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Photochemical transformation of zearalenone in aqueous solutions under simulated solar irradiation: Kinetics and influence of water constituents

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HIGHLIGHTS

- The transformation of ZEN has been studied under simulated solar irradiation.
- Conversion of *trans*- to *cis*-ZEN was observed predominantly during the irradiation.
- Half-lifes varied from 28 to 136 (natural waters) to 1777 min (deionized water).
- Influence of natural water constituents on the rate of photolysis was reported.
- First publication reporting the ZEN phototransformation in natural waters.

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ABSTRACT

The presence of estrogenic mycotoxins, such as zearalenone (ZEN), in surface waters is an emerging environmental issue. Little is known about its phototransformation behavior, which may influence its environmental fate. In this context, the phototransformation of ZEN was investigated in pure water, river water and estuarine water using simulated sunlight irradiation. Kinetic studies revealed that two concomitant processes contribute to the fate of ZEN under solar irradiation: photoisomerization and photodegradation. This phototransformation followed a pseudo-first order kinetics. ZEN degrades quickly in natural waters and slowly in deionized water, with half-lives ($t_{1/2}$) of 28 ± 4 min (estuarine water), 136 ± 21 min (river water) and 1777 ± 412 min (deionized water). The effects of different water constituents on the phototransformation of ZEN in aqueous solution have been assessed (NaCl, Ca^{2+}, Mg^{2+}, Fe^{3+}, NO_3^- and oxalate ions, synthetic seawater, Fe(III)-oxalate and Mg(II)-oxalate complexes, humic acids, fulvic acids and XAD-4 fraction). In the presence of synthetic seawater salt ($t_{1/2}$ = 18 ± 5 min) and Fe(III)-oxalate complexes ($t_{1/2}$ = 61 ± 9 min), the transformation rate increased considerably in relation to other water constituents tested. The solution pH also had a considerable effect in the kinetics with maximum transformation rates occurring around pH 8.5. These results allow us to conclude that phototransformation by solar radiation can be an important degradation pathway of ZEN in natural waters.

1. Introduction

Mycoestrogens are naturally occurring estrogens produced as secondary metabolites by several molds of the *Fusarium* genus that colonize a wide variety of crops, including wheat, barley, oats, rice and corn (Kinani et al., 2008). Amongst the well-known mycoestrogens are zearalenone (ZEN) and its metabolites which have estrogenic activities similar to those of natural estrogens (estrone and estriol) (Le Guevel and Pakdel, 2001) and higher than those of many notorious synthetic endocrine disruptors, such as bisphenol A, DDT and atrazine (Coldham et al., 1997; Sforza et al., 2006).

Although ZEN possesses a relatively low acute toxicity (oral LD

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50 values of >2000–20,000 mg kg^{-1} b.w.) after oral administration in mice, rats and guinea pigs, ZEN causes pronounced estrogenic symptoms including vulvovaginitis, uterine enlargement, prolonged or interrupted estrus, infertility in farm animals and it is occasionally implicated in hypoestrogenic syndromes in humans (Zinedine et al., 2007). In addition, it is suspected to be a triggering factor for central precocious puberty development in girls (Massart et al., 2008). Experiments exposing zebrafish (*Danio rerio*) to ZEN confirm its estrogenic potential to influence sexual differentiation and reproduction. Decreased frequency of spawning and fecundity and stimulation of plasma vitellogenin were observed after 21 day exposure of adult zebrafish to 0.1–1 μg L^{-1} of ZEN (Schwartz et al., 2010).

Because of the high stability of ZEN during milling, food processing and heating, among others, it is reasonable to assume that this compound is persistent in the environment (Ryu et al., 2003). The occurrence of mycoestrogens has been extensively studied in food and feed products, however fewer studies focused on their occurrence in the natural aqueous environment (Jarosová et al., 2015). Potential aqueous environmental contamination pathways by mycoestrogens include: (1) runoff and drainage water from fields cultivated with infected plants, (2) runoff from livestock facilities or fields receiving livestock manure applications, and (3) human excretions via wastewaters (Schenzel et al., 2012). Several studies have examined the occurrence of ZEN with concentrations in surface waters ranging from 1.4 to 96.0 ng L^{-1} (Gromadzka et al., 2009; Kolpin et al., 2014), in groundwater between <0.3 and 0.5 ng L^{-1} (Gromadzka et al., 2009) and in influents and effluents of wastewater treatment plants (WWTP) in the range of 1.0–19.8 ng L^{-1} (Gromadzka et al., 2015; Lagana et al., 2001), providing evidence of both diffuse and point sources of this compound into the environment. Runoffs from agricultural activities and sites downstream of the WWTP's effluent discharge have been identified as high risk factors for mycoestrogen exposure.

