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The impact of chromophoric dissolved organic matter on the photodegradation of 17α-ethinylestradiol (EE2) in natural waters

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HIGHLIGHTS

- Photodegradation of 17α-ethinylestradiol (EE2) was studied natural water samples.
- Photodegradation was enhanced in presence of chromophoric dissolved organic matter.
- Half-life times in river and sea water were about one and two days, respectively.

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ABSTRACT

17α-Ethinylestradiol (EE2), the potent estrogen which forms the basic constituent of the contraceptive pill, can undergo degradation in natural waters by sunlight and via secondary reactions initiated by photo-excited dissolved organic matter. The current paper presents the findings of an investigation into the irradiation process of EE2 when dissolved in natural waters. This investigation was carried out under simulated sunlight in samples of sea, river and distilled water at a 17α-ethinylestradiol concentration of 300 ng L^{-1}.

Several notes of significance may be made on the basis of these results. Firstly, an enhancement of the degradation, observed in the presence of co-absorbing dissolved organic matter, was shown to be proportional to the absorbance of the sample. Secondly, the kinetics of the process obtained during this investigation were within the range of previously reported findings, despite the fact that significantly higher concentrations of EE2 were used in earlier studies. Finally, the environmental half-life times for 17α-ethynyloestradiol, calculated from the results of the experiments, were found to be one and two days in the top layer of river and sea water respectively.

1. Introduction

17α-Ethinylestradiol (EE2), the basic constituent of the contraceptive pill, is released into surface waters from communal sewage treatment plants and, despite occurring at very low concentrations (in the range of ng L^{-1}), can exert noticeable effects on aquatic biota (Sumpter and Johnson, 2005; Kidd et al., 2007). It is not only more stable in the natural environment than natural estrogens (Ying and Kookana, 2003; Robinson and Hellou, 2009) but also possesses the greatest estrogenic potency (Thorpe et al., 2003; van den Belt et al., 2004).

The light absorption band of EE2 partly overlaps with the solar spectrum and this xenobiotic may therefore be subject to degradation via direct/primary photoreactions. Indeed, there are studies showing that radiation representative to that of sunlight (wavelength > 280 nm) decreases the concentration of 17α-ethynyloestradiol in solutions (Table 2). Aside from direct photolysis, a significant role in the removal of EE2 is played by indirect (sensitized) reactions initiated by other light absorbers. Reports of experiments with natural water samples (Table 2) clearly show enhancement of EE2 photodegradation as a result of secondary reactions initiated by photo-excited chromophoric dissolved organic matter (CDOM), the main component in the pool of dissolved natural organic substances. This material, referred to in the past as humic substances, is the most important sunlight absorber in natural waters (Lean, 1998). Its significance in aquatic photochemistry has been proved in numerous studies (see Mopper and Kieber, 2002 and references therein).

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Table 1
Physico-chemical characteristics of irradiated waters.

	pH	Salinity (practical salinity units)	DOC (mg L^{-1})	Fe_{tot} (μM)	$NO_3^- + NO_2^-$ (μM)
Baltic Sea	8.1	6.9	4.9 ± 0.2	b.d[a]	b.d[b]
Vistula River	7.9	0.2	10.8 ± 0.3	0.18 ± 0.05	6.2 ± 1.2

[a] Below detection limit (0.02 μM).
[b] Below detection limit (0.8 μM).

Table 2
Degradation rate constant (k) and half-life for EE2 photodegradation under different experimental conditions.

