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Photoinductive degradation of 17 β -estradiol and isoproturon by natural dissolved organic matter under simulated sunlight

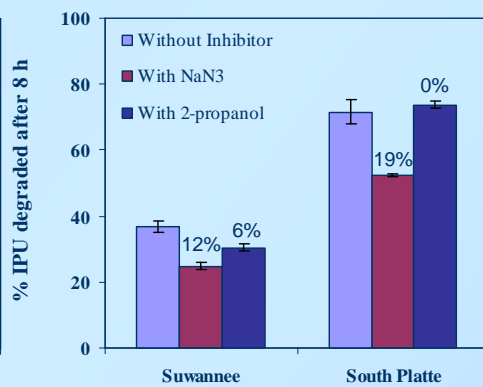
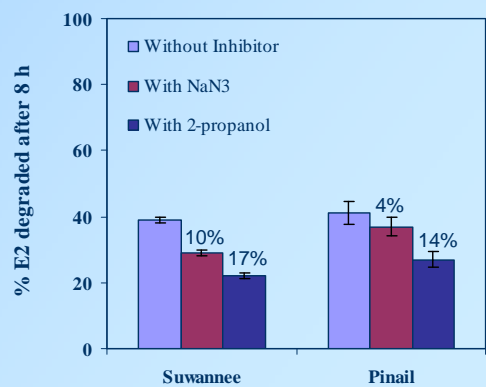
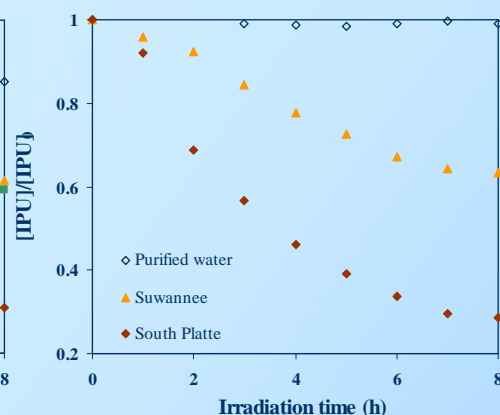
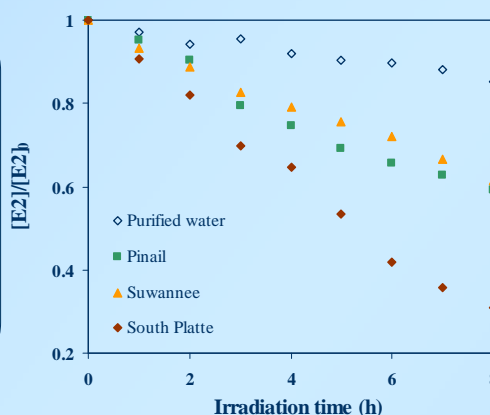
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- > Pesticides are common micropollutants of surface waters. Beside them, pharmaceuticals are now detected, coming from natural excretions or WWTPs.
- > Natural Dissolved Organic Matter (DOM) is ubiquitous in surface waters. It is a complex organic mixture formed by natural decomposition of ecosystems.
- > Photodegradation of aquatic micropollutants can be enhanced through DOM sensitization pathway involving the formation of reactive species.

- > The natural photodegradation of a natural hormone (17 β -estradiol, E2) and a pesticide (isoproturon, IPU) has been studied in the presence of DOM.
- > Sunlight irradiation was performed by a Suntest CPS+ solar simulator (290 nm < λ < 700 nm, 250 W/m², 8h). Concentrations used in the experiments were approximately 1 μ M. Photodegradation efficiencies have been measured in the presence of DOM (20 mg/L) isolated from surface waters.
- > The formation of reactive species was investigated and photoproducts were identified through LC-MS analyses.

A – Photodegradation in the presence of DOM

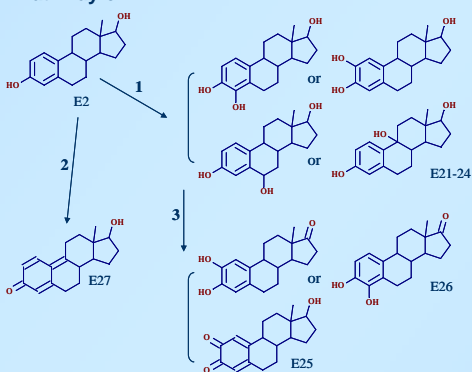
- Pollutants degradation is always faster in the presence of DOM than in purified water
- Enhancement effect strongly depends on the nature of DOM extracts
- An order of DOM efficiency is observed :
 South Platte (69%, E2; 72%, IPU) >>
 Pinail (41%, E2) >
 Suwannee (39%, E2; 37%, IPU)



B – DOM production of reactive species

- Photodegradation only weakly decreases with the addition of inhibitors (azide \rightarrow 1O_2 ; 2-propanol \rightarrow OH^\bullet)
- For E2 :
 Without inhibitor > with NaN₃ > with 2-propanol
- For IPU :
 Without inhibitor \geq with 2-propanol > with NaN₃
- Reactive species involved :
 > 1O_2 : participation in the photodegradation about 4 – 19%
 > OH^\bullet : participation in the photodegradation about 0 – 17%

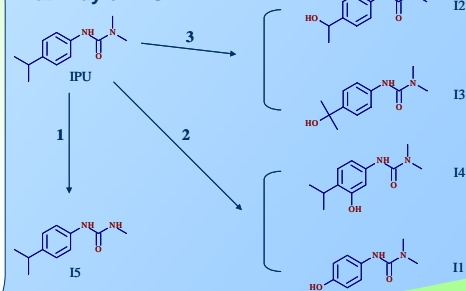
Pathway of E2



C – Pathways and photoproducts

- 8 and 5 photoproducts have been identified during the degradation of E2 and IPU respectively
- Pathway of E2 :
 1: hydroxylation of aromatic cycle or cycle closed to aromatic one (E21-E24)
 2: E2 quinone methide derivative (E27)
 3: hydroxylation of aromatic cycle and oxidation of phenolic groups (E25 and E26)
- Pathway of IPU :
 1: demethylation of dimethylurea group (I5)
 2: hydroxylation of aromatic cycle (I1 and I4)
 3: simultaneous demethylation and hydroxylation of isopropyl group (I2 and I3)

Pathway of IPU



Conclusions

- > DOM presents an ability to photoinduce the degradation of micropollutants; its efficiency depending on the micropollutant and on its own properties (nature of the extract)
- > During photoinductive degradation, reactive species such as singlet oxygen and hydroxyl radicals are produced by DOM and react with the pollutants. However, the participation of these 2 molecules has only been observed. Excited triplet states may contribute to a large extent in the reaction.
- > Photoproducts have been observed. They come from hydroxylation, oxidation and demethylation/dealkylation mechanisms of the parent compound.