

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

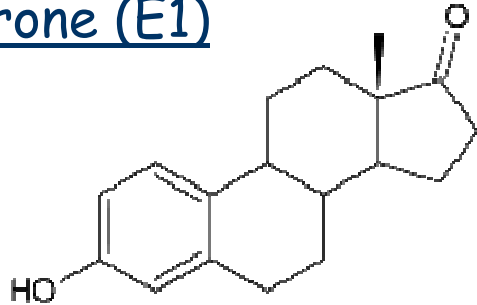
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EMEC 10 Limoges 12/04/09

Introduction

Estrone (E1)



➤ Presence in the environment

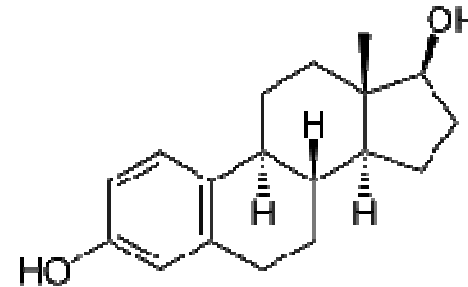
- natural estrogens (steroidal hormones) present in aquatic media (through animals excretion)

- 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)

17β-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)

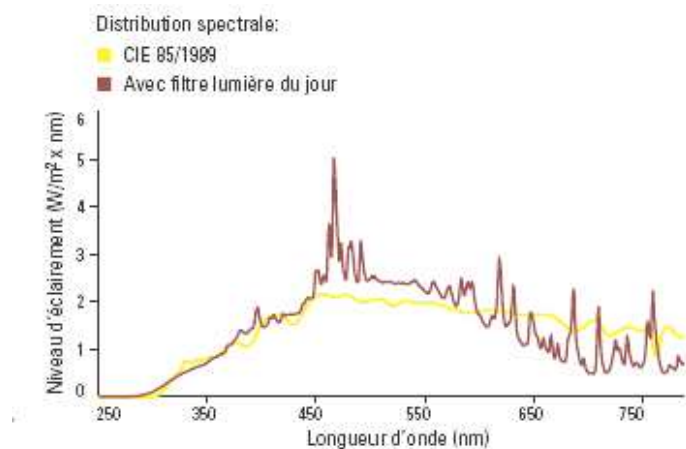
➤ Photodegradation

- 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

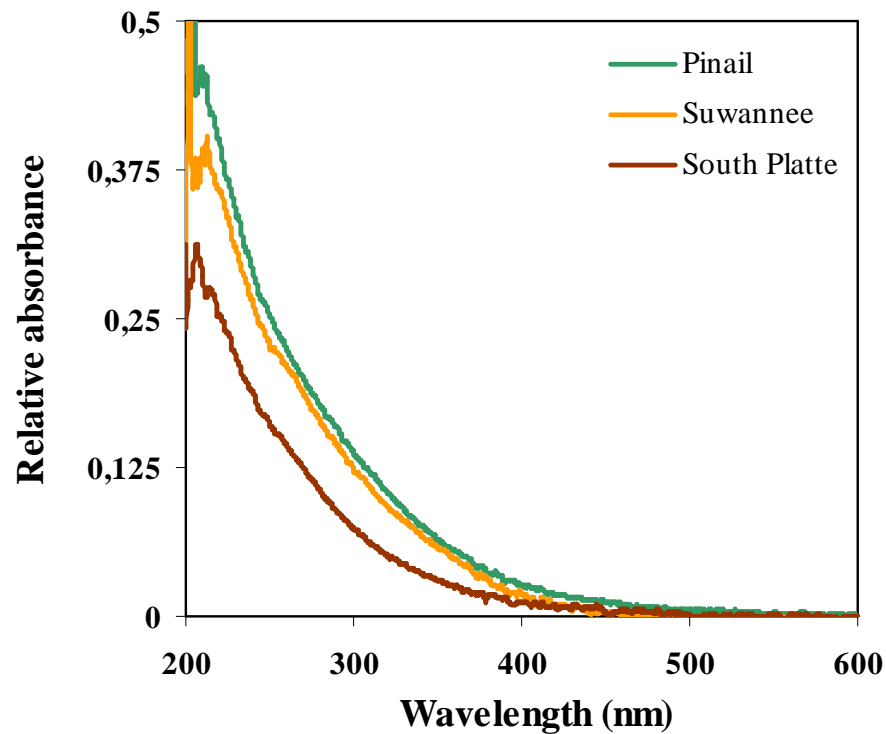
Analysis

- 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 >

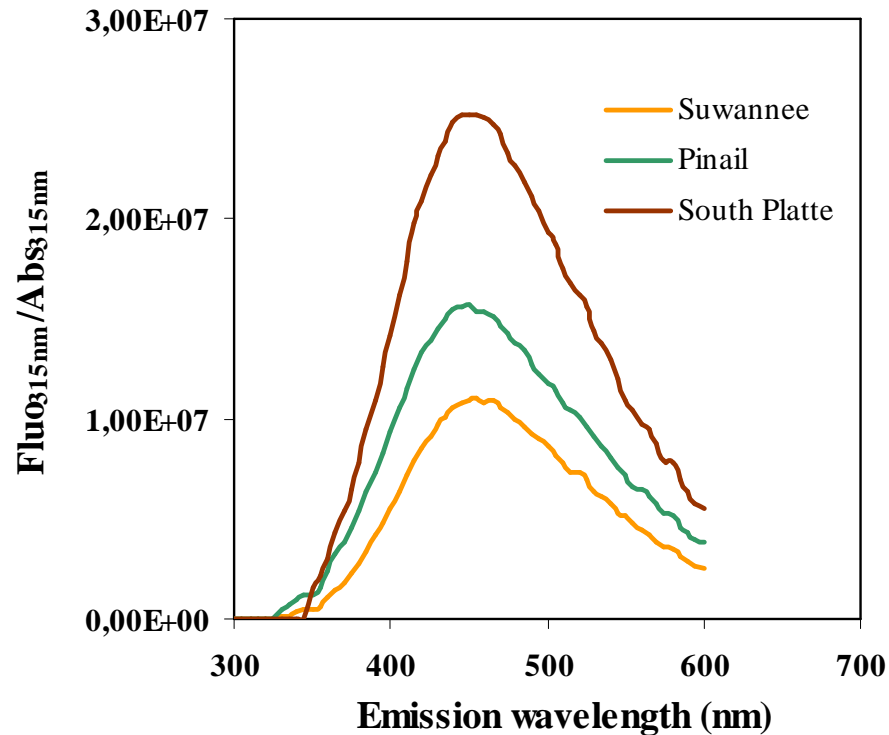
Suwannee >>

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

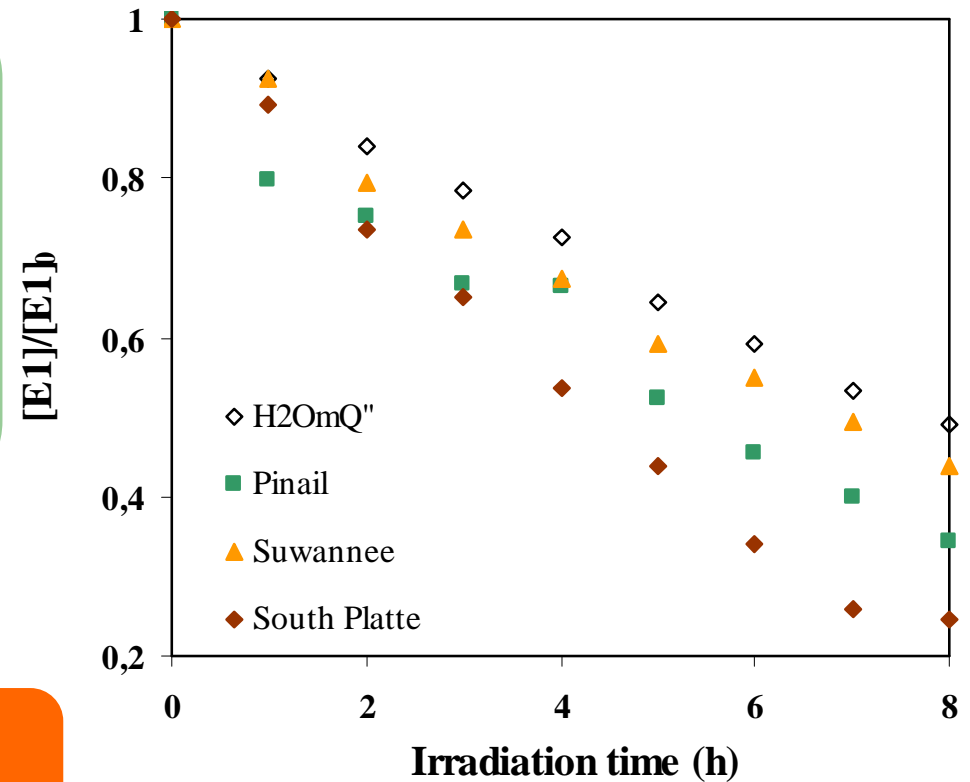
South P. 76% >

