



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

Emilie Caupos, Jean-Philippe Croue, Patrick Mazellier

► To cite this version:

Emilie Caupos, Jean-Philippe Croue, Patrick Mazellier. PHOTOINDUCTIVE DEGRADATION OF TWO ESTROGENS BY NATURAL DISSOLVED ORGANIC MATTER UNDER SIMULATED SUNLIGHT. EMEC 10, Limoges, France. 2009. <hal-00822552>

HAL Id: hal-00822552

<https://hal-enpc.archives-ouvertes.fr/hal-00822552>

Submitted on 14 May 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

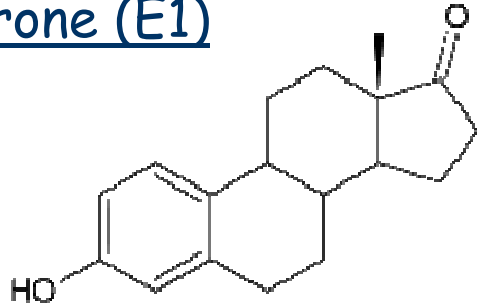
Emilie Caupos, Patrick Mazellier, Jean-Philippe Croué

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

EMEC 10 Limoges 12/04/09

Introduction

Estrone (E1)



➤ Presence in the environment

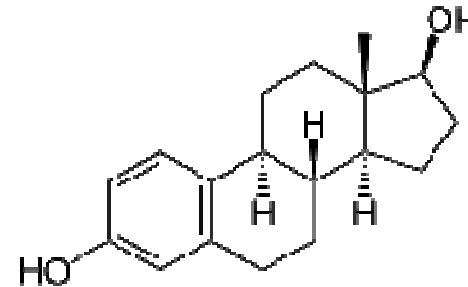
- natural estrogens (steroidal hormones) present in aquatic media (through animals excretion)

- 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)

17 β -estradiol (E2)



Introduction

➤ Effects on aquatic organisms

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

- **estrogenic effects** detected for vertebrates and invertebrates, fishes, amphibians, reptiles (feminisation, ... Orlando 2004, Brion 2004, Lai 2002)

➤ Human impacts

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

- reduced fertility of men (Harrison 1997, Colburn 1995, Carlsen 1995)

- 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** ($^1\text{O}_2$, OH° , RO° , solvated electrons, ... Aguer 1999)

