Effect of UV treatment on formation of disinfection by-products in chlorinated seawater swimming pools

Cheema, Waqas Akram; Manasfi, Tarek; Kaarsholm, Kamilla Marie Speht; Andersen, Henrik Rasmus; Boudenne, Jean-Luc

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INNOVATIONS AND APPLICATIONS 2

Effect of UV treatment on formation of disinfection by-products in chlorinated seawater swimming pools
Waqas A. Cheema¹, Tarek Manasfi², Kamilla M. S. Kaarsholm¹, Henrik R. Andersen¹, Jean-Luc Boudenne²
¹Technical University of Denmark, Denmark
²Aix Marseille Université, France
³National University of Sciences and Technology, Pakistan

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

- **Particles**: Hair, Skin cells
- **Dissolved matters**: Sweat, Urine, Lotion, Shampoo, Make-up

Disinfection By-Products (DBPs)
- Dissolved Organic Carbon (DOC) + Chlorine
  - 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*

HOCl + Br⁻ → HOBr + Cl⁻

HOBr + DM → Br⁻-DBPs

Seawater pools disinfection resulted in brominated DBPs
Approach
Emerging treatment technologies

Particles → DOC + chlorine → DBPs

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><strong>THMs</strong></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><strong>HANs</strong></td>
<td>Dichloroacetonitrile</td>
<td>DCAN</td>
</tr>
<tr>
<td></td>
<td>Bromochloroacetanotile</td>
<td>BCAN</td>
</tr>
<tr>
<td><strong>Misc. DBPs</strong></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><strong>HAAs</strong></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:

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

$EC_{50}$ 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

% Br-THM

2.5% 2.5% 2.7%
2.9% 3.3% 3.5%

Br-THM (% Br-THM)

Initial Control, Cl2 UV UV, Cl2 UV UV, Cl2 UV UV, Cl2

0.0 0.2 0.4 0.6

EED (kWh/m3)

Time (min)

C/C0

Hansen et al., (2013)

- Increased bromine substitution → increasing UV photolysis

UV treatment followed by Cl2 → increased Br-THM
UV treatment → decreased Br-THM
Br-Cl-DBP Formation Theory

UV Irradiation

Reaction I

OH
CH₂ Cl
Br-CH-CH-C-COOH
Cl Br-CH₂-CH₂-C-CH₂-CH≡CH-COOH
CH₂-Br
O
OH
Cl

Cl₂

Reaction II

Further reaction

Reaction III

Spiliotopoulou et al., (2015)
Experimental setup

Sampling
Seawater Pool

Treatment
Medium pressure batch reactor
24 hr 25 °C
Residual Chlorine 3±0.3 mg/L

Analysis
LLE – GC-ECD
UV in seawater pools

Results

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

Results

**Total Haloacetonitriles**

<table>
<thead>
<tr>
<th>Sample</th>
<th>tHAN (μmol/L)</th>
<th>% Br-HAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.00</td>
<td>95%</td>
</tr>
<tr>
<td>Control, Cl₂</td>
<td>0.05</td>
<td>95%</td>
</tr>
<tr>
<td>UV₁/₂d, Cl₂</td>
<td></td>
<td>93%</td>
</tr>
<tr>
<td>UV₁d, Cl₂</td>
<td></td>
<td>94%</td>
</tr>
</tbody>
</table>

**Genotoxicity**

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

- UV treatment followed by Cl₂ → increased total HAN
- UV treatment followed by Cl₂ → increased toxicity
Future work

Seawater pools

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