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% >>

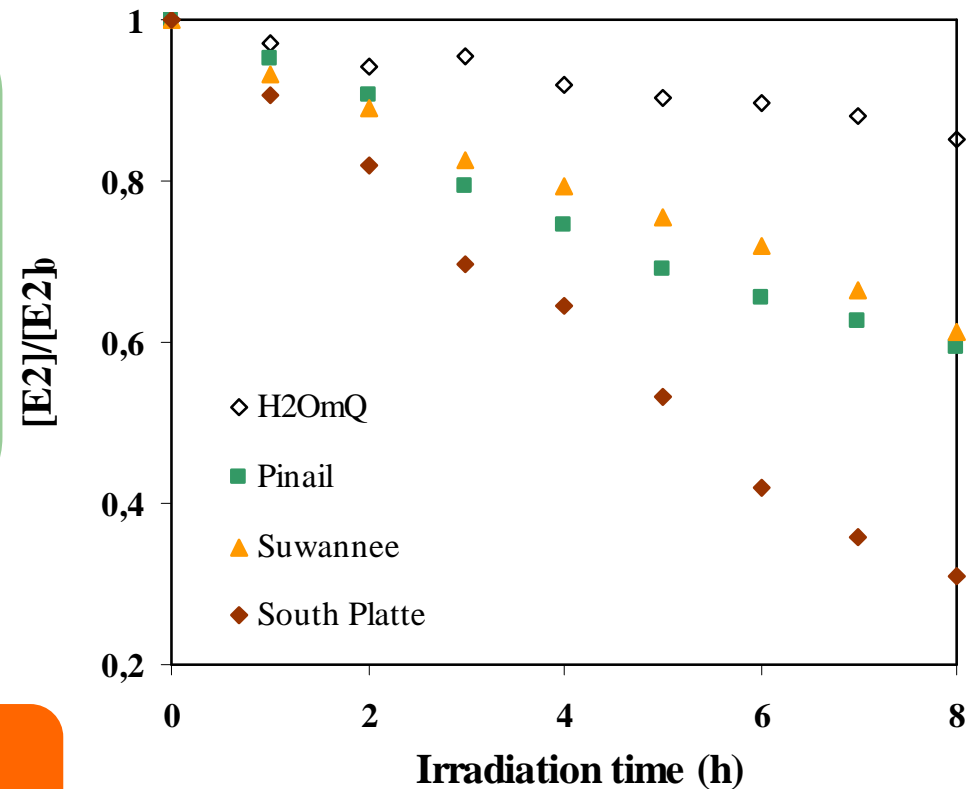
Pinail 41% >

Suwannee 39%

Relationship between
DOM nature –
photoinductive efficiency

The more fluorescent the
more photoinductive efficient

Suntest 8h, 250 W/m², 700 nM E2, pH7



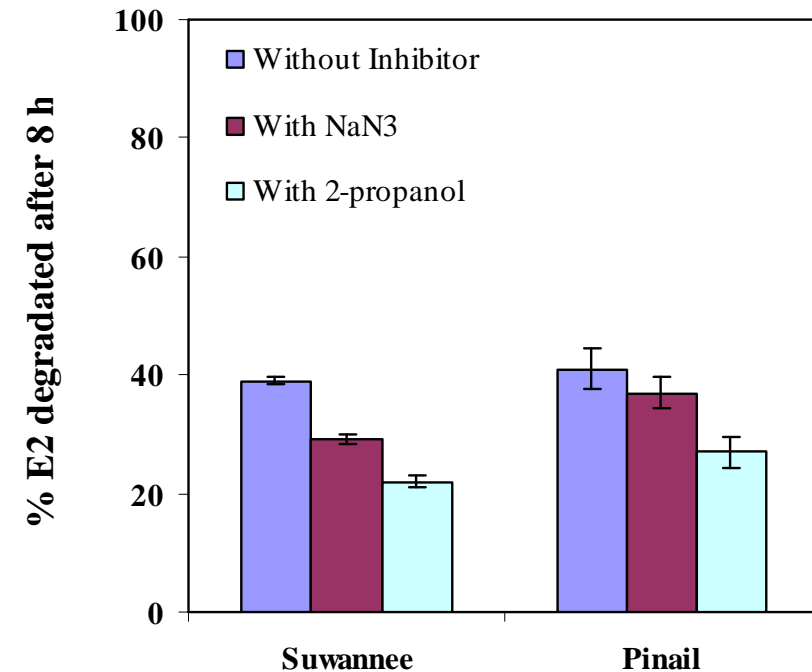
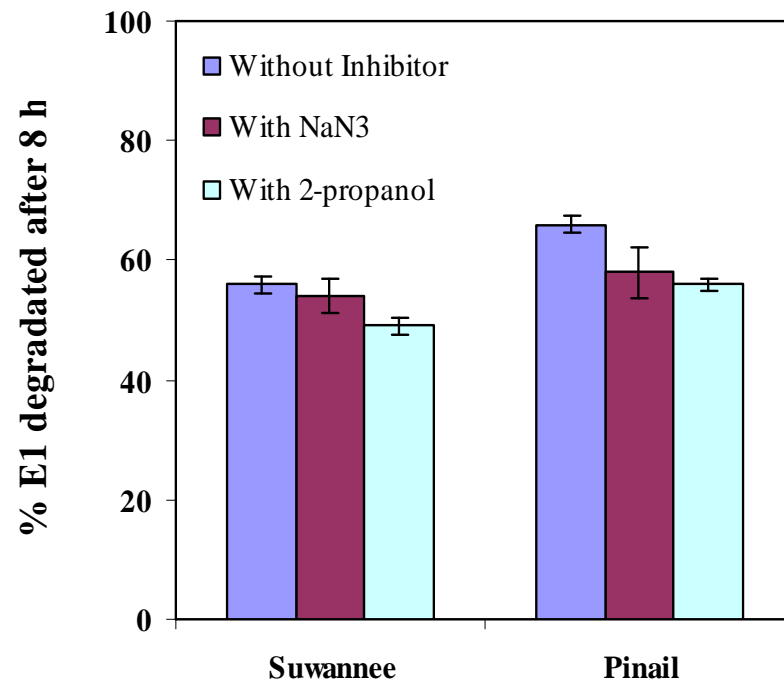
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Indirect photolysis

