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To cite this version:

Emilie Caupos, Patrick Mazellier, Jean-Philippe Croué. Photoinductive degradation of two pesticies by natural dissolved organic matter under simulated sunlight. TransCon 2010, Sep 2010, Monte Verita, Switzerland. hal-00822551

HAL Id: hal-00822551

https://enpc.hal.science/hal-00822551v1

Submitted on 14 May 2013

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

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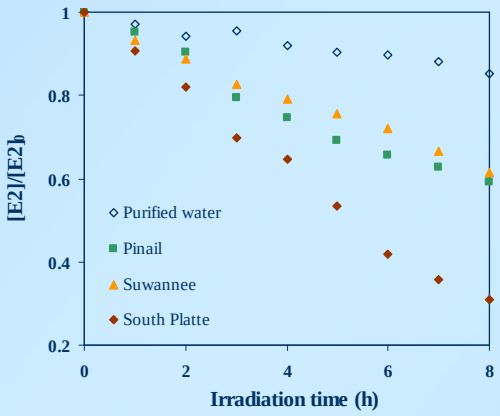
- Pesticides are common micropollutants of surface waters. Beside them, pharmaceuticals are now detected, coming from natural excretions or WWTPs.
- Natural Dissolved Organic Matter (DOM) is ubiquitous in surface waters. It is a complex organic mixture formed by natural decomposition of ecosystems.
-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

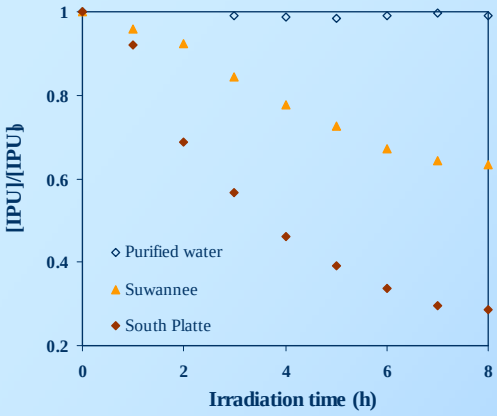
- The natural photodegradation of a natural hormone (17β-estradiol, E2) and a pesticide (isoproturon, IPU) has been studied in the presence of DOM.
- Sunlight irradiation was performed by a Suntest CPS+ solar simulator (290 nm < λ < 700 nm, 250 W/m², 8h). Concentrations used in the experiments were approximately 1 µM. 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.

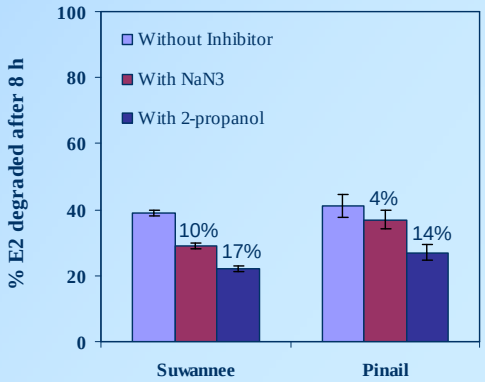
A – Photodegradation in the presence of DOM

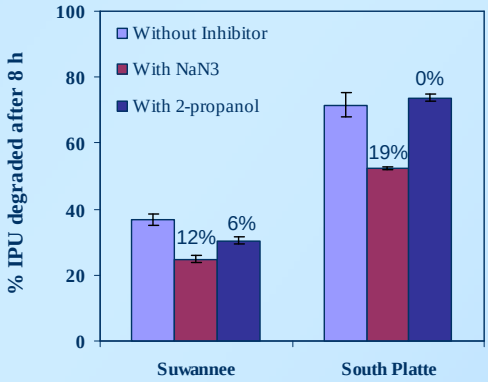
- Pollutants degradation is always faster in the presence of DOM than in purified water
- Enhancement effect strongly depends on the nature of DOM extracts
- An order of DOM efficiency is observed :

South Platte (69%, E2; 72%, IPU) >>
Pinail (41%, E2) >
Suwannee (39%, E2; 37%, IPU)





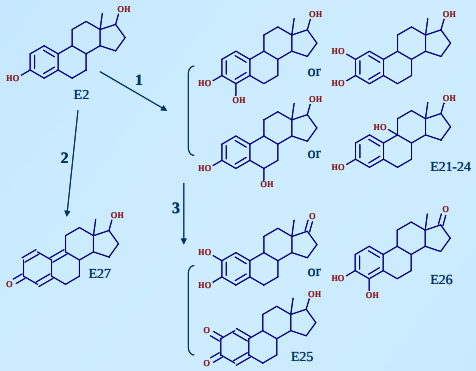




B – DOM production of reactive species

- Photodegradation only weakly decreases with the addition of inhibitors (azide → $^1O_2$; 2-propanol → OH°)
  - For E2 :
  Without inhibitor > with NaN_3 > with 2-propanol
  - For IPU :
  Without inhibitor ≥ with 2-propanol > with NaN_3
- Reactive species involved :
  - $^1O_2$: participation in the photodegradation about 4 – 19%
  - OH°: participation in the photodegradation about 0 – 17%

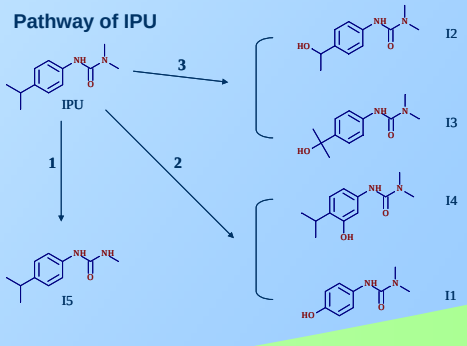
Pathway of E2



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 dimetylurea 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.

TransCon2010, Monte Verità, September 12-17, 2010