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

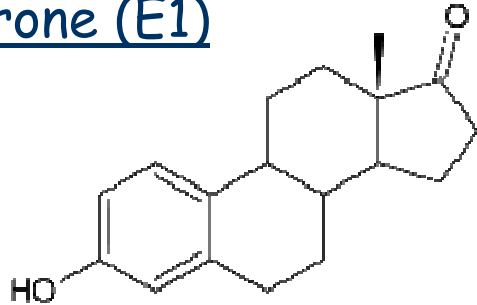
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EMEC 10 Limoges 12/04/09

# Introduction

## Estrone (E1)



### ➤ Presence in the environment

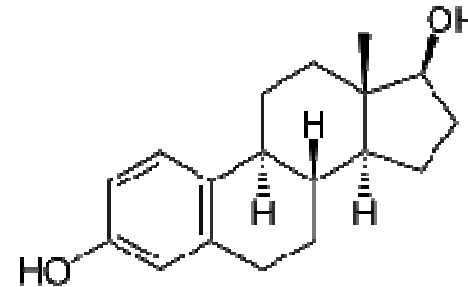
- natural estrogens (steroidal hormones) present in aquatic media (through animals excretion)

- 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)

## 17 $\beta$ -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)

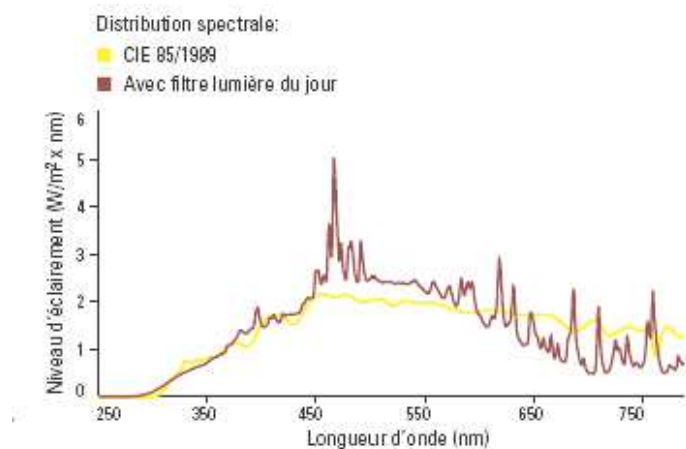
### ➤ Photodegradation

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

# Materials and Methods

## Photolysis

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



Suntest 8h, 250  $W/m^2$ , 900 kJ/h :  
- ~ 800 nM E1 or E2  
- 20 mg/L DOM  
- pH = 7