Although often ignored, ZEN can occur in two configurations. The double bond between C_{11} and C_{12} (Fig. 1) may isomerize from the *trans* to the *cis* configuration (Drzymala et al., 2014). Since the 1970s it is known that this isomerization can easily be achieved by artificial UV light or sunlight (Peters, 1972). The structure of *cis*-ZEN was primarily confirmed by nuclear magnetic resonance and recently by X-ray crystallography (Köppen et al., 2012b). The *cis*-ZEN is chemically stable and retains its configuration in biological systems. Reports on the occurrence of *cis*-ZEN as natural product (Muñoz et al., 1989; Richardson et al., 1985) may be due to exposure of the *trans*-isomer to light. The *cis*-isomer has been described in edible oils, raw grains and especially wet ground maize for feeding. Isomerization occurs at high extent under sunlight, but the *cis-trans* ratio may largely vary depending on the environmental conditions (Brezina et al., 2013; Köppen et al., 2012a). Due to analytical limitations, data about the occurrence of the two isomers are still scarce and a preliminary risk assessment study has never been done.

Recently, Drzymala et al. (2015) compared the estrogenicity of eleven different ZEN congeners using the E-Screen assay. Overall, a change in the configuration from *trans* to *cis* retains significant estrogenic activity. In the cited work, *cis*-ZEN was slightly more active (EC_{50} = 0.41 nM) than *trans*-ZEN (EC_{50} = 0.62 nM).

Among the several environmental degradation processes (abiotic/biotic), photodegradation is one of the most important for determining the fate of contaminants in aquatic environments (Chowdhury et al., 2011). Solar phototransformation of organic compounds in aquatic environments may occur either by direct or indirect photolysis within the photic zone. Direct photolysis occurs due to the absorbance of photons of certain energy by the substrate and depends on both the rate of light absorption and the reaction quantum yield of the excited state (Chowdhury et al., 2010). On the other hand, indirect photolysis occurs via light absorption by photosensitizers, some of the most important being dissolved organic matter (DOM), nitrate/nitrite ions, and Fe(III)/Fe(II)-organic substance complexes (Zhan, 2009). Excited photosensitizers generate singlet oxygen ($^1O_2$), OH radicals (•OH), DOM-derived peroxy radicals (ROO•), triplet-state DOM ($^3DOM^*$), solvated electrons, (e^-_{aq}) and other photoreactants that can react with the compounds of interest and therefore influence their environmental fate, persistence and ecological risk in natural water systems (Lin and Reinhard, 2005).

The objective of this study was to determine the kinetics of the phototransformation of ZEN in natural waters and to understand the effects of water constituents on its photolysis. Up to now, the photochemical behavior and especially the contribution of photolysis to the degradation of this compound in environmental water samples have not been studied.

2. Material and methods

2.1. Chemicals

ZEN (Empirical formula: $C_{18}H_{22}O_5$, CAS registry number: 17924-92-4) solid standard was purchased from Sigma–Aldrich (St. Louis, MO, USA) with purity higher than 99%. Methanol (MeOH) for HPLC analysis was of HPLC–grade and purchased from Fisher Scientific (Ottawa, Ontario, Canada). Tropic Marin® (synthetic seawater salt, contains all major and minor elements, for a total of 70 elements, to reproduce the natural concentrations found in the ocean) was purchased from Marinus Inc. (Long Beach, CA). All other reagents used for solutions were reagent grade and used without further purification. Deionized water was obtained from a Millipore

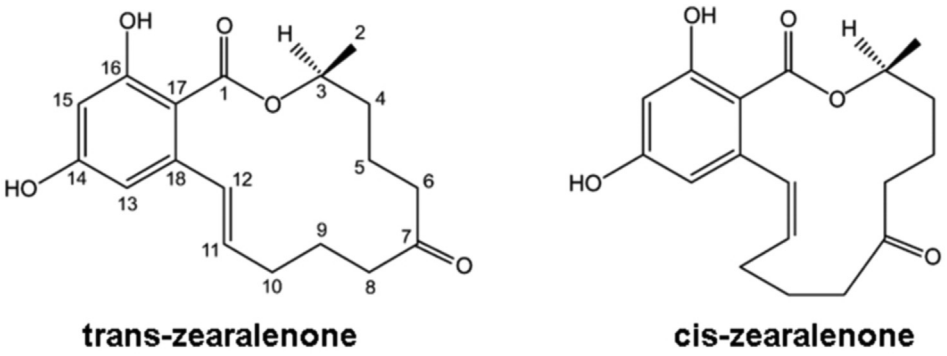

Fig. 1. Chemical structures of *trans*-zearalenone and *cis*-zearalenone.

purification system (Milli-Q plus 185). Stock solutions of ZEN were prepared in deionized water at concentration of 2.7 mg L^{-1}. The solution was stored at 4 °C in sealed flasks, protected from light to prevent any degradation. Irradiated samples were prepared by diluting the ZEN stock solution to a final concentration of 100 μg L^{-1}. The stock solution was also used to prepare calibration standard solutions.

