UV Photolysis of DBPs in Chlorinated Recreational Water

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Presentation Outline

• Use of UV Radiation in Water Treatment
• Photochemistry Basics
• Swimming Pool Chlorination (DBPs)
• Experimental Methods
• Results
• Implications
• Future Work
• Acknowledgements
Uses of UV Radiation in Water Treatment

• Disinfection
  – Broad-Spectrum Antimicrobial Agent
    • Bacteria (spores, vegetative cells)
    • Viruses
    • Protozoa (Cryptosporidium parvum, Giardia lamblia)
  – Fast Reactions → Small Footprint
  – Low Cost
  – Minimal DBP Formation
  – Doses up to 200-300 mJ/cm²
  – Wavelength Dependence (UV Source Dependence)

• Photolysis
  – Only Effective Against Absorbing Compounds
  – Dose Range Often Higher Than With Disinfection
  – Application Less Common Than Disinfection
  – Wavelength Dependence (UV Source Dependence)
Photochemistry Basics

• Photochemical Reactions Require:
  – Absorption of Radiation by Target Molecule
  – Sufficient Photon Energy to Break or Form a Chemical Bond

• Photon Energy Depends on Wavelength

• Bond Energy Often Similar to Photon Energy Within Ultraviolet (UV) Spectrum
Absorption Spectra of Relevant Biological Molecules (Jagger, 1967)
Emission Spectrum
Low-Pressure Hg Lamp

Relative Radiant Power

Wavelength (nm)
Emission Spectra: Medium Pressure Lamps
C. parvum UV\textsubscript{254} Dose-Response Behavior

B. anthracis (Sterne) Spore UV$_{254}$ Dose-Response Behavior

Chlorination of Recreational Waters (Swimming Pools)

- Microbial Inactivation
  - Effective control of (most)
    - Bacteria
    - Viruses
  - Poor control of protozoa
    - *C. parvum*
    - *G. lamblia*

- Recommended Concentration: 1-3 mg/L as Cl₂

- Disinfection By-Products (DBPs)
Organic Precursors in Swimming Pools

- **Creatinine**: Breakdown product of creatine phosphate in muscle tissue; present in sweat, urine
- **Urea**: Metabolic conversion of NH$_3$ in liver; present in sweat, urine
- **Amino acids**: Present in sweat, urine
- **Personal care products**
  - Deodorants
  - Make-up
  - Etc.
DBP Formation Experiments


• Pure Compounds
  – Creatinine
  – Urea
  – L-histidine
  – L-arginine
• Body Fluid Analog
• Pool Water Samples
Chlorination of Creatinine

\[ [P] = 1.8 \times 10^{-4} \text{ M}, \ Cl:P = 5; \ \text{pH} = 7.5 \]
# Volatile DBP Measurement in Samples of Recreational Water

<table>
<thead>
<tr>
<th>Sample</th>
<th>NC\textsubscript{3}Cl\textsubscript{2} (mg/L as Cl\textsubscript{2})</th>
<th>CHCl\textsubscript{3} (mg/L)</th>
<th>CNCHCl\textsubscript{2} (mg/L)</th>
<th>Free Chlorine (mg/L as Cl\textsubscript{2})</th>
<th>Inorganic Chloramine (mg/L as Cl\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.08</td>
<td>0.07</td>
<td>0.01</td>
<td>1.5</td>
<td>1.34</td>
</tr>
<tr>
<td>B</td>
<td>0.07</td>
<td>0.13</td>
<td>0.03</td>
<td>1.95</td>
<td>0.25</td>
</tr>
<tr>
<td>C</td>
<td>0.09</td>
<td>0.14</td>
<td>0.01</td>
<td>0.68</td>
<td>1.36</td>
</tr>
<tr>
<td>D</td>
<td>0.16</td>
<td>0.08</td>
<td>0.02</td>
<td>6.52</td>
<td>1.76</td>
</tr>
<tr>
<td>E</td>
<td>0.1</td>
<td>0.13</td>
<td>0.01</td>
<td>5.92</td>
<td>1.28</td>
</tr>
<tr>
<td>F</td>
<td>0.07</td>
<td>0.08</td>
<td>0.01</td>
<td>1.72</td>
<td>0.76</td>
</tr>
</tbody>
</table>

A, C, E, F: Indoor lap Swimming Pool; B: Outdoor General Use Swimming Pool; D: Outdoor Recreation Park