Materials and Methods

Photolysis

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



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

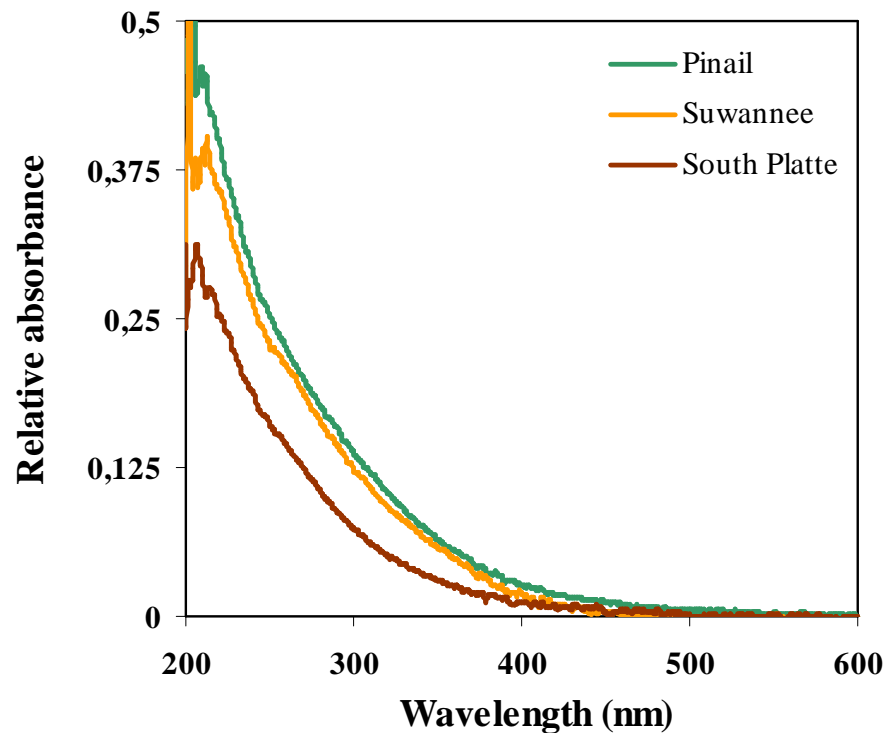
Analysis

- HPLC-UV
- Spectrophotometer, Fluorimeter, TOCmeter

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



Order of UV-Visible absorbance