2.2. Water samples

Surface water samples were collected in October 2015. One surface water sample (estuarine origin) was collected from *Ria de Aveiro* located in the urban city center of Aveiro, (*Cais da Fonte Nova*, *Ria de Aveiro*, Aveiro, Portugal). This sampling site is typically known to have high contents of organic matter and salinity. The other tested surface water sample was collected from *Rio Novo do Príncipe* (located in a rural agricultural area of Aveiro, Portugal), which is situated in the confluence of the Vouga River with the *Ria de Aveiro* coastal lagoon. Salinity, pH, total carbon (TC), inorganic carbon (IC), dissolved organic carbon (DOC) and total iron contents were measured for the surface water samples. These techniques are described below in Section 2.4.2.

Samples were collected in 1 L glass bottles, previously washed with dilute alkaline soap solution, distilled water, acetone, evaporated to dryness, and rinsed with sampling water before sample collection. All samples were immediately filtered through 0.22 μm PVDF filter membranes (Red Analytical, UK) to remove any particles and microorganisms and stored in the dark at 4 °C. The water samples were used within a period of time as short as possible (less than 2 weeks).

2.3. Irradiation experiments

2.3.1. Solar simulator device

Photodegradation experiments were carried out under simulated solar radiation using a Solarbox 1500 (CO.FO.ME.GRA, Milano, Italy), equipped with a 1500 W Xenon lamp and outdoor UV filters that allowed the transmission of light only at wavelengths above 290 nm. During the irradiation experiment, the irradiance of the lamp was kept constant at 55 W m^{-2} (290–400 nm), corresponding to 550 W m^{-2} for the whole spectrum (290–800 nm). A multimeter (CO.FO.ME.GRA, Italy) equipped with a black standard temperature sensor and a UV 290–400 nm large band sensor was used to monitor the temperature and irradiance levels, respectively. The temperature of the device chamber was maintained by an air cooled system and irradiation uniformity was guaranteed by a parabolic reflector chamber. A scheme of the irradiation apparatus is presented in Fig. S1 (in Supplementary Data).

2.3.2. Kinetics experiments

ZEN aqueous solutions, with 100 μg L^{-1} concentration, were irradiated in triplicate using 25 mL quartz tubes (internal diameter of 1.5 cm and height of 20 cm). For each set of experiments, dark controls were also performed in triplicate, foiled several times with aluminum paper. The quartz tubes were suspended inside the irradiation chamber using a home-made metallic holder which assured that samples were homogeneously irradiated.

Phototransformation kinetics experiments of ZEN were performed in the following aqueous matrices: deionized water, freshwater and estuarine water. Quartz tubes (for samples and dark controls) were filled with 15 mL of solution. Aliquots (1 mL) were collected between 0 and 180 min for freshwater and estuarine water samples, and between 0 and 1680 min for the deionized water sample. Aliquots were stored at 4 °C (refrigerator) until analysis.

Other irradiation experiments were performed testing the role of different natural water constituents, on the phototransformation of ZEN. These experiments were performed in deionized water by adding (separately) Ca^{2+} (added salt, $CaCl_2$), Mg^{2+} (added salt, $MgCl_2$), Fe^{3+} (added salt, $FeCl_3$), NO_3^- (added salt, $NaNO_3$) and oxalate ions (added salt, $Na_2C_2O_4$), NaCl, synthetic seawater, Fe(III)-oxalate and Mg(II)-oxalate complexes, and different humic substances (humic acids (HA), fulvic acids (FA) and XAD-4 fraction). Concentrations for each constituent were set according to naturally-occurring levels in waters. HA, FA and XAD-4 fraction were extracted and isolated from a local riverine water sample (Esteves et al., 1995). Humic substances were used to simulate natural dissolved organic matter. Ultrasonication was used for the solubilization of humic acids in water (30 min, at 80 W). Sodium phosphate buffer solution (0.01 M, pH 7.3) was added in order to eliminate the effect of pH variations, except in the presence of HA, FA and XAD-4 fraction. The phosphate buffer solution was also evaluated separately without adding any constituent (blank test). The influence of pH on ZEN transformation was studied in sodium phosphate buffers (0.01 M) at different pH values (5.5; 6.5; 7.5 and 8.5) during a 180 min irradiation time.

Experimental kinetic data were fitted to a pseudo-first order kinetic model by non-linear regression analysis. In this context, the concentration values for ZEN were represented as a function of time $C(t) = C_0 e^{-kt}$, where C_0 and C are the concentrations of ZEN at time zero and reaction time t (min), k is the first order transformation rate constant (min^{-1}), and the half-life of ZEN was determined as $t_{1/2} = \ln(2)k^{-1}$. Data analysis was carried out using GraphPad Prism software, version 5.03.