Reactive species

- Addition of inhibitors : NaN_3 and 2-propanol



Photodegradation decrease with the addition of inhibitors

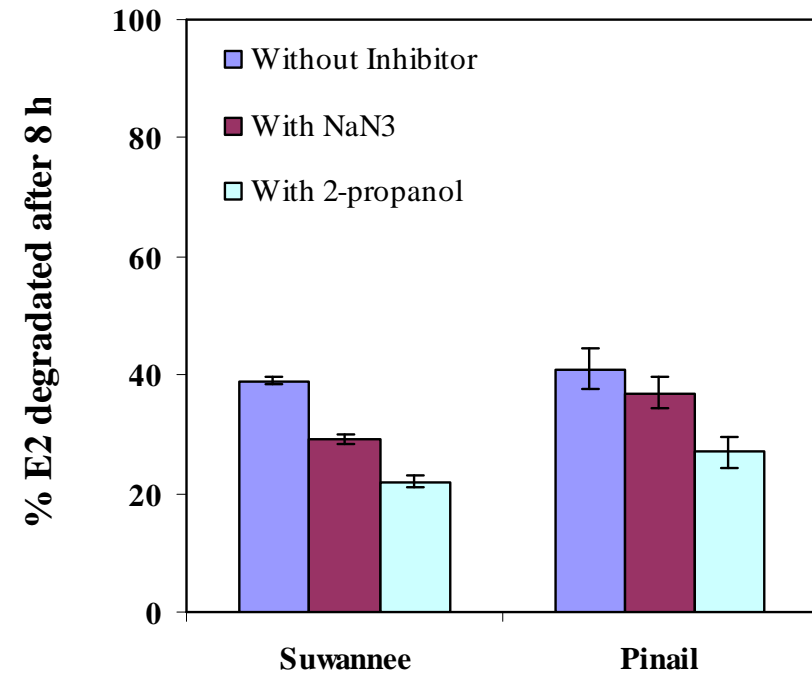
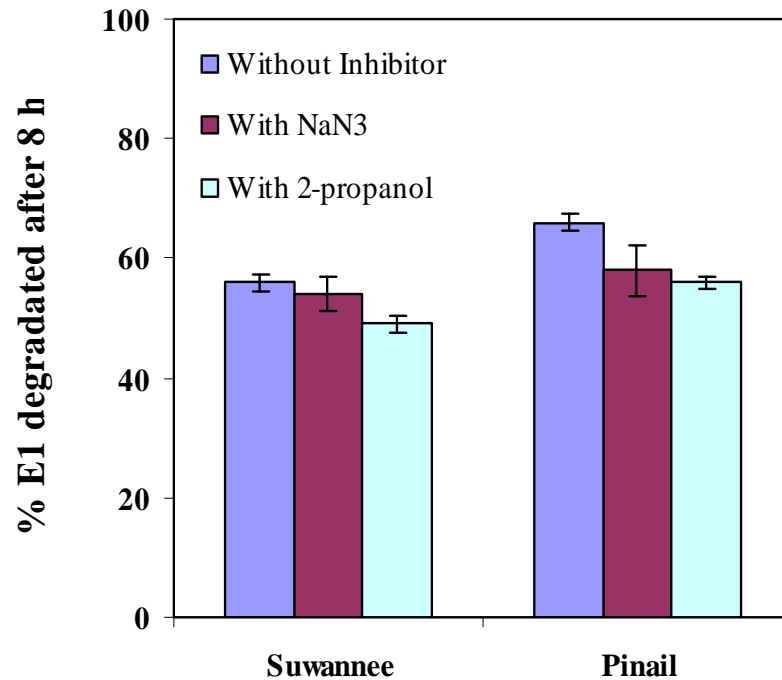
For every DOM :

Degradation without inhibitor > with NaN_3 > with 2-propanol