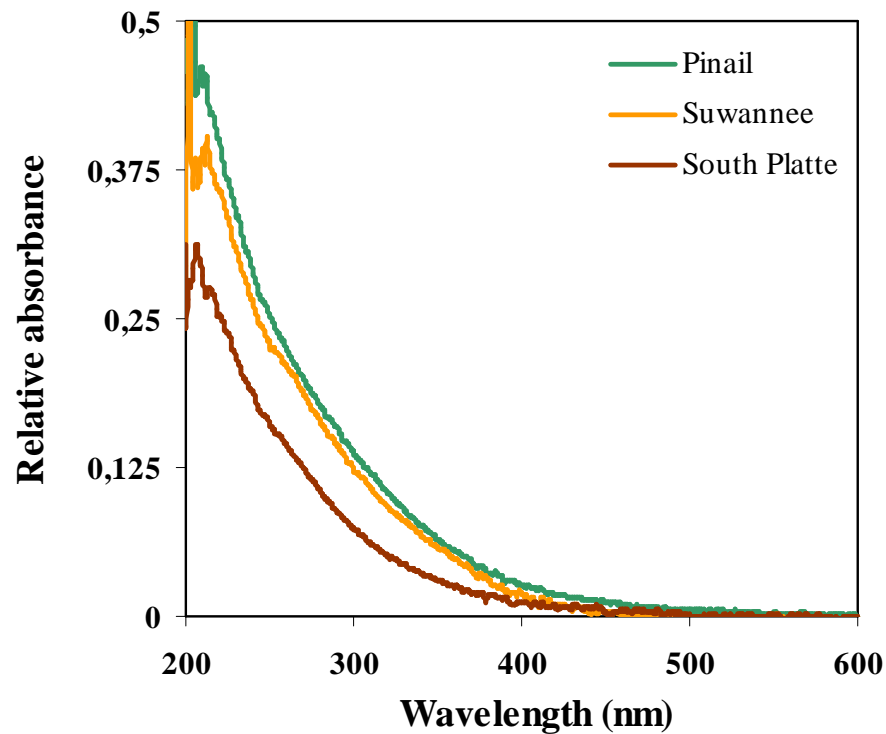
## Analysis

- 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 >

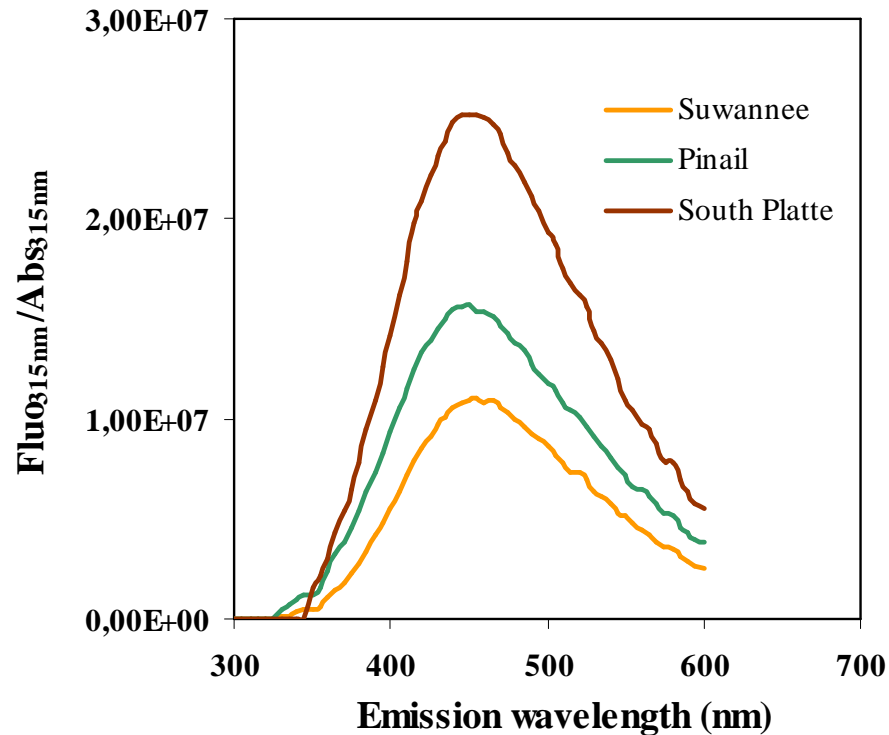
Suwannee >>

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

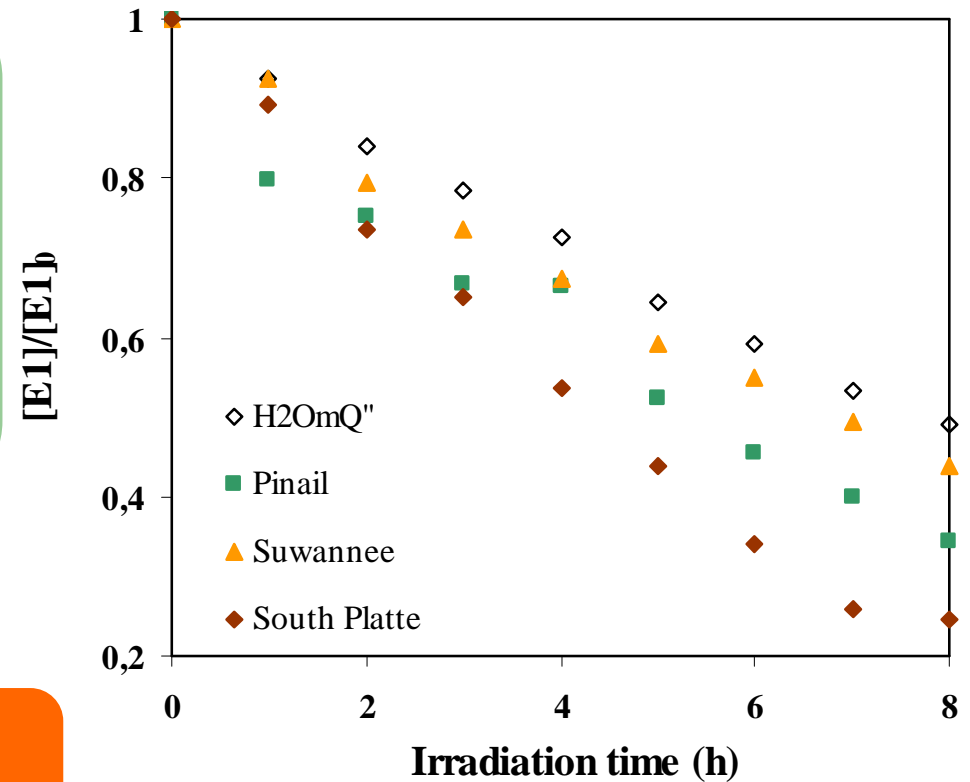
South P. 76% >

Pinail 66% >

Suwannee 56%