2.4. Analytical methods

2.4.1. Analysis of ZEN samples

Quantitative analysis of ZEN was performed on a Shimadzu Prominence HPLC system (Kyoto, Japan) equipped with a DGU-20A5 on-line degasser, LC-20AD solvent delivery module, CTO-10ASVP column oven, and RF-20A XS fluorescence detector. Separations were carried out with a New ACE® C18 column-PFP (150 mm × 4.6 mm, 5 μm) connected to an ACE® 5 C18 4.6 mm i.d. guard column. The mobile phase consisted of a mixture of MeOH and ultra-pure water (75:25, *v/v*), at a flow rate of 0.5 mL min^{-1} with an injection volume of 20 μL. Mobile phase constituents were filtered through 0.2 μm polyamide membrane filters (Whatman Inc., USA). Detection was performed using a Shimadzu RF-20A XS Prominence fluorescence detector, set to excitation and emission wavelength of 275 nm and 460 nm, respectively. The column temperature was maintained at 30 °C, and the detector flow cell at 35 °C. The used HPLC method of analysis satisfactorily separates the *trans*- from *cis*-zearalenone (t_R = 8.1 min and t_R = 8.6 min, respectively).

Two calibration curves were obtained for ZEN quantification in the concentration range of 2–75 μg L^{-1} and 5–150 μg L^{-1}. The first curve was used for the quantification of the lowest ZEN concentrations and the second curve was used for the establishment of linearity over the specified range. Each concentration was measured in triplicate. Limits of detection (LOD) and quantification (LOQ) were determined by the calibration curve method according to International Conference on Harmonization (ICH) guidelines (ICH, 2005), for the curve considering the concentration range of 2–75 μg L^{-1}. LOD was defined as $3.3 \times (\sigma)/S$ and LOQ was computed as $10 \times (\sigma)/S$, where σ is the standard deviation of the y-intercepts and S is the slope of the calibration curve. LOD and LOQ values were 1 and 4 μg L^{-1}, respectively. The calibration linearity for ZEN was established in the range between LOQ and 150 μg L^{-1}.

The UV-visible spectra of ZEN solutions were obtained with a

T90 + UV/VIS Spectrophotometer (PG Instruments Ltd.) in a 1 cm path length rectangular quartz cuvette. Spectra were measured over the wavelength range of 270 and 820 nm.

2.4.2. Chemical characterization of environmental water samples

The concentrations of dissolved total carbon (TC) and dissolved inorganic carbon (IC) were determined using a Shimadzu TOC-VCPN analyzer. The dissolved organic carbon (DOC) content of the samples was calculated as the difference between TC and IC. The pH was measured using a pH meter (Ecoscan, EUTECH. Instruments, Singapore). The total iron concentration was determined using an atomic absorption spectrometer AAnalyst 100 (Perkin Elmer, Norwalk, CT, EUA).

3. Results and discussion

3.1. Identification of trans/cis-zearalenone

In our phototransformation experiments, ZEN was eluted as two separate peaks, which corresponded to *trans*-ZEN and *cis*-ZEN ($t_R = 8.1$ min and $t_R = 8.6$ min, respectively). The identification was carried out in part based on the retention time using HPLC elution on C_{18} column under isocratic conditions (MeOH:H_2O). The isomer with the shorter retention time is assigned the *trans* configuration (*trans*-ZEN) and that with the longer retention time is assigned the *cis* configuration (*cis*-ZEN). These results (HPLC elution) are in agreement with Köppen et al. (2012a) and Brezina et al. (2013). Additional verification was achieved with simulated sunlight irradiation of aqueous solutions (in pure water) of ZEN because the *trans-cis* transformation is known to be promoted by light (Peters, 1972). Apart from the identification of the two isomers during the irradiation, no other fluorescent byproducts were detected.

3.2. Phototransformation in pure water

Phototransformation of ZEN was investigated in deionized water, irradiating the solution during 28 h (1680 min). In the dark controls, no obvious transformation of ZEN was observed, indicating that the decay by microbiological, thermal, or hydrolytic processes was negligible during the time of the photolysis experiments. Thus, the observed concentration decay was assumed to be due only to photolysis.

The results obtained allowed the identification of two distinct phototransformation phenomena: (1) conversion of *trans*- to *cis*-ZEN; (2) phototransformation of *trans*-ZEN and *cis*-ZEN. During the initial period of the irradiation, the decrease of *trans*-ZEN was accompanied by an increase of *cis*-ZEN (monitored as the *cis*-ZEN peak area in the chromatograms). The *cis*-ZEN peak area reached a maximum after 180 min of irradiation time, corresponding to about 50.2% of transformation of *trans*-ZEN. After 180 min of irradiation time a decrease of both *trans*- and *cis*-ZEN was observed. The graphical representation of the concentration of *trans*-ZEN along the irradiation (Fig. 2(A) and (B)) suggests that the two phenomena described above result into two different decay kinetics: the first part is marked mainly by the *trans*/*cis* photoisomerization, while the second part of the kinetics is dominated by photodegradation of *trans*-ZEN (and also by the photodegradation of *cis*-ZEN). Consequently, the experimental data of phototransformation of *trans*-ZEN were divided into two parts (from 0 to 180 min and from 180 min to 1680 min) and each part was separately fitted to a pseudo-first order kinetic model. In Fig. 2(B), the curve was extrapolated between 0 and 180 min by assuming that the kinetics of photodegradation of *trans*-ZEN in this time interval is equal to that observed after 180 min of irradiation time. The values of rate constants and determination coefficient were $k_{obs} = (4.3 \pm 0.6) \times 10^{-3}$ min^{-1} and $R^2 = 0.977$ (mainly isomerization), $k_{obs} = (3.9 \pm 0.7) \times 10^{-4}$ min^{-1} and $R^2 = 0.965$ (mainly degradation), respectively, which evidences that the irradiation period dominated by photoisomerization has a rate constant that is 10 times higher than the subsequent period, dominated by photodegradation processes. Therefore, the contribution of the photodegradation of *trans*-ZEN to the decrease of total ZEN concentration during the first part of the irradiation, dominated by the isomerization process, was considered to be negligible.