EE2 concentration (solute)	k (h^{-1})/half-life time	Irradiation device; optical path length (l)	Source
300 ng L^{-1}			
(Distilled water)	0.04 ± 0.02/17 h	See text	This study
(Baltic Sea)	0.06 ± 0.02/12 h		
(Vistula River)	0.11 ± 0.03/6 h		
0.6 mg L^{-1}			
(Lake water)	0.03/23 h	Sunlight, summer sunny day 41°N; l = 1.4 cm	Zuo et al. (2013)
10 μg L^{-1}			
(Distilled water)	0.08 ± 0.02/7 h	Solar simulator $\lambda > 300$ nm; l = 1 cm	Whidbey et al. (2012)
(10 mg L^{-1} Solution of Swuanee River fulvic acid)	0.13 ± 0.03/5 h		
500 ng L^{-1}			
(Distilled water)	0.013 ± 0.006/53 h	Fluorescent lamp UVB = 133 μW cm^{-2}	Atkinson et al. (2011)
(Ottawa River)	0.001 ± 0.004/693 h		
(Lake Cromwell)	0.021 ± 0.014/33 h		
(Raisin River)	0.010 ± 0.011/69 h		
1 mg L^{-1}			
(Distilled water)	~0.09/7 h	Fluorescent lamp UVA = 115.6 Wm^{-2}; $\lambda > 300$ nm; l = 25.5 cm	Puma et al. (2010)
10–40 mg L^{-1}			
(Distilled water)	0.61/1 h	Sunlight simulator (300–800 nm); $l \approx 2$ cm	Matamoros et al. (2009)
(Ebre river)	0.69/1 h		
(Besos River)	0.73/1 h		
(Mediterranean Sea)	0.62/1 h		
(Besos River)	0.007/99 h	Sunlight, May, 41°N; $l \approx 2$ cm	
0.150 mg L^{-1}			
(Distilled water)	~0.12/6 h	Fluorescent lamp ($\lambda > 290$ nm); l = 6.75 cm	Mazellier et al. (2008)
8 mg L^{-1}			
(Estuarine seawater)	~0.05/14 h	Sunlight 41°N; l = 1.4 cm	Zuo et al. (2006)
1–2 μg L^{-1}			
(Milli-Q water)	0.02 ± 0.002/28 h	Sunlight simulator (290–700 nm) 765 W m^{-2}; l = 1.5 cm	Lin and Reinhard (2005)
(Santa Ana River)	0.30 ± 0.015/2 h		
100 μg L^{-1}			
(Thames River)	0.0055/126 h	Solar light simulator	Jürgens et al. (2002)

In the majority of laboratory experiments EE2 concentrations exceeded "natural" levels by three to six orders of magnitude. Those results can still be reasonably extrapolated to natural aquatic systems, however, provided that the irradiated water sample contains low amounts of other light absorbing species (as is the case, for example, with ocean water), thus showing EE2 photodegradation to be driven mainly by the primary reactions. However, in samples of high concentration of natural organic matter the reactions sensitized by CDOM have to be taken into account. As already mentioned, much of the research has been conducted with EE2 concentrations comparably high to that of natural organic matter. The question arises therefore whether the relative share of indirect reactions could have been underestimated in those studies. This issue was addressed within the current study which purpose was to examine the photodegradation of EE2 in solutions where its concentration was several orders of magnitude lower than that of natural organic matter.

2. Materials and methods

River and sea water samples were taken from the Vistula River at Tczew (Poland) and from Gdansk Bay (Baltic Sea) respectively. The samples were aged at room temperature for several months. The physico-chemical parameters were determined for water samples filtered through ~0.8 μm Whatman GFF filters. The concentration of dissolved organic carbon was measured using a Shimadzu TOC-5000 analyser. The total iron concentration was determined by a colorimetric method (Collins et al., 1959) using 100 mm long glass cuvette. Prior to performing the analysis the samples were UV irradiated in order to release organically bound iron (for details see Kononets et al., 2002). The sum of nitrate and nitrite was measured colorimetrically as described by Grashoff et al. (1983). The changes in oxygen concentration in water were monitored using a dissolved oxygen meter.

Directly before photochemical experiment, the filtered samples of river, sea and Millli-Q water were shaken vigorously for 5 min in glass jars then enriched with 17α-ethinylestradiol (Merck) to concentration of 300 ng mg L^{-1} and poured into quartz glass tubes (1 cm inner diameter). The tubes contained small air-filled headspaces. The samples were irradiated in triplicates, with the tubes tightly sealed with ground glass stoppers to prevent evaporation and dark control samples additionally covered with aluminum foil. The tubes were placed horizontally in a shallow water bath, the temperature of which was kept below 30 °C using tap water cooling, and irradiation was then performed using a solar simulator (SOL 500, Dr. Hönle, Germany) equipped with a H1 filter. Sub-samples of 0.5 ml were withdrawn during the irradiation process. Radiation intensity was measured with UV-B SKU 430 (280–315 nm) and UV-A SKU 420 (315–380 nm) broadband