→ Relationship between  
DOM nature –  
photoinductive efficiency

Suntest 8h, 250 W/m<sup>2</sup>, 800 nM E1, pH7



%Error (duplicates) : 2-5 %

# Indirect photolysis

Nature of DOM Influence → E2

Photoinductive efficiency

South P. 69% >>

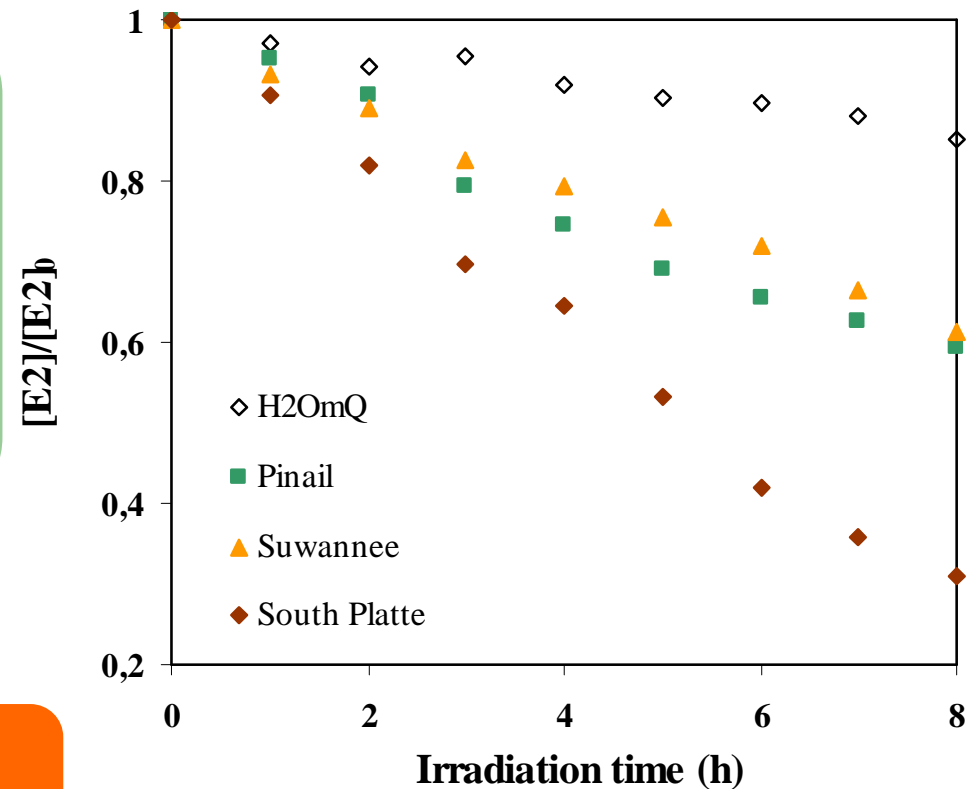
Pinail 41% >