This behavior (isomerization/degradation) is consistent with that observed by Köppen et al. (2012a) for ZEN in corn oil. The naturally occurring *trans*-ZEN is assumed to be transformed by ultraviolet irradiation to the more stable *cis*-ZEN, causing both isomers to co-occur. *Cis*-ZEN was reported in edible oils and wet maize when exposed to UV-light (UVA 315–380 nm) (Brezina et al., 2013; Köppen et al., 2012a). As observed by Avetta et al. (2014) for dimethomorph isomerization, it is acceptable to assume that a photostationary equilibrium is reached between *cis*- and *trans*-ZEN and that a steady-state dynamic constant ratio is maintained under irradiation.

3.3. Phototransformation in natural waters

Similarly to phototransfomation of ZEN in pure water, the results were divided into two phenomena occurring at two different kinetic rates (isomerization and degradation). The pseudo-first order kinetic model was adequate to describe the experimental data in both cases (R^2 values ranged from 0.985 to 0.995). Within the experimental error, no obvious transformation of ZEN was observed in the dark during the experiments. Similarly to deionized water, there was a noticeably faster transformation (photo-isomerizarion) in the first 15 min (river water) and 30 min (estuarine water) of irradiation followed by a slow transformation up to 180 min (photodegradation). Phototransformation (isomerization and photodegradation) plots of ZEN in the tested natural waters are depicted in Fig. 3. In Fig. 3 (A2) and (B2), photodegradation plots were extrapolated between the initial time and 30 min for river water and 15 min for estuarine water, supposing that the rate of the photodegradation of the *trans*-ZEN was equal before and after the given time.

The phototransformation rate of ZEN decreased in the following order: estuarine > river > deionized water illustrating a strong dependence on the composition of the irradiated media. Compared with pure water, natural waters contain optically active substances, which are prone to the generation of some active species (e.g., •OH and $^1O_2$) contributing to the indirect photodegradation of ZEN under sunlight irradiation. Table 1 describes some physico-chemical characteristics of these natural waters.

Half-lifes (degradation) decreased from 1777 ± 412 min (deionized water) to 136 ± 21 min (river water) and 28 ± 4 min (estuarine water). These half-life times are strictly dependent on the experimental conditions used during the irradiation experiments (namely irradiance level and lamp spectrum). To transform the obtained results into data with environmental relevance, the half-life times of ZEN were converted into units equivalents to summer sunny days (SSD). Taking into consideration that the total energy reaching the ground in a summer cloudless day (45°N latitude) is 7.5×10^5 J m^{-2}, one summer sunny day (SSD) will correspond to 3.8 h of irradiation (Calisto et al., 2011). By employing this conversion, it is possible to better estimate the half-life time of ZEN in real conditions. According to the obtained results, this compound can persist in the environment for between 0.12 ± 0.02 and 8 ± 2 SSD (Table 2).

The faster phototransformation of ZEN in the two natural waters compared to that observed in deionized water (half-lives of 13–63

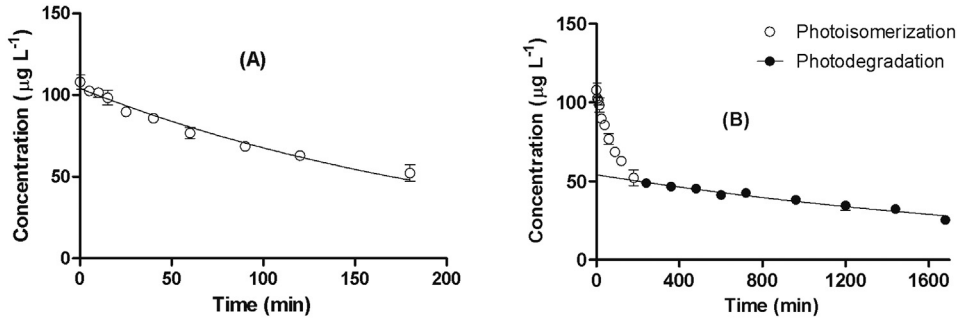

Fig. 2. Photoisomerization/degradation plots for first-order kinetics obtained under simulated solar irradiation in deionized water. (A) Photoisomerization of *trans*- to *cis*-ZEN. (B) Photodegradation of *trans*-ZEN. Shown error bars are standard deviations (n = 3).