Pool A: 10 ppb dichloromethylamine; CNCl\textsubscript{2} never found
### Health Effects of Recreational Water Halogenated DBPs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Toxicology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloramine</td>
<td>NCl$_3$</td>
<td>Eye, nose, throat irritant, may promote asthma</td>
</tr>
<tr>
<td>Dichloroacetonitrile</td>
<td>N≡CHCCl$_2$</td>
<td>Possible mutagen, respiratory irritant</td>
</tr>
<tr>
<td>Dichloromethylamine</td>
<td>CH$_3$NCl$_2$</td>
<td>Malodor, ?</td>
</tr>
<tr>
<td>Cyanogen chloride</td>
<td>N≡CCl</td>
<td>Suspected neurotoxicant, respiratory toxicant, skin and sense organ toxicant</td>
</tr>
</tbody>
</table>

- Volatile DBPs not limited to NCl$_3$, CHCl$_3$
- N-Containing DBPs may display greater toxicity than other DBPs
Effects of Swimming Pool DBPs on Human Health

- Increased Incidence of Respiratory Problems (Asthma)
- Incidence of Asthma Relatively High Among Swimmers, Lifeguards
- Effects Related to Chlorine Concentration
- Generally Attributed to NCl$_3$
- Swimming Often Prescribed as Therapy for Asthmatics
- Translation to Other Water Treatment Settings
UV Use in Swimming Pools and Recreational Water

• Alternative Disinfectant
  – *Cryptosporidium parvum*
  – NY Water Park Outbreak
    • 3000 cases
    • UV now required in NY water parks

• Chloramine Control
  – Inorganic chloramines photodegrade
  – Free chlorine photodecays slowly
  – Selective removal of inorganic chloramines

• Effects on Chlorinated Organic-N Compounds?
DBP Photochemistry

• Spectrophotometry
• Wavelength-dependent photodegradation
• Collimated beams
  – KrCl excimer lamp ($\lambda \approx 222$ nm)
  – LP Hg lamp ($\lambda \approx 254$ nm)
  – XeBr excimer lamp ($\lambda \approx 282$ nm)
• Monitor reaction progress with MIMS
Collimated Beam (UV Source)
Collimated Beam Types Used in This Research

- Low-Pressure Hg
- Excimer Lamp
  - XeBr (282 nm)
  - KrCl (222 nm)
Membrane Introduction Mass Spectrometry (MIMS): Membrane Cell

Other Analytical Methods

- Ion Chromatography
- UV-Visible Spectrophotometry
- Wet Chemistry
  - DPD/FAS Titration
  - DPD Colorimetric
  - Alkalinity Titration
- pH Probe
UV Absorbance Spectra:
Free Chlorine (HOCl + OCl\(^-\))
UV Absorbance Spectra: Inorganic Combined Chlorine
\((\text{NH}_2\text{Cl}, \text{NHCl}_2, \text{NCl}_3)\)
UV Absorbance: Free Chlorine and Inorganic Chloramines

• Free Chlorine:
  – HOCl, OCl⁻
  – Poor Absorbers of Germicidal UV
  – Minimal Potential to Photodegrade

• Inorganic Combined Chlorine
  – NH₂Cl, NHCl₂, NCl₃
  – Moderate to Strong Absorbers of UV (λ)
  – May Photodegrade
UV$_{254}$ Irradiation: Free Chlorine + NCl$_3$

$I_0 = 560$ $\mu$W/cm$^2$

\[ \frac{C}{C_0} \]

Irradiation time / min
NH$_2$Cl Photodecay; pH = 7.5
Alkalinity = 120 mg/L as CaCO$_3$
NH$_2$Cl Photodecay; pH = 6.5
Alkalinity = 120 mg/L as CaCO$_3$
NHCl₂ Photodecay; pH = 7.5
Alkalinity = 120 mg/L as CaCO₃

![Graph showing UV dose (mJ/cm²) versus C/C₀ over time (min) with different wavelengths and extinction coefficients for NHCl₂ photodecay at pH = 7.5 and alkalinity = 120 mg/L as CaCO₃.](image-url)
$\text{NCl}_3$ Photodecay; $\text{pH} = 7.5$

Alkalinity = 120 mg/L as CaCO$_3$
Photodegradation of Inorganic Chloramines

\[ \text{NH}_2\text{Cl} \xrightarrow{h\nu} \bullet\text{NH}_2 + \text{Cl} \bullet \rightarrow \text{???} \]
\[ \text{NHCl}_2 \xrightarrow{h\nu} \bullet\text{NHCl} + \text{Cl} \bullet \rightarrow \text{???} \]
\[ \text{NCl}_3 \xrightarrow{h\nu} \bullet\text{NCl}_2 + \text{Cl} \bullet \rightarrow \text{???} \]
Byproducts of UV$_{254}$ Irradiation:

\[ \text{NH}_2\text{Cl} \xrightarrow{hv} \text{NO}_2^- + \text{NO}_3^- + ? \]