Suwannee 39%

Relationship between  
DOM nature –  
photoinductive efficiency

The more fluorescent the  
more photoinductive efficient

Suntest 8h, 250 W/m<sup>2</sup>, 700 nM E2, pH7



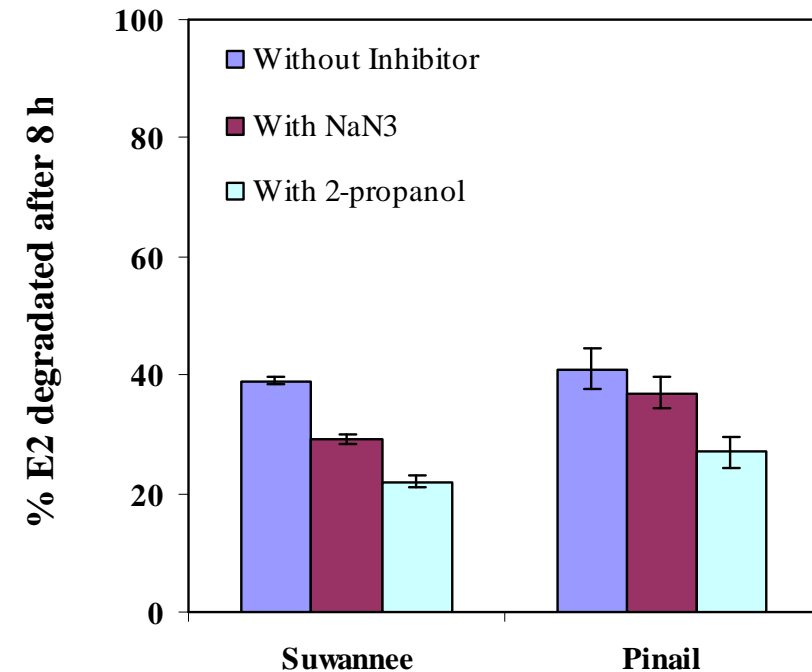
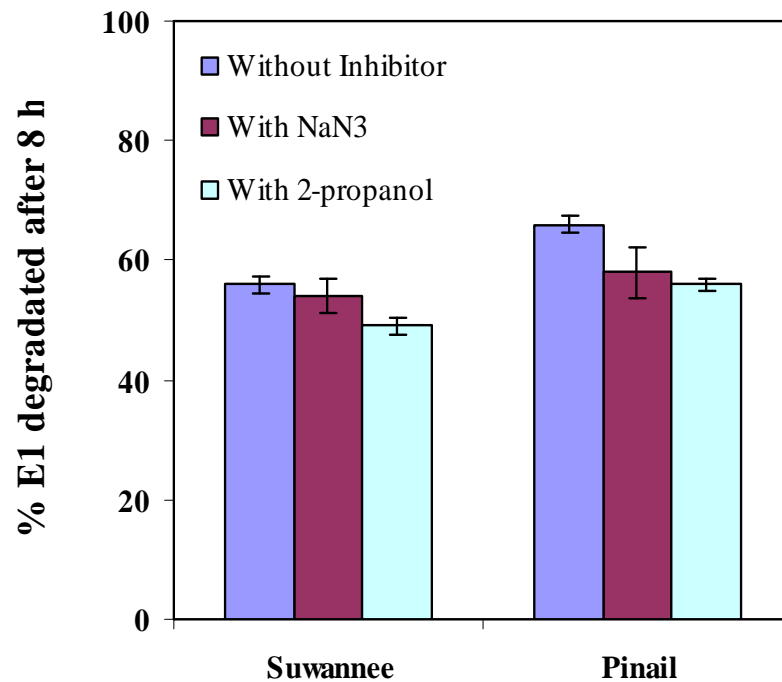
%Error (duplicates) : 3-6 %

