followed by Cl₂ → decreased total HAA
UV in seawater pools

Results

**Total Haloacetonitriles**

- UV treatment followed by Cl₂ → increased total HAN

**Genotoxicity**

- UV treatment followed by Cl₂ → increased toxicity

\[
Toxicity = \sum \frac{C_i}{EC_{50,i}}
\]
Future work

Seawater pools

• Repeated treatment investigations for seawater pools
Thanks for your attention!