Pinail >

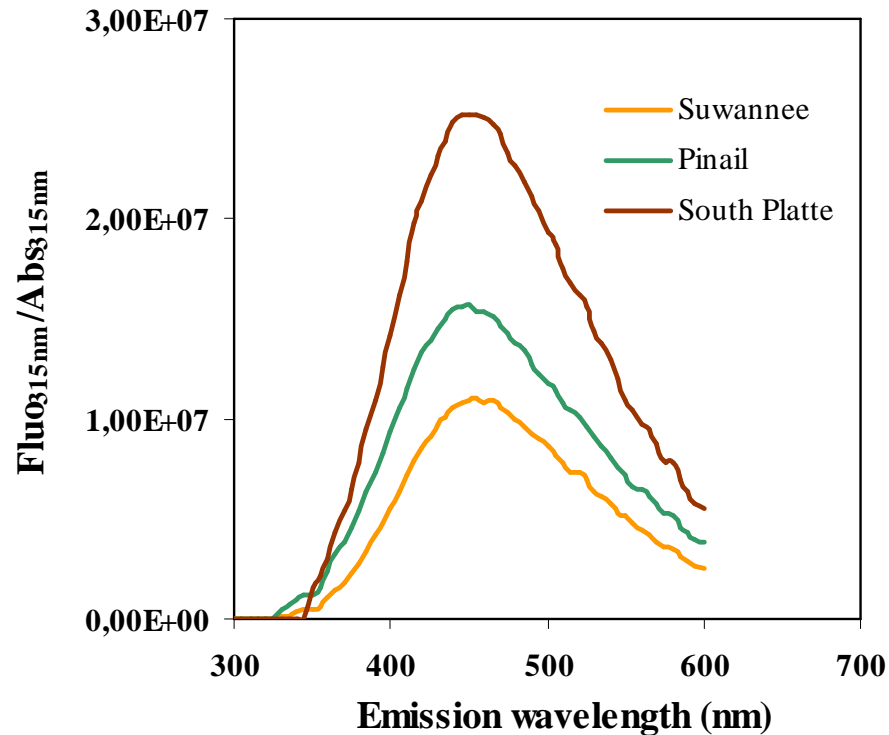
Suwannee >>

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



South Platte

The most efficient

Indirect photolysis

Nature of DOM Influence → E1

Photoinductive efficiency

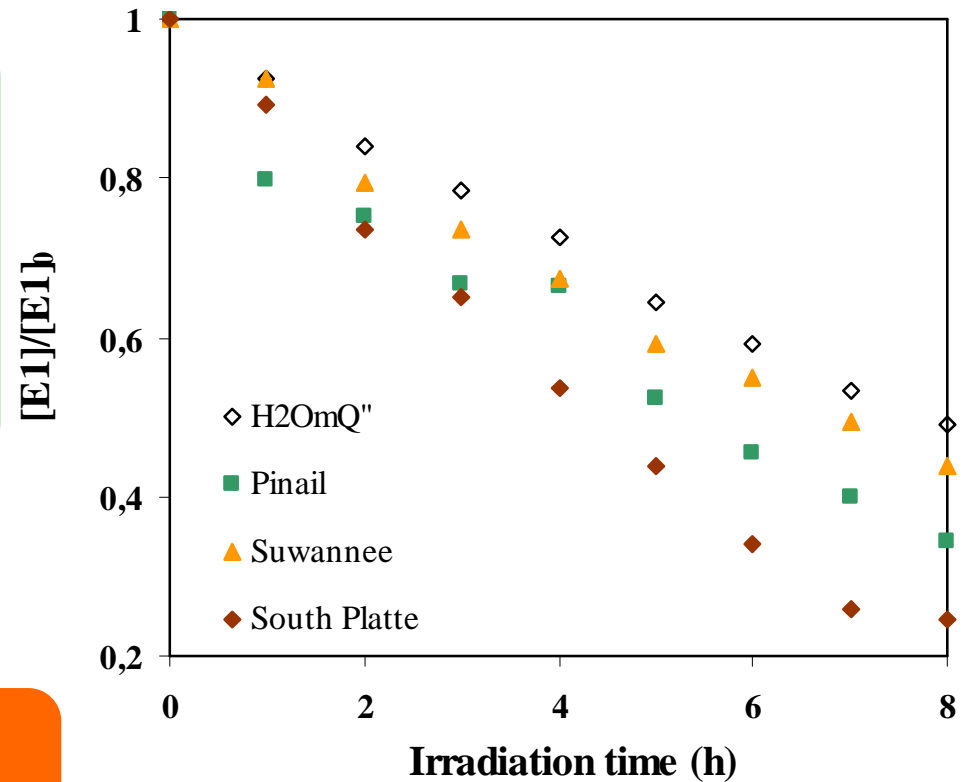
South P. 76% >