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# Indirect photolysis

## Reactive species

- Addition of inhibitors :  $\text{NaN}_3$  and 2-propanol



Photodegradation decrease with the addition of inhibitors

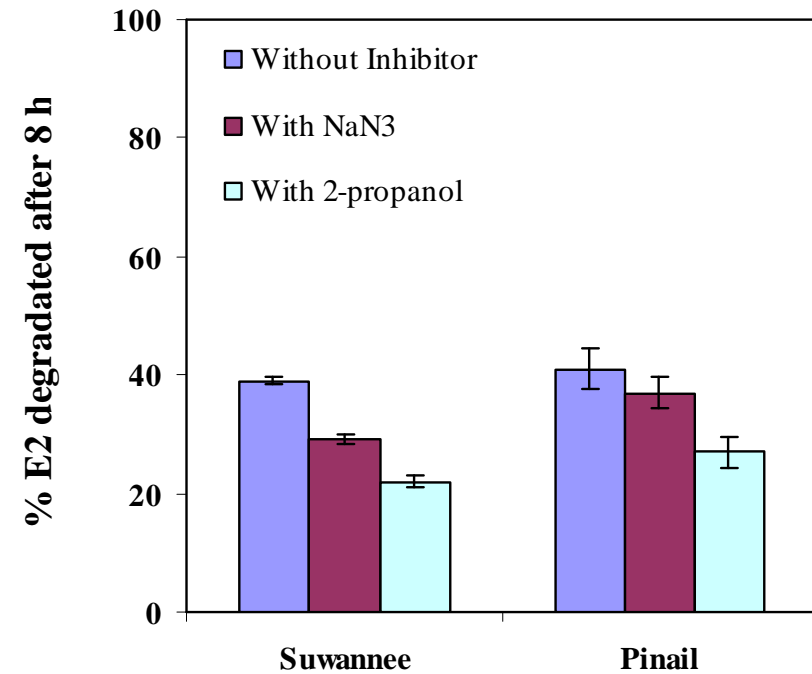
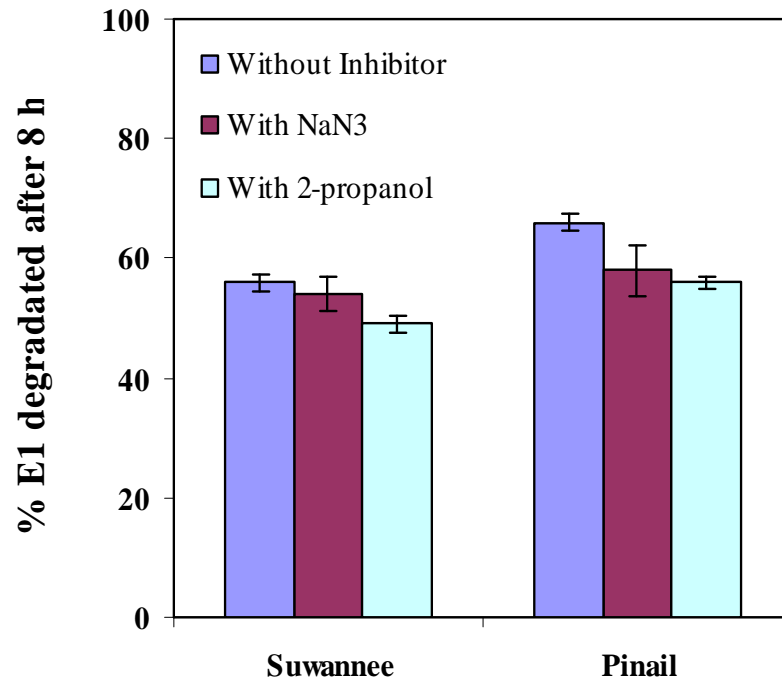
For every DOM :