NO$_2^-$ Formation from NH$_2$Cl Photodegradation (\( \lambda = 254 \text{ nm} \))

\[ (I_0 = 150 \mu\text{W/cm}^2; [\text{NH}_2\text{Cl}]_0 = 14.1 \mu\text{M}) \]

\[ \text{NO}_2^- \text{ and NO}_3^- \text{ formed account for 13-20\% of Original Reduced-N Concentration} \]
Byproducts of UV$_{254}$ Irradiation:

\[ NHCl_2 \xrightarrow{h\nu} NO_2^- + NO_3^- + ? \]

$\text{NO}_2^-$ Formation from NHCl$_2$ Photodegradation ($\lambda = 254$ nm)

(I$_0 = 150$ $\mu$W/cm$^2$; [NHCl$_2$]$_0 = 7.04$ $\mu$M)

$\text{NO}_3^-$ Formation from NHCl$_2$ Photodegradation ($\lambda = 254$ nm)

(I$_0 = 150$ $\mu$W/cm$^2$; [NHCl$_2$]$_0 = 7.04$ $\mu$M)

$\text{NO}_2^-$ and $\text{NO}_3^-$ formed account for 10-20% of Original Reduced-N Concentration
Byproducts of UV$_{254}$ Irradiation:

\[
NCl_3 \xrightarrow{h\nu} NO_2^- + NO_3^- + ?
\]

\begin{align*}
\text{NO}_2^- \text{ Formation from NCl}_3 \text{ Photodegradation} (\lambda = 254 \text{ nm}) \\
(I_0 = 150 \mu W/cm^2; [NCl_3]_0 = 4.69 \mu M)
\end{align*}

\begin{align*}
\text{NO}_3^- \text{ Formation from NCl}_3 \text{ Photodegradation} (\lambda = 254 \text{ nm}) \\
(I_0 = 150 \mu W/cm^2; [NCl_3]_0 = 4.69 \mu M)
\end{align*}

\begin{align*}
\text{pH} = 6.5 & \quad \text{pH} = 7.5 & \quad \text{pH} = 8.6 \\
\end{align*}

\text{NO}_2^- \text{ and } \text{NO}_3^- \text{ formed account for } 80\% \text{ of Original Reduced-N Concentration}
UV Photolysis of Residual Chlorine

- Free Chlorine Degrades Slowly
- Inorganic Chloramines Degrade at Germicidal UV Doses
- Products of Inorganic Chloramine Photolysis Include NO$_2^-$ and NO$_3^-$
- Amounts of NO$_2^-$ and NO$_3^-$ Formed Depend on pH, Free Chlorine
- NCl$_3$ is Most Susceptible to Photodegradation, and Most Likely to be Present in Swimming Pools
Volatile DBP Absorbance Spectra

\[ \varepsilon = \text{Molar Absorptivity (M}^{-1}\text{cm}^{-1}) \]

Wavelength (nm)

\[ 200 \quad 220 \quad 240 \quad 260 \quad 280 \quad 300 \]

\[
\begin{array}{c}
0 \\
1000 \\
2000 \\
3000 \\
4000 \\
5000 \\
\end{array}
\]

CNCHCl$_2$

CNCI

CH$_3$NCl$_2$
UV Absorbance: Chlorinated Organic-N Compounds

- **CNCHCl₂, CNCl**
  - Poor Absorbers of Germicidal UV
  - Minimal Potential to Photodegrade

- **CH₃NCl₂**
  - Moderate to Strong Absorber of UV (\(\lambda\))
  - May Photodegrade
CNCHCl₂ Photodecay; pH = 7.5
Alkalinity = 120 mg/L as CaCO₃

UV Dose (mJ/cm²)

C/C₀

λ = 282 nm (ε = 0.477 M⁻¹cm⁻¹)
λ = 254 nm (ε = 0.659 M⁻¹cm⁻¹)
λ = 222 nm (ε = 25.3 M⁻¹cm⁻¹)
CNCl Photodecay; pH = 7.5
Alkalinity = 120 mg/L as CaCO$_3$
CH$_3$NCl$_2$ Photodecay; pH = 7.5
Alkalinity = 120 mg/L as CaCO$_3$
Photodecay of Chlorinated DBPs