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% >

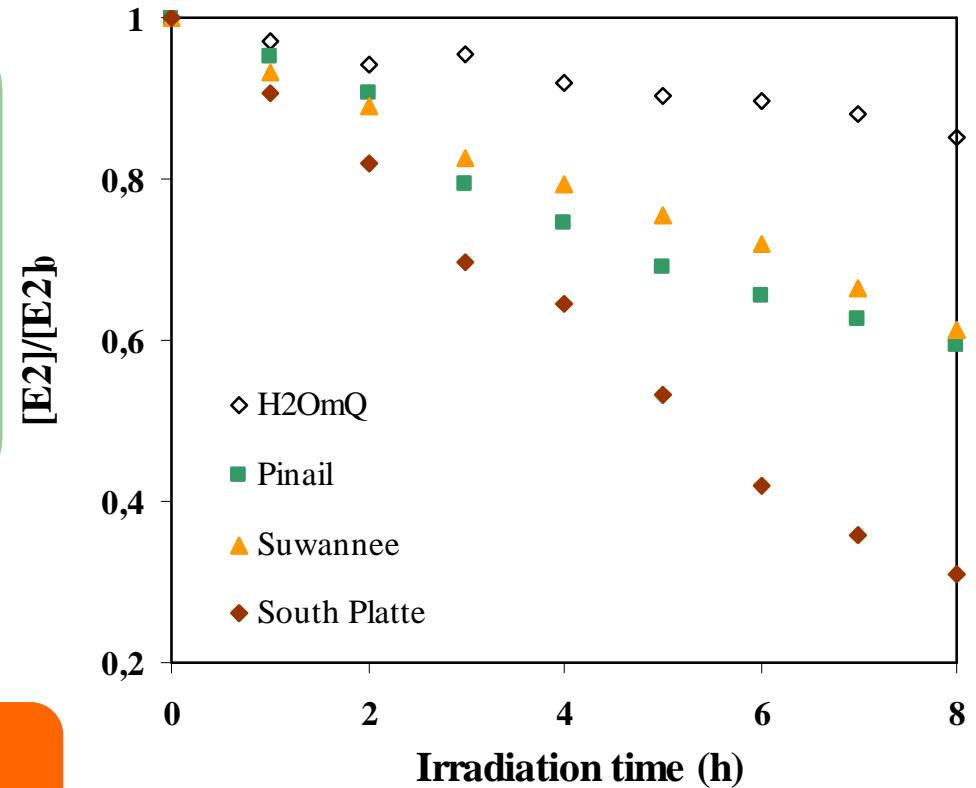
Suwannee 39%



**Relationship between
DOM nature –
photoinductive efficiency**

The more fluorescent the
more photoinductive efficient

Suntest 8h, 250 W/m², 700 nM E2, pH7

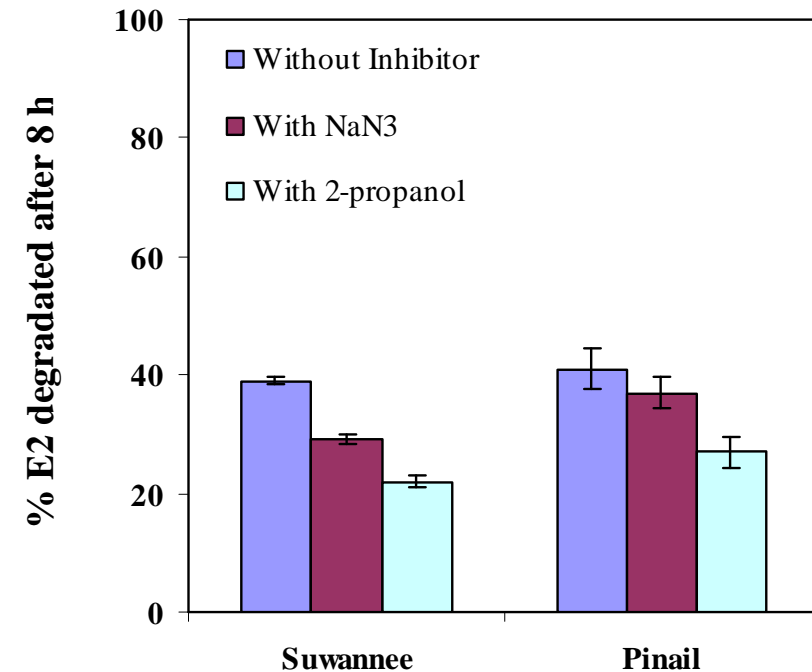
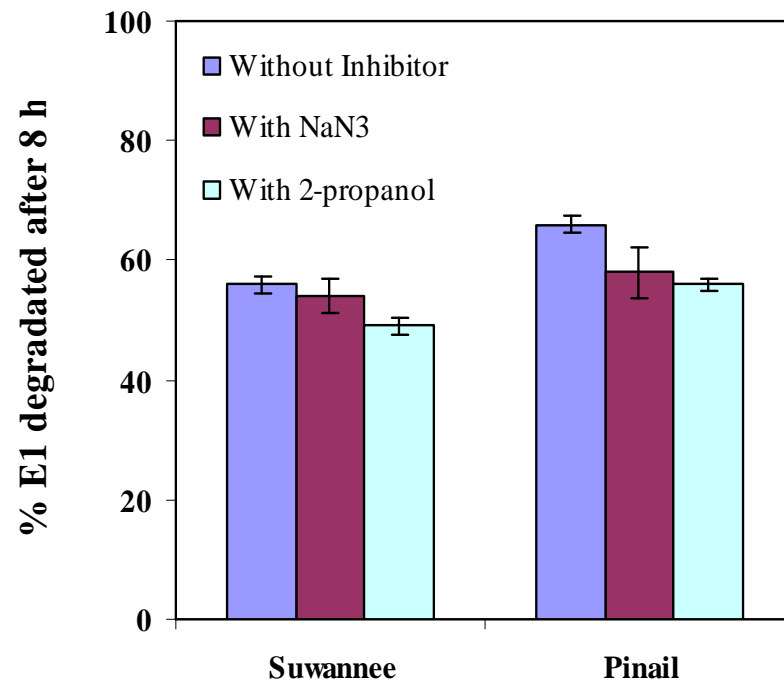