Indirect photolysis

Reactive species

➤ Addition of inhibitors : NaN_3 and 2-propanol



Reactive species in the inductive photodegradation

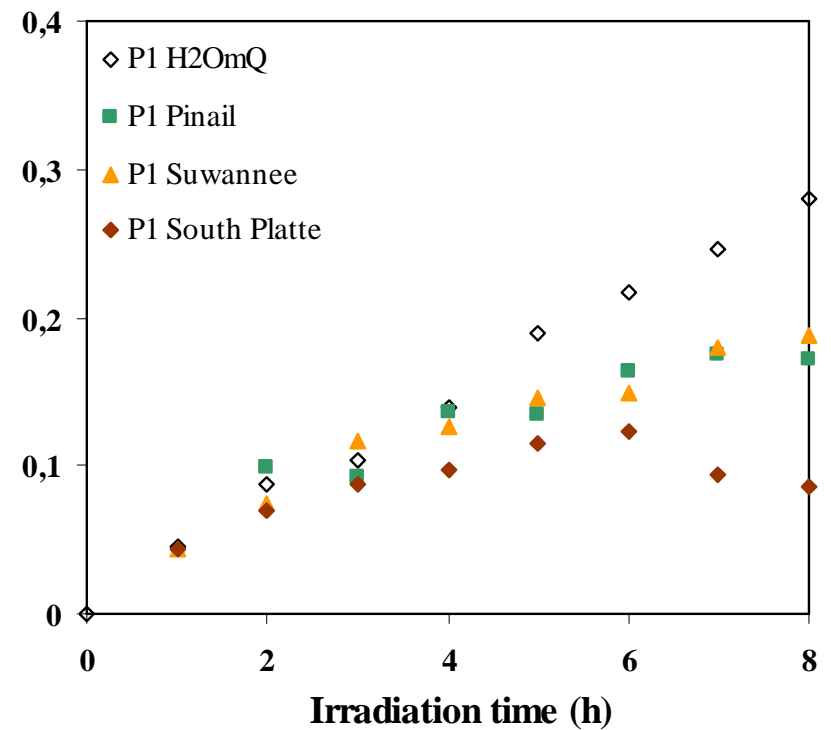
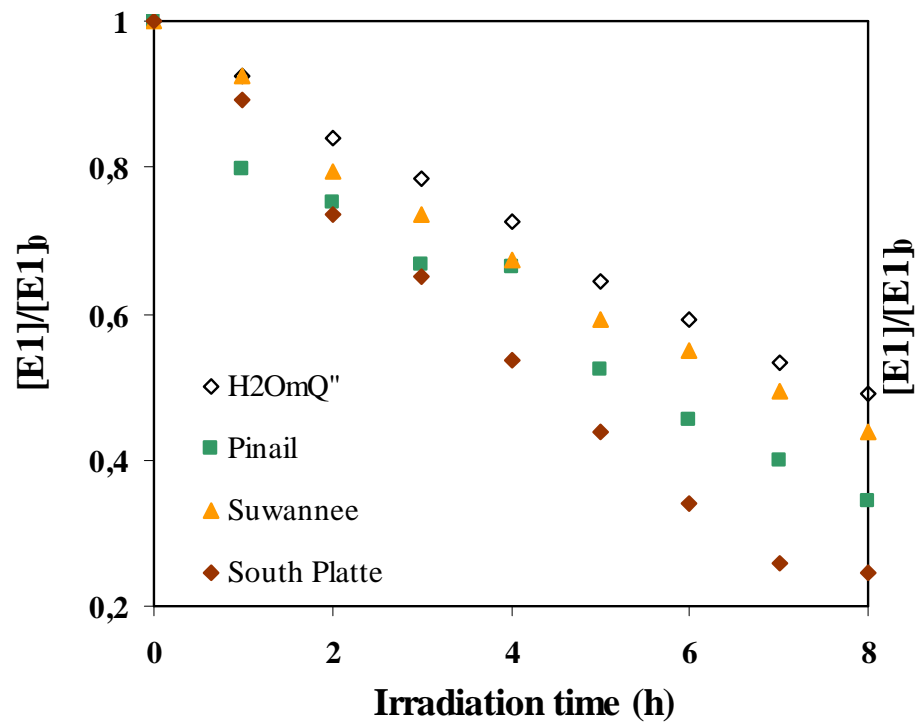
$^1\text{O}_2$: participation in the photodegradation about 2 – 10 %