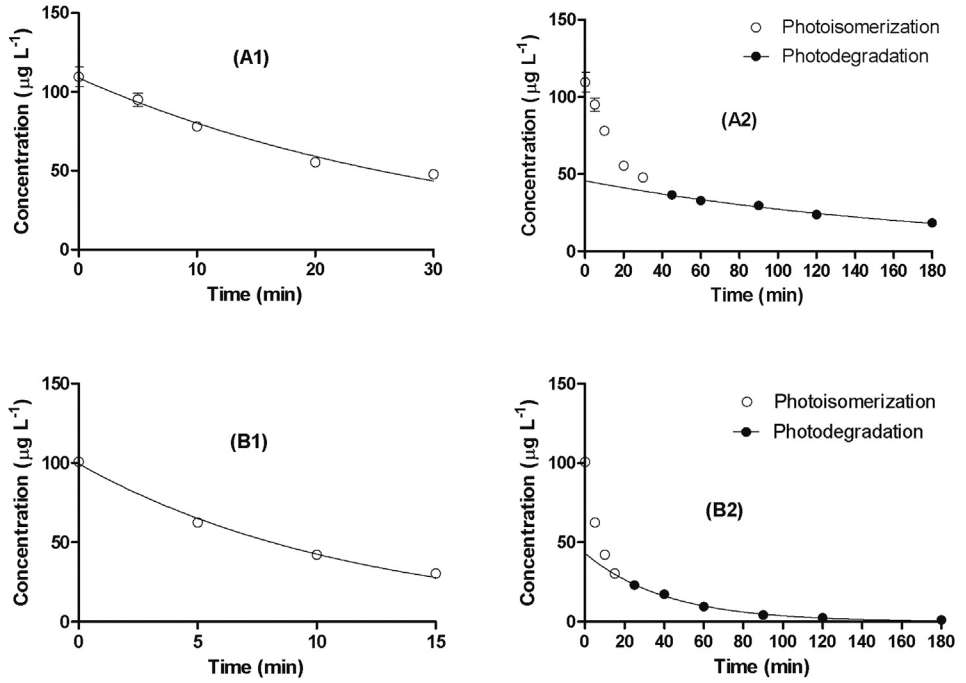

Fig. 3. Photoisomerization/degradation plots for first-order kinetics obtained under simulated solar irradiation in natural waters. (A1) Photoisomerization of *trans*- to *cis*-ZEN in river water. (A2) Photodegradation of *trans*-ZEN in river water. (B1) Photoisomerization of *trans*- to *cis*-ZEN in estuarine water. (B2) Photodegradation of *trans*-ZEN in estuarine water. Shown error bars are standard deviations (n = 3).

Table 1
Physico-chemical characteristics of natural waters.

Sample	pH	Salinity (‰)	TC (mg L^{-1})	IC (mg L^{-1})	DOC (mg L^{-1})	Fe_{tot} (mg L^{-1})
Estuarine water (Ria Aveiro)	7.3	23	33.7	29.3	4.4	b.q[a]
Riverwater (Rio Novo do Principe)	7.7	b.d[b]	8.0	4.8	3.2	b.q[a]

[a] Below quantification limit (0.1 mg L^{-1}).
[b] Below detection limit.

Table 2
Pseudo-first-order rate coefficients for the phototransformation of ZEN in river and estuarine water.

Sample	R^2	k_{iso} (min^{-1})	k_{deg} (min^{-1})	$t_{1/2}$ (min)	$t_{1/2}$ (SSD)
Deionized water	0.965–0.977	$(4 \pm 1) \times 10^{-3}$	$(4 \pm 1) \times 10^{-4}$	1777 ± 412	8 ± 2
River water	0.985–0.989	$(3 \pm 1) \times 10^{-2}$	$(5 \pm 1) \times 10^{-3}$	136 ± 21	0.6 ± 0.1
Estuarine water	0.994–0.995	$(8 \pm 2) \times 10^{-2}$	$(24 \pm 4) \times 10^{-3}$	28 ± 4	0.12 ± 0.02

times lower) is expected to be primarily due to oxidation reactions triggered by the reactive species generated by natural photosensitizers, such as humic substances, transition metals, nitrate or nitrite.

Previous studies have pointed out that some aquatic constituents (e.g., dissolved organic matter (DOM), nitrate, bicarbonate, halides) can affect the photolysis of organic pollutants (Zhou et al., 2015). However, it is still unclear whether ZEN can be susceptible to these or other factors under irradiation. In the next step, studies were conducted to evaluate the rates of ZEN phototransformation and the influence of some estuarine water constituents (note that higher transformation rate of ZEN was observed in the estuarine water sample), which could accelerate or retard the photolytic process (Table 1).