%Error (duplicates) : 3-6 %

Indirect photolysis

Reactive species

- Addition of inhibitors : NaN_3 and 2-propanol



Photodegradation decrease with the addition of inhibitors

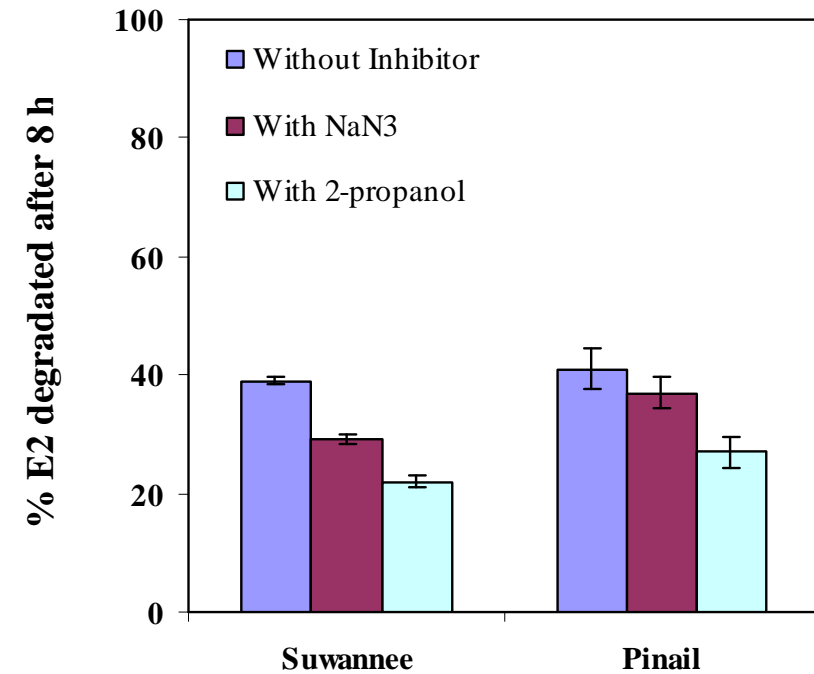
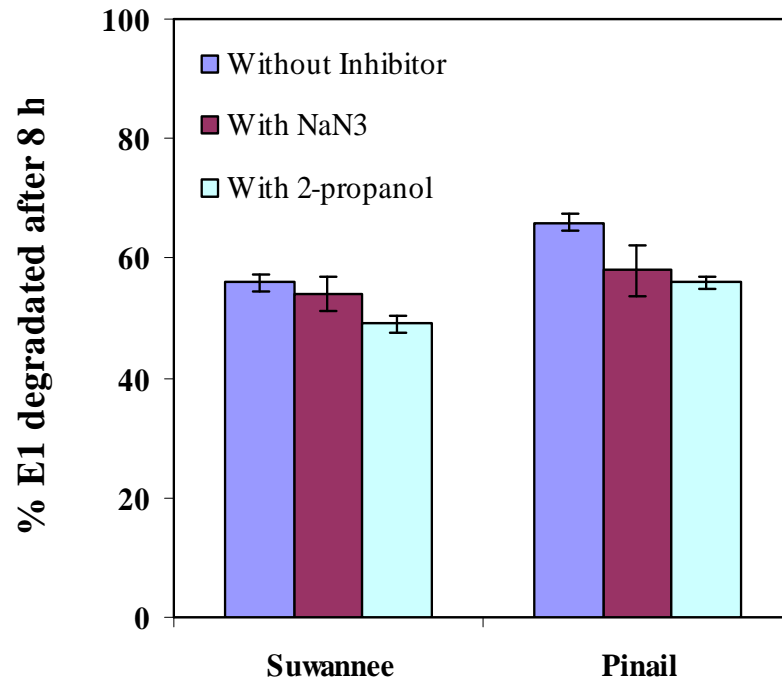
For every DOM :