Degradation without inhibitor > with  $\text{NaN}_3$  > with 2-propanol

# Indirect photolysis

## Reactive species

➤ Addition of inhibitors :  $\text{NaN}_3$  and 2-propanol



**Reactive species in the inductive photodegradation**

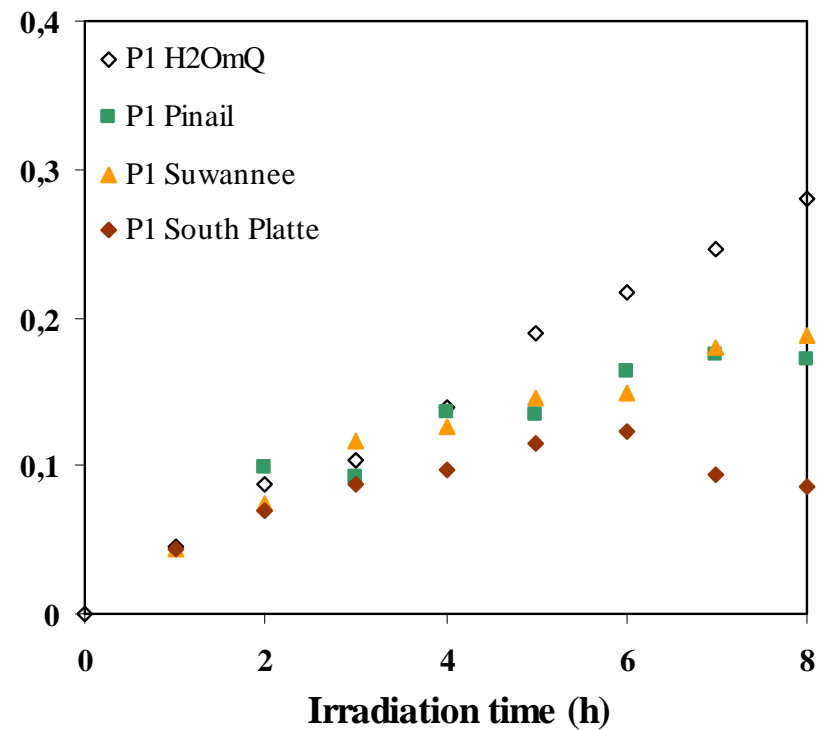
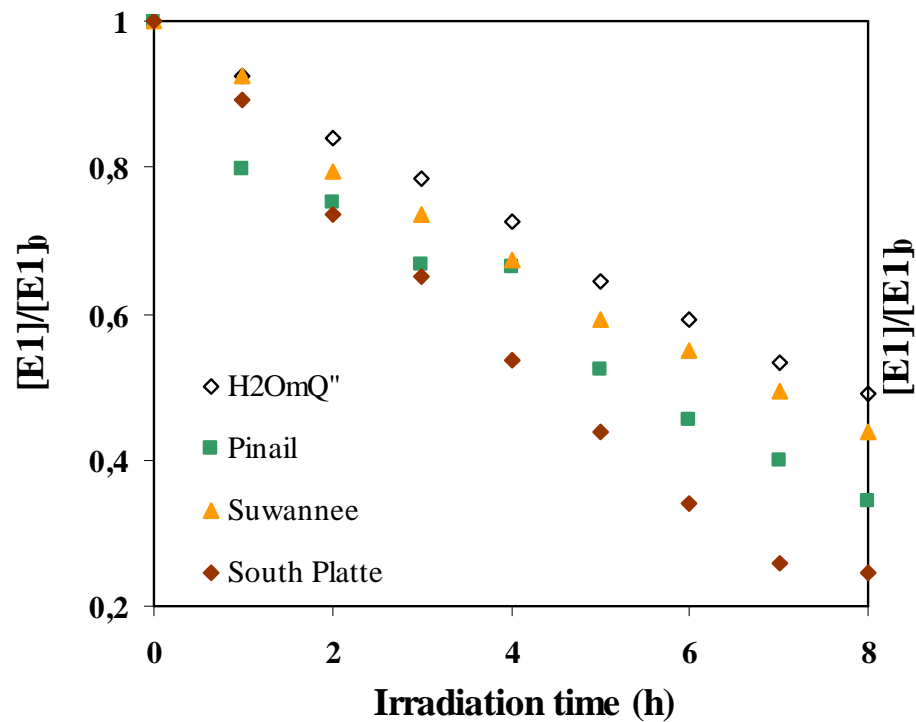
$^1\text{O}_2$  : participation in the photodegradation about 2 – 10 %