3.4. Effects of some water constituents on zearalenone phototransformation

Natural water constituents are often used in controlled experiments with the goal of determining their specific influence in indirect photolysis (i.e., which photosensitizing species are involved) (Challis et al., 2014). In previous studies, humic acids, Cl^-, Br^-, I^-, Fe(III), NO_3^-, and HCO_3^- were observed to accelerate, inhibit or have minor effect on the photolysis rate of organic contaminants (Ge et al., 2009, 2010; Li et al., 2011; Li et al., 2014).

Under simulated sunlight with different water constituents, degradation was observed throughout the 180 min of irradiation time. The rate of phototransformation of ZEN varied from $(4 \pm 1) \times 10^{-3}$ to $(39 \pm 17) \times 10^{-3}$ min^{-1} with half-life times between 18 ± 5 min and 172 ± 25 min (Table 3). The isomerization of *trans*- to *cis*-ZEN was also observed for the irradiation with all the evaluated constituents.

ZEN transformation rate was much higher ($k = (39 \pm 17) \times 10^{-3}$ min^{-1}, $t_{1/2} = 18 \pm 5$ min) in synthetic seawater compared to solutions with other water constituents (Table 3), presumably due to the presence of natural photo-sensitizers in seawater. Sensitized photolysis of target compounds in seawater depends on the formation, and subsequent reactivity of reactive intermediates (indirect photolysis), such as singlet oxygen ($^1O_2$), hydroxyl radical (HO•), triplet excited dissolved organic matter (^{3}DOM*) and halide radicals (X•, $X_2^{\bullet -}$) (Glover et al., 2014). Compounds such as triclosan (Aranami and Readman, 2007), carbofuran (Campbell et al., 2004) and carbamazepine (Chiron et al., 2006) have increased degradation in saltwater in comparison to freshwater, which was attributed to the formation of halide radicals. Al Housari et al. (2010) found that HO•, $^1O_2$, and chromophoric dissolved organic matter triplet state concentrations were higher in an estuarine water compared to freshwater.

Besides synthetic seawater, experiments with the addition of [Fe(III)]/[oxalate] (0.4/6.0 μM) in deionized water resulted in the second largest increase in the transformation rate of ZEN (Table 3). After 180 min of irradiation time, 83% of ZEN transformation was achieved. In sunlit surface waters, photochemical reactions of oxalate complexes with Fe(III) can produce Fe(II) and a series of reactive oxygen species (ROS) such as $O_2^{\bullet -}$, $HO_2^{\bullet}$, H_2O_2 and HO•. The resulting production of OH radicals is very significant as they can oxidize a wide variety of natural and anthropogenic organic and inorganic substances (Liu et al., 2010). For example, the phenolic ring of estrogens is a crucial component of their potential to scavenge free radicals, and it might be readily oxidized by ROS (Zhou et al., 2004). However, differently from laboratory experiments with pure species, in natural waters •OH would be scavenged by DOM and, in brackish waters, by bromide as well. Photo-bleaching of DOM by halides can destroy the chromophores necessary to produce ^{3}DOM* and, without this precursor, the •OH induced degradation is decreased.

The study of the effects of Fe(III) and oxalate ions separately resulted in half-lives similar to those obtained in deionized water, confirming specifically that is the interaction between Fe(III) and oxalate ions which increased the transformation rate of ZEN. However, the combination of magnesium and oxalate ions did not result in the same effect as the Fe(III)-oxalate complexes. In this case, unlike iron, the transformation rate with Mg(II)-oxalate was slower than the isolated effect of Mg^{2+} in aqueous solution.

It is worth noting that the ZEN transformation rates did not show remarkable differences in the presence of the different fractions of DOM (humic acids, fulvic acids and XAD-4 fraction) in comparison with some other water constituents (Table 3). These results are in agreement with a previous study published by Qu et al. (2012) for ZEN metabolites, at pH 7.0, where α-zearalanol loss was observed in all solutions in the presence of 5 mg L^{-1} of DOM, with the greatest rate of decay being observed for soil humic acid ($t_{1/2}$ ~ 3 h and $k = 0.214 \pm 0.009$ h^{-1}) with simulated sunlight.

Overall, some water constituents had no influence on the transformation rate constant compared to deionized water, including Fe(III), nitrate, oxalate ions and Mg(II)-oxalate. Despite the relevant transformation for ZEN in estuarine water and synthetic seawater, a NaCl solution (salinity = 23‰) did not show the same effect, i.e., salinity alone does not explain the increase of the phototransformation rate for estuarine water in comparison to river water. The participation of other reactive species that were not investigated here cannot be ruled out.

Table 3
Kinetic parameters for the phototransformation of zearalenone in different aqueous solutions.

