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

Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
INNOVATIONS AND APPLICATIONS 2

Effect of UV treatment on formation of disinfection by-products in chlorinated seawater swimming pools
Waqas A. Cheema1,3, 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.
Effect of UV treatment on formation of disinfection by-products in chlorinated seawater swimming pools

Waqas A. Cheema\textsuperscript{1,3}, Tarek Manasfi\textsuperscript{2}, Kamilla M. S. Kaarsholm\textsuperscript{1}, Henrik R. Andersen\textsuperscript{1}, Jean-Luc Boudenne\textsuperscript{2}

\textsuperscript{1}Technical University of Denmark, Denmark
\textsuperscript{2}Aix Marseille Université, France
\textsuperscript{3}National University of Sciences and Technology, Pakistan

2017 IUVA Americas Conference
February 5-8, 2017
Austin, Texas
USA

DTU Environment
Department of Environmental Engineering
Disinfection By-Products

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

Particles: Hair, Skin cells

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

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

Seawater pools disinfection resulted in brominated DBPs
Approach
Emerging treatment technologies

Particles $\rightarrow$ DOC + chlorine $\rightarrow$ 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>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:

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

$EC_{50}$ 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**

<table>
<thead>
<tr>
<th>Cycle</th>
<th>tTHM (µmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2.5%</td>
</tr>
<tr>
<td>Control</td>
<td>2.5%</td>
</tr>
<tr>
<td>UV</td>
<td>2.7%</td>
</tr>
<tr>
<td>UV, Cl₂</td>
<td>3.1%</td>
</tr>
<tr>
<td>UV</td>
<td>2.9%</td>
</tr>
<tr>
<td>UV, Cl₂</td>
<td>3.3%</td>
</tr>
<tr>
<td>UV</td>
<td>3.0%</td>
</tr>
<tr>
<td>UV, Cl₂</td>
<td>3.5%</td>
</tr>
</tbody>
</table>

---

**UV photolysis**

- Increased bromine substitution → increasing UV photolysis

---

UV treatment followed by Cl₂ → increased Br-THM

UV treatment → decreased Br-THM

---

**Hansen et al., (2013)**

**EED (kWh/m³)**

- Chloroform
- Bromodichloromethane
- Dibromochloromethane
- Bromoform

---

**Time (min)**

0 20 40 60 80
Br-Cl-DBP Formation Theory

UV Irradiation

Reaction I

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

Results

- UV treatment followed by Cl$_2$ → increased total HAN
- UV treatment followed by Cl$_2$ → increased toxicity

**Total Haloacetonitriles**

<table>
<thead>
<tr>
<th>tHAN (µmol/L)</th>
<th>Initial</th>
<th>Control, Cl$_2$</th>
<th>UV$_{1/2d}$, Cl$_2$</th>
<th>UV$_{1d}$, Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Br-HAN</td>
<td>95%</td>
<td>95%</td>
<td>93%</td>
<td>94%</td>
</tr>
</tbody>
</table>

**Genotoxicity**

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

- UV treatment followed by Cl$_2$ → increased total HAN
- UV treatment followed by Cl$_2$ → increased toxicity
Future work

Seawater pools

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