$\text{OH}^\bullet$  : participation in the photodegradation about 7 – 17 %

# Indirect photolysis

## Photoproduct (P1)

### ➤ Formation kinetics



# Indirect photolysis

## Photoproduct (P1)

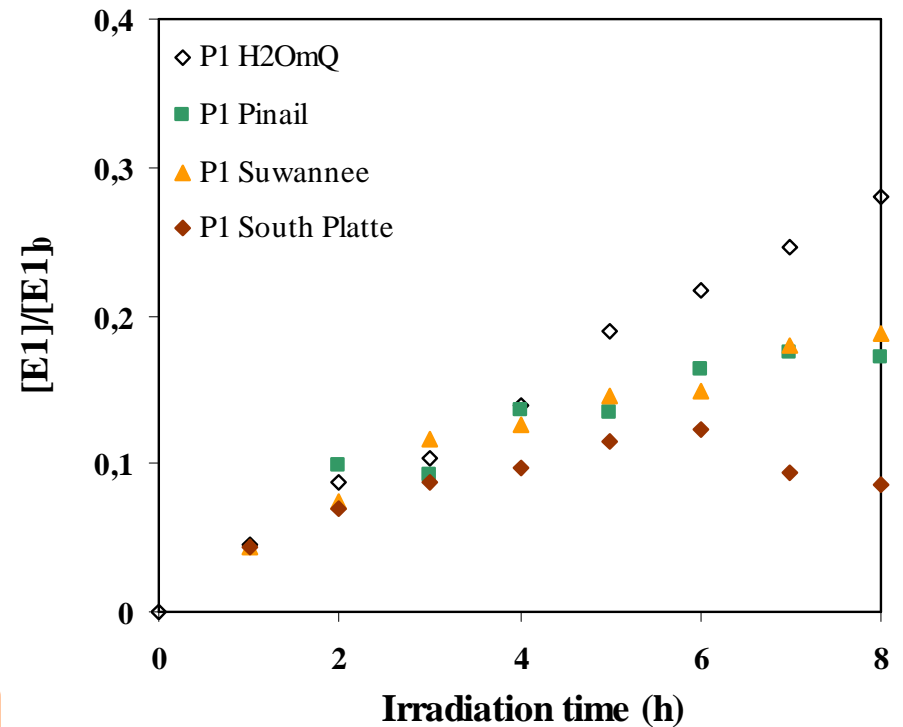
### ➤ Formation kinetics

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 <sup>-1</sup> ) |                       | $k_{O_2+NaN_3}$ (h <sup>-1</sup> ) |                       | $k_{O_2+Pro}$ (h <sup>-1</sup> ) |                       |
|-------------------------|------------------------------|-----------------------|------------------------------------|-----------------------|----------------------------------|-----------------------|
| <b>H<sub>2</sub>OmQ</b> | 0,09                         | R <sup>2</sup> =0,998 |                                    |                       |                                  |                       |
| <b>Pinail</b>           | 0,13                         | R <sup>2</sup> =0,977 | 0,11                               | R <sup>2</sup> =0,994 | 0,10                             | R <sup>2</sup> =0,984 |
| <b>Suwannee</b>         | 0,10                         | R <sup>2</sup> =0,997 | 0,09                               | R <sup>2</sup> =0,964 | 0,08                             | R <sup>2</sup> =0,986 |
| <b>South Platte</b>     | 0,18                         | R <sup>2</sup> =0,981 | *                                  | *                     | 0,16                             | R <sup>2</sup> =0,978 |

| E2                      | $k_{O_2}$ (h <sup>-1</sup> ) |                       | $k_{O_2+NaN_3}$ (h <sup>-1</sup> ) |                       | $k_{O_2+Pro}$ (h <sup>-1</sup> ) |                       |
|-------------------------|------------------------------|-----------------------|------------------------------------|-----------------------|----------------------------------|-----------------------|
| <b>H<sub>2</sub>OmQ</b> | 0,02                         | R <sup>2</sup> =0,958 |                                    |                       |                                  |                       |
| <b>Pinail</b>           | 0,07                         | R <sup>2</sup> =0,985 | 0,05                               | R <sup>2</sup> =0,922 | 0,04                             | R <sup>2</sup> =0,959 |
| <b>Suwannee</b>         | 0,06                         | R <sup>2</sup> =0,993 | 0,04                               | R <sup>2</sup> =0,990 | 0,03                             | R <sup>2</sup> =0,963 |
| <b>South Platte</b>     | 0,14                         | R <sup>2</sup> =0,973 | *                                  | *                     | 0,11                             | R <sup>2</sup> =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  $^{13}\text{C}$ , 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