Degradation without inhibitor > with NaN_3 > with 2-propanol

Indirect photolysis

Reactive species

➤ Addition of inhibitors : NaN_3 and 2-propanol



Reactive species in the inductive photodegradation

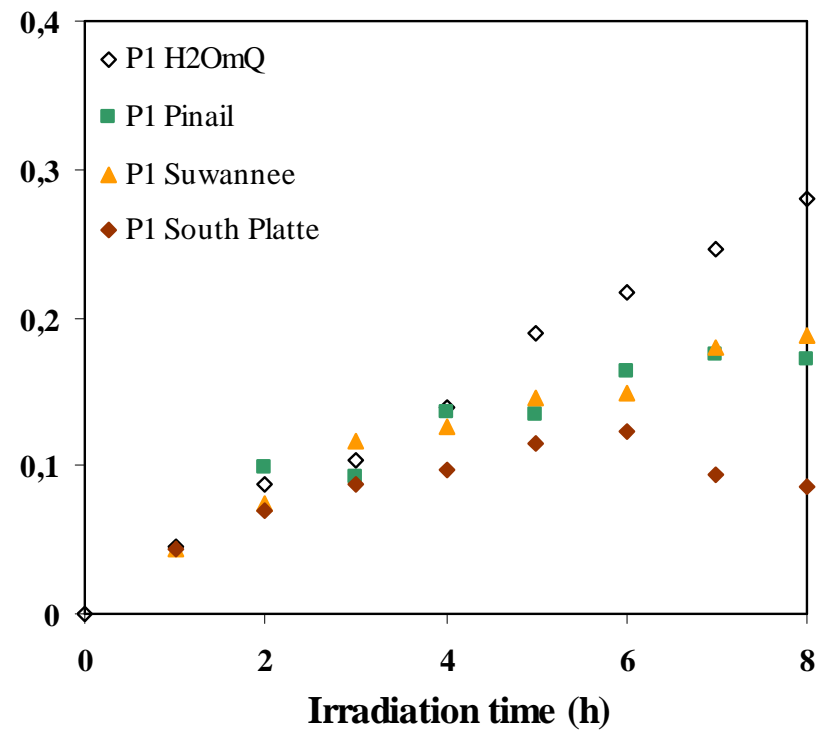
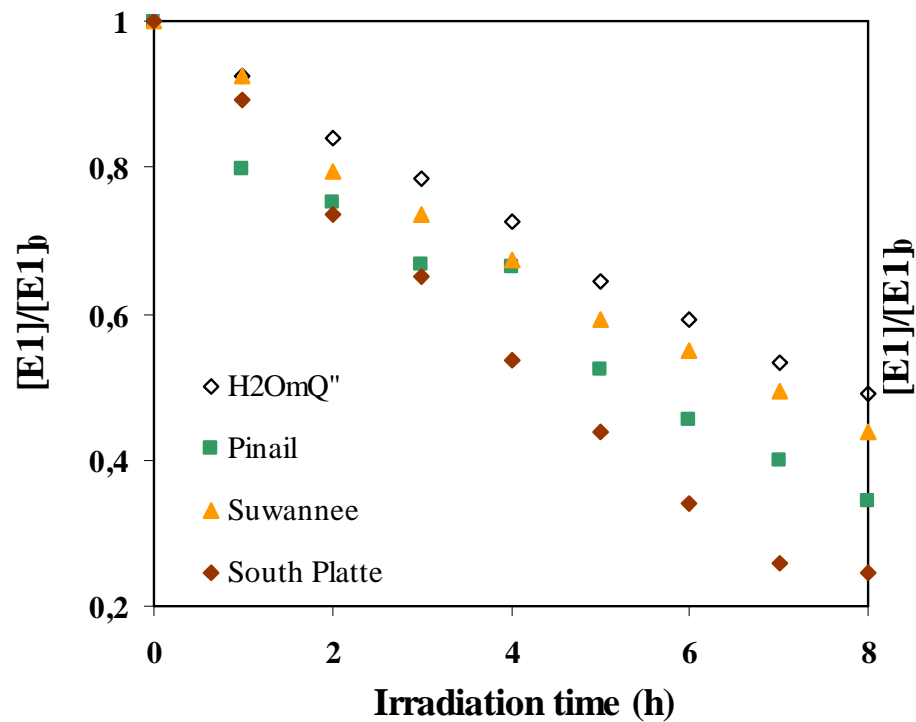
$^1\text{O}_2$: participation in the photodegradation about 2 – 10 %

