Involvement of NOM in the Photochemical Fate of Beta-Blockers in Water

Haomin Xu, Ph.D.
William J. Cooper, Ph.D.
Weihua Song, Ph.D.
Outline

- Introduction
- Photochemical Fate
- Photodegradation Results
- Conclusions
Introduction

- Human and animal excretion
- Improper disposal of expired medications
- Agricultural and aquacultural activities
Introduction

Figure 1. Sources and distribution of pharmaceuticals in the environment (modified from Ternes (1998)).
Some of the common water purification methods are sedimentation or settling, boiling, chemical disinfection and filtration.

- Ultraviolet
- Ozone
- Membrane
- Reverse Osmosis
Little is known about the environmental occurrence, transport, and ultimate fate of pharmaceuticals.

Biodegradation, sorption and photodegradation are the main removal processes in surface waters.

In some cases, pharmaceuticals have been designed to be resistant to biodegradation.

The sediment type has been shown to significantly affect the sorption of pharmaceuticals.
Photochemical Fate

- Hydrolysis
- Direct photolysis
- Indirect photolysis, by reaction with reactive oxygen species (ROS), e.g. hydroxyl radical (•OH) and singlet oxygen (¹ΔΟ₂)
- Direct reactions with triplet excited state DOM (³DOM*)
- Light screening, season of the year, latitude of the location
• Beta-blockers is a class of drugs used for the management of cardiac arrhythmias, cardioprotection after myocardial infarction (heart attack), and hypertension.

• In the US market by dispensed prescriptions in 2009, atenolol ranked 85th and metoprolol 9th.

• Dissolved organic matter (DOM), fulvic acid (2S101F), was used to simulate natural water conditions.
Figure 2. Molecular Structure of Beta-blockers.

Atenolol
MW: 266.34 g/mol

Metoprolol
MW: 267.36 g/mol
Figure 3. Hydrolysis of solutions of 75 µM beta-blockers at pH 4, 7 and 10, (a) atenolol; (b) metoprolol, in the dark at 20 °C.
Figure 4. Loss of atenolol (75 µM) in pH 7 buffered distilled water (■) dark control; (●) direct photolysis in pH buffered distilled water; and, (▲) containing 20 mg L\(^{-1}\) DOM (2S101F). All experiments were at 20 °C.
Photodegradation Results — •OH, ¹ΔO₂, ³DOM*

**Figure 5.** Overall photolysis of atenolol (75 µM) in 20 mg L⁻¹ DOM (2S101F) solutions irradiated in solar simulator at 20 °C, pH 7: (a) in H₂O (■), in D₂O (▲), and with the addition of 2-propanol (65 mM) (●); (b) Photolysis with DOM (2S101F) (■), with addition of sorbic acid (0.18 mM), a ³DOM* quencher (●); purged with nitrogen (to enhance the formation of the ³DOM*) (▲).
Photodegradation Results – •OH

Figure 6. Solutions of terephthalic acid (0.6 mM, TA) containing 20 mg L\(^{-1}\) DOM (2S101F) irradiated in solar simulator at 20 °C, air-saturated (■), oxygen purged (●), and air-saturated with anionic surfactant sodium dodecylbenzenesulfonate (57 µM, SDBS) (▲), 2-hydroxyterephthalic acid (2OHTA) being its photoproduct.
Figure 7. Solution of 20 mg L⁻¹ DOM (2S101F) containing furfuryl alcohol (1.5 mM, FFA) irradiated in solar simulator at 20 °C.
Figure 8. Solutions of 75 µM beta-blockers (atenolol and metoprolol), with furfuraldehyde (or furan-2-carbaldehyde, 1.6 mM, FAD), containing 0.103 mM Rose Bengal (RB) irradiated in the solar simulator at 20 °C respectively.
Table 1. Measured steady-state concentrations (M) and first-order reaction rate (s\(^{-1}\)) for reactions of 75 µM selected beta-blockers with •OH and \(^{1}O_2\) at presence of 20 mg L\(^{-1}\) DOM (2S101F).

<table>
<thead>
<tr>
<th>Beta-blocker</th>
<th>([•OH]_{ss} \times 10^{-17} \text{ M})</th>
<th>(k_{•OH} \times 10^{-7} \text{ s}^{-1})</th>
<th>([^{1}ΔO_2]_{ss} \times 10^{-13} \text{ M})</th>
<th>(k_{1ΔO2} \times 10^{-9} \text{ s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atenolol</td>
<td>14.35 ± 0.74</td>
<td>10.12 ± 0.52</td>
<td>2.94 ± 0.01</td>
<td>2.49 ± 0.010</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>14.35 ± 0.74</td>
<td>12.04 ± 0.62</td>
<td>2.94 ± 0.01</td>
<td>1.84 ± 0.007</td>
</tr>
</tbody>
</table>
Table 2. Contributions (%) of hydrolysis, direct photolysis, reactions with •OH, $^{1}\text{O}_2$, and $^3\text{DOM}^*$ to the overall photodegradation rate of 75 µM selected beta-blockers at presence of 20 mg L$^{-1}$ DOM (2S101F).

<table>
<thead>
<tr>
<th>Beta-blocker</th>
<th>Hydrolysis</th>
<th>Direct Photolysis</th>
<th>•OH</th>
<th>$^{1}\text{O}_2$</th>
<th>$^3\text{DOM}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atenolol</td>
<td>0.5</td>
<td>6.9</td>
<td>7.2</td>
<td>0.02</td>
<td>85.4</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>1.1</td>
<td>6.1</td>
<td>26.6</td>
<td>0.04</td>
<td>66.2</td>
</tr>
</tbody>
</table>
Figure 9. Effect of anionic surfactant sodium dodecyl benzene sulfonate (SDBS) on sorption of beta-blockers to DOM.
Table 3. Half-life (hr) of 75 µM selected beta-blockers at presence of 20 mg L^{-1} DOM (2S101F) irradiated in solar simulator at 20 °C, with and without anionic surfactant sodium dodecylbenzenesulfonate (57 µM, SDBS) respectively.

<table>
<thead>
<tr>
<th>Beta-blocker</th>
<th>Half-life (hr)</th>
<th>No SDBS</th>
<th>With SDBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atenolol</td>
<td>13.7</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>Metoprolol</td>
<td>42.5</td>
<td>32.4</td>
<td></td>
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</tbody>
</table>
Photodegradation Results – Concentration Effect

**Figure 10.** Overall photolysis of beta-blockers in 20 mg L$^{-1}$ DOM (2S101F) solutions irradiated in solar simulator at 20 °C, pH 7: (a) 75 µM (■) and 3.8 µM (●) atenolol; (b) 75 µM (■) and 3.8 µM (●) metoprolol; (c) Sorption of beta-blockers at two different concentrations (75 µM and 3.8 µM) to DOM.
Conclusions

- Hydrolysis, direct photolysis, and reactions with $^1\Delta O_2$ and •OH radicals are from negligible to slightly important to the overall photodegradation of selected beta-blockers.
- The direct reactions with $^3$DOM* are exclusively a predominant degradation pathway of the selected beta-blockers in sunlit natural waters.
- The photodegradation rates of selected beta-blockers are significantly increased at the presence of sodium dodecylbenzenesulfonate (SDBS), presumably by facilitating the direct energy/electron transfer from $^3$DOM* to the substrates due to the enhanced sorption of beta-blockers on DOM.
References

Thank you for your attention!

Questions, remarks, feedbacks are welcome!!