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

Indirect photolysis

Photoproduct (P1)

➤ Formation kinetics



Indirect photolysis

Photoproduct (P1)

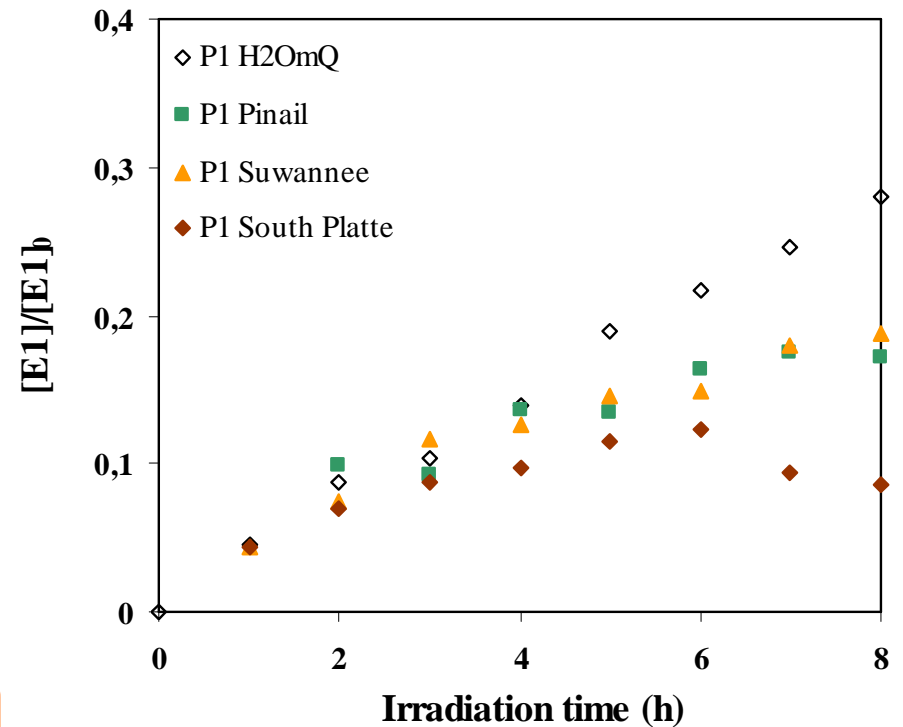
➤ Formation kinetics

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)	
H ₂ OmQ	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)	
H ₂ OmQ	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 photosensitivity
- 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