OH^\bullet : participation in the photodegradation about 7 – 17 %

Indirect photolysis

Photoproduct (P1)

➤ Formation kinetics



Indirect photolysis

Photoproduct (P1)

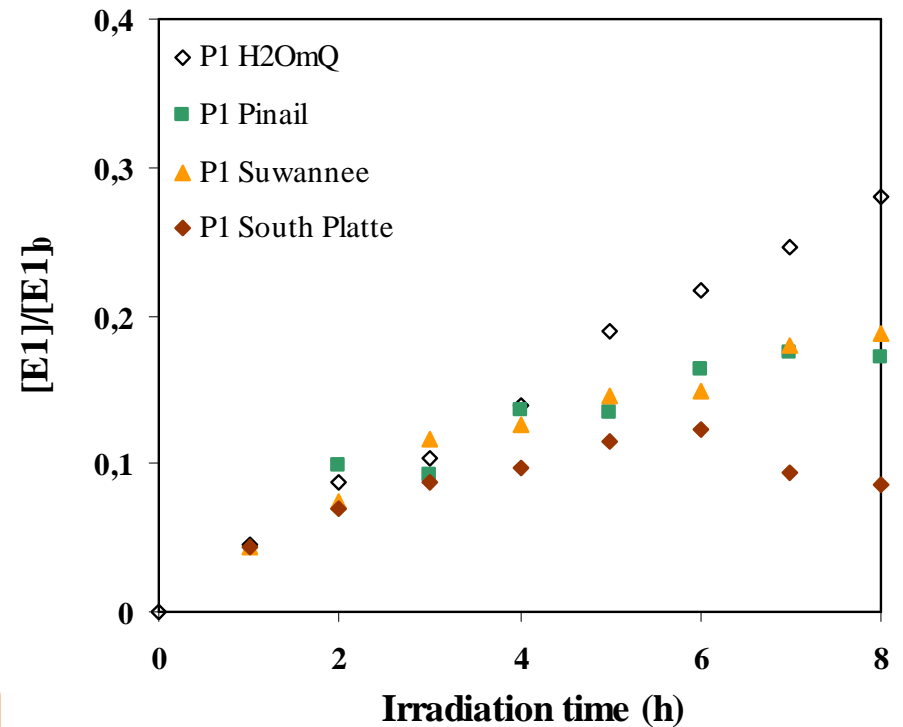
➤ Formation kinetics

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

E1	k_{O_2} (h ⁻¹)		$k_{O_2+NaN_3}$ (h ⁻¹)		k_{O_2+Pro} (h ⁻¹)	
H₂OmQ	0,09	R ² =0,998				
Pinail	0,13	R ² =0,977	0,11	R ² =0,994	0,10	R ² =0,984
Suwannee	0,10	R ² =0,997	0,09	R ² =0,964	0,08	R ² =0,986
South Platte	0,18	R ² =0,981	*	*	0,16	R ² =0,978

E2	k_{O_2} (h ⁻¹)		$k_{O_2+NaN_3}$ (h ⁻¹)		k_{O_2+Pro} (h ⁻¹)	
H₂OmQ	0,02	R ² =0,958				
Pinail	0,07	R ² =0,985	0,05	R ² =0,922	0,04	R ² =0,959
Suwannee	0,06	R ² =0,993	0,04	R ² =0,990	0,03	R ² =0,963
South Platte	0,14	R ² =0,973	*	*	0,11	R ² =0,937

* 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}C , oxidation of DOM to the hydrophilic fraction)
- Study of by-product toxicity (osters)

A large green L-shaped graphic is positioned on the left side of the slide. It consists of a vertical bar on the left and a horizontal bar at the top, meeting at a rounded corner.

Thank you