Matrix[a]	k, min^{-1}	$t_{1/2}$, min	R^2
Deionized water	$(4 \pm 1) \times 10^{-3}$	161 ± 4	0.977
NaCl salinity (‰) = 23	$(6 \pm 1) \times 10^{-3}$	107 ± 18	0.983
Synthetic sea water salt salinity (‰) = 23	$(39 \pm 17) \times 10^{-3}$	18 ± 5	0.955
Phosphate buffer (0.01 M)	$(6 \pm 1) \times 10^{-3}$	121 ± 28	0.969
Fulvic acids (9 mg L^{-1})	$(6 \pm 1) \times 10^{-3}$	111 ± 24	0.976
XAD-4 (9 mg L^{-1})	$(6 \pm 1) \times 10^{-3}$	118 ± 24	0.978
Humic acids (9 mg L^{-1})	$(6 \pm 1) \times 10^{-3}$	127 ± 21	0.985
Ca^{2+} (9.2 mg L^{-1})	$(5 \pm 1) \times 10^{-3}$	130 ± 21	0.986
Mg^{2+} (24.1 mg L^{-1})	$(8 \pm 1) \times 10^{-3}$	91 ± 17	0.978
Fe^{3+}(0.1 mg L^{-1})	$(4 \pm 1) \times 10^{-3}$	161 ± 26	0.984
NO_3^- (0.7 mg L^{-1})	$(5 \pm 1) \times 10^{-3}$	151 ± 24	0.986
[Fe(III)]/[Oxalate] 0.4/6.0 (μM)	$(11 \pm 2) \times 10^{-3}$	61 ± 9	0.987
Oxalate (6.0 μM)	$(4 \pm 1) \times 10^{-3}$	172 ± 25	0.977
[Mg^{2+}]/[Oxalate] 100/6.0 (μM)	$(4 \pm 1) \times 10^{-3}$	154 ± 33	0.984

[a] Except for humic substances, all matrices were added a sodium phosphate buffer solution (0.01 mol L^{-1}).

3.5. Influence of pH on phototransformation of zearalenone

In comparison with some other phenolic compounds it can be presumed that deprotonated ZEN reacts faster than the undissociated compound (Neamtu and Frimmel, 2006). The study of the pH effect revealed that after 180 min of irradiation at pH 5.5 and pH 8.5, 55% and 72% of ZEN was transformed, respectively, which showed a considerable increase in phototransformation when the medium was more basic. This is probably due to the fact that in alkaline medium the molar absorption coefficients of the dissociated ZEN are slightly higher than at acidic pH (Li et al., 2015).

Because ZEN has a pK_{a1} value of approximately 7.6, it occurs in the neutral form at acidic pH, whereas the corresponding phenolate anion occurs in solution at pH 7.0 (in equilibrium with the protonated form) and predominates at pH 9.0 (Gajęcka et al., 2011). Therefore, both the protonated form and the phenolate are present in natural waters. The results obtained in the experiments performed at different environmentally relevant pH values are summarized in Fig. 4.

3.6. Determination of the direct photolysis quantum yield for zearalenone

The efficiency of a phototransformation process can be expressed in terms of quantum yield (ϕ), which is the ratio between the total number of molecules of the compound transformed by a chemical reaction per total moles of photons absorbed (Leifer, 1988). Quantum yields serve as a much better predictor of direct photolytic fate than just simply rate constants and half-lives; however, fewer studies tend to measure them as their determination is more complex. Direct photolysis quantum yields measure the efficiency with which a compound breaks down upon absorption of light. This property should be independent of the light source over a single electronic transition (absorption band) of a compound. Therefore, the quantum yield is essential for predictive and comparative purposes (Challis et al., 2014). In real aquatic environments, however, there are a wide variety of absorbing species that can indirectly contribute to the degradation of organic compounds. In this context, a direct photolysis quantum yield cannot be determined but, instead, one can define an overall reaction quantum yield that takes into account all the photo-induced reactions that result in the transformation of the target compound.

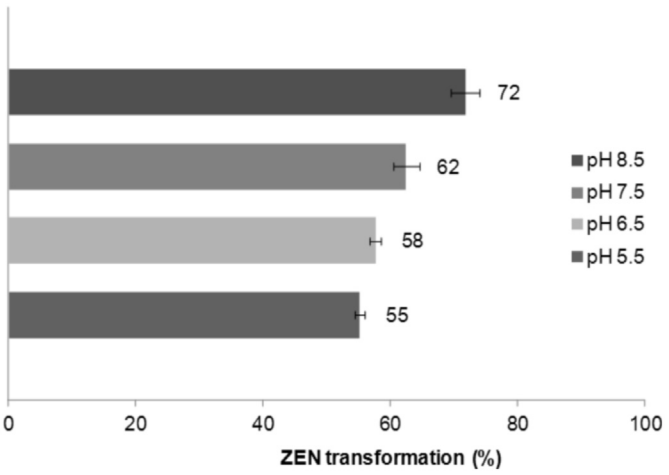

Fig. 4. Effect of pH on the phototransformation of ZEN. Conditions: irradiation time, 180 min; 100 μg L^{-1} of ZEN in sodium phosphate buffers.

The quantum yield for the photolysis of ZEN in ultrapure, estuarine and riverine water was determined as an overall average over the lamp emission range (290–800 nm). Accordingly, the ZEN average quantum yield (ϕ_{ave}) was calculated using Eq. (1) (Calisto et al., 