Stability of Chlorinated Creatinine

1:1 Cl:P Ratio; pH = 7.5

![Graph showing absorbance against wavelength for different time points of chlorinated creatinine and creatinine.](image)
UV$_{254}$ Photodecay of Chlorinated Creatinine
1:1 Cl:P Ratio; pH = 7.5
Nitrite and Nitrate Formation from UV_{254} Irradiation of Chlorinated Creatinine

Initial Creatinine Concentration = 100 µmole/L; I_0 = 150 µW/cm²

NO_2^- and NO_3^- formed account for 5% of Original Reduced-N Concentration
Next Steps

• Effects of Solution Chemistry on Photochemical Kinetics
  – pH
  – Alkalinity
• Photochemical By-Products
• Combined Effects of Solution Chemistry and Photochemistry
• Other DBPs
  – Polar fraction
  – Low volatility
• Field Measurements of DBPs in Water, Air
• System Optimization
Long-Term Research Objectives: Engineering Systems Approach

• Improve Understanding of Swimming Pool Chemistry and Treatment Processes
• Define Rates of Gas:Liquid Transfer
• Simulate System Behavior
  – Reactions
  – Treatment Processes
  – Gas:Liquid Exchange
  – Mixing in Water and Air
• Optimize System Performance
Conceptual Model

$$\text{HOCl} + R \rightarrow ???$$
Future Research Direction on DBP Chemistry and Facility Operations

- Informal Meeting
- Thursday, October 4, 2007  7:30 AM
- Same Room as DBP Session
Acknowledgements

• DuPont Experimental Station
• National Swimming Pool Foundation
**Organic-N Precursors**

- Creatinine
- Histidine
- Urea
- Arginine

**Volatile DBPs**

- Trichloramine
- Dichloromethylamine
- Chloroform
- Dichloroacetonitrile
- Cyanogen Chloride
Molar Absorptivity Values (M⁻¹cm⁻¹) for volatile DBPs and free chlorine at different wavelengths

<table>
<thead>
<tr>
<th>Species</th>
<th>$\lambda=222\text{ nm}$</th>
<th>$\lambda=254\text{ nm}$</th>
<th>$\lambda=282\text{ nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNCHCl₂</td>
<td>25</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>CNCl</td>
<td>-</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>CH₃NCl₂</td>
<td>1662</td>
<td>211</td>
<td>562</td>
</tr>
<tr>
<td>NCl₃</td>
<td>4938</td>
<td>367</td>
<td>54</td>
</tr>
<tr>
<td>NaOCl(HOCl) pH=7</td>
<td>71</td>
<td>64</td>
<td>71</td>
</tr>
<tr>
<td>NHCl₂</td>
<td>1126</td>
<td>142</td>
<td>221</td>
</tr>
<tr>
<td>NH₂Cl</td>
<td>221</td>
<td>388</td>
<td>78</td>
</tr>
</tbody>
</table>
Pool A: Competition Pool
Chlorination of L-Histidine

\[ [P] = 1.8 \times 10^{-4} \text{ M, Cl:P} = 5; \text{ pH} = 7.5 \]

![Diagram of chlorination products and m/z values]

- \( \text{CNCHCl}_2 \)
- \( \text{CNCl} \)
- \( \text{NCl}_3 \)
- \( \text{CHCl}_3 \)

Abundance vs. \( m/z \) graph:
- Peaks at 61, 63, 74, 76, 82, 84, 85, 108, 119
- M/z values for the products:
  - 61: CNCl
  - 63: NCl₃
  - 74: CNCHCl₂
  - 76: CNCHCl₂
  - 82: CNCHCl₂
  - 84: NCl₃
  - 85: CHCl₃
  - 108: CNCHCl₂
  - 119: NCl₃
  - 120: CHCl₃

Chemical structures and reactions:
- HOCl + H₂N\( \text{CH₂CH₂COOH} \) → CNCHCl₂, CNCl, NCl₃, CHCl₃
Chlorination of Urea

\[ [P] = 1.8 \times 10^{-4} \text{ M, Cl:P = 5; pH = 7.5} \]
Chlorination of L-Arginine

\[ [P] = 1.8 \times 10^{-4} \text{ M}, \text{ Cl:P} = 8; \text{ pH} = 7.5 \]
Mass spectra of volatile byproducts from chlorination of BFA

L-Histidine: 12.1 ppm
L-Arginine: 5 ppm
Creatinine: 18 ppm
Urea: 148 ppm