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PHOTOINDUCTIVE DEGRADATION OF TWO ESTROGENS BY NATURAL DISSOLVED ORGANIC MATTER UNDER SIMULATED SUNLIGHT

Emilie Caupos, Patrick Mazellier, Jean-Philippe Croué

Laboratoire de Chimie et Microbiologie de l’Eau (LCME) UMR 6008
40 avenue du Recteur Pineau
86022 Poitiers

EMEC 10 Limoges 12/04/09
Estrone (E1) 17β-estradiol (E2)

➢ Presence in the environment

- natural estrogens (steroidal hormones) present in aquatic media (through animals excretion)

- released into surface and ground waters through wastewater effluents

- detected in soils adjacent to agricultural fields fertilized with animals waste

- E1 and E2 = two main estrogens detected in fresh and marine waters ~ in ng/L, Hohenblum 2004, Zuo 2006)
Introduction

- **Effects on aquatic organisms**
  - impact on reproductive system and development of reproductive organs (Jobling 2002, Rodgers-Gray 2000)

- **Human impacts**
  - increased incidents of breast, testicular and prostate cancer

  - no conclusive relationships established between endocrine disruptor exposure and human health

- **Photodegradation**: half-lives under simulated solar system
  - E1 : 4,7 h (Lin et Reinhard 2005)
  - E2 : 13,6 h (Leech 2008)
Introduction

Natural Dissolved Organic Matter (DOM)

- Presence in the environment
  - complex matrix
  - natural decomposition of ecosystems: terrestrial and aquatic origins
    - composition and concentration depending on the nature and origin of the media (Thurman 1985)

- Photodegradation
  - degradation (break of aromatic structures Carvalho 2008)
  - light absorption and production of reactive species \( ^1\text{O}_2, \text{OH}^\circ, \text{RO}^\circ, \text{solvated electrons, ...} \) (Aguer 1999)
Materials and Methods

Photolysis

- Photodegradation under **simulated sunlight** (Suntest Atlas CPS+)

Analysis

- HPLC-UV
- Spectrophotometer, Fluorimeter, TOCmeter

**Suntest 8h, 250 W/m², 900 kJ/h:**
- ~ 800 nM E1 or E2
- 20 mg/L DOM
- pH = 7
Optical properties of DOM

- 3 extracts used in photolysis experiments: fulvic acids of Pinail (France), Suwannee and South Platte (US rivers) at 20 mg DOM/L or 10 mg C/L

Order of UV-Visible absorbance:
- Pinail > Suwannee >> South Platte
Materials and Methods

Optical properties of DOM

- 3 extracts used in photolysis experiments: fulvic acids of Pinail (France), Suwannee and South Platte (US rivers) at 20 mg DOM/L or 10 mg C/L

Fluorescence/Absorbance Order

South Platte > Pinail > Suwannee

The most efficient

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Indirect photolysis

**Nature of DOM Influence → E₁**

**Photoinductive efficiency**

- South P. 76% > Pinail 66% > Suwannee 56%

Relationship between DOM nature – photoinductive efficiency

**Suntest 8h, 250 W/m², 800 nM E₁, pH7**

- [%Error (duplicates) : 2-5 %](#)
Indirect photolysis

Nature of DOM Influence → E2

Photoinductive efficiency

South P. 69% >>
Pinail 41% >
Suwannee 39%

Relationship between DOM nature – photoinductive efficiency

The more fluorescent the more photoinductive efficient

Sunset 8h, 250 W/m², 700 nM E2, pH7

%Error (duplicates) : 3-6 %

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Indirect photolysis

Reactive species

- Addition of inhibitors: NaN$_3$ and 2-propanol

Photodegradation decrease with the addition of inhibitors

For every DOM:
Degradation without inhibitor > with NaN$_3$ > with 2-propanol
Indirect photolysis

**Reactive species**

- Addition of inhibitors: NaN$_3$ and 2-propanol

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**Reactive species in the inductive photodegradation**

- $^{1}$O$_2$: participation in the photodegradation about 2 – 10 %
- OH$: participation in the photodegradation about 7 – 17 %
Indirect photolysis

Photoprodut (P1)

- Formation kinetics

![Graph showing formation kinetics of photoprodut (P1) with different water sources.](image-url)
**Indirect photolysis**

**Photoproduction (P1)**

- Formation kinetics

**P1 formation decreases in the presence of DOM**

Degradation of P1 by S. P. after 6 h

**P1 degraded by DOM or Optical filter effect of DOM**
**Indirect photolysis**

**Kinetics**

- Pseudo-first order kinetic rate constants obtained for E1 and E2 during inductive photodegradation by DOM solutions

<table>
<thead>
<tr>
<th></th>
<th>$k_{O2}$ (h$^{-1}$)</th>
<th>$k_{O2+NaN3}$ (h$^{-1}$)</th>
<th>$k_{O2+Pro}$ (h$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td><strong>E1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$OmQ</td>
<td>0.09</td>
<td>R$^2$=0.998</td>
<td></td>
</tr>
<tr>
<td>Pinail</td>
<td>0.13</td>
<td>R$^2$=0.977</td>
<td>0.11</td>
</tr>
<tr>
<td>Suwannee</td>
<td>0.10</td>
<td>R$^2$=0.997</td>
<td>0.09</td>
</tr>
<tr>
<td><strong>South Platte</strong></td>
<td>0.18</td>
<td>R$^2$=0.981</td>
<td>*</td>
</tr>
<tr>
<td><strong>E2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$OmQ</td>
<td>0.02</td>
<td>R$^2$=0.958</td>
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</tr>
<tr>
<td>Pinail</td>
<td>0.07</td>
<td>R$^2$=0.985</td>
<td>0.05</td>
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<tr>
<td>Suwannee</td>
<td>0.06</td>
<td>R$^2$=0.993</td>
<td>0.04</td>
</tr>
<tr>
<td><strong>South Platte</strong></td>
<td>0.14</td>
<td>R$^2$=0.973</td>
<td>*</td>
</tr>
</tbody>
</table>

* Not done
Conclusion

- Photodegradation of E1 and E2 is possible under natural sunlight

- Observation of DOM photosensibility

- Participation of singlet oxygen and hydroxyl radicals in the reaction

- Formation of a by-product
Future works

- Identification of the by-product (LC-MS)

- Development on the relationship between nature of DOM and its photoinductive properties (RMN $^{13}\text{C}$, oxidation of DOM to the hydrophilic fraction)

- Study of by-product toxicity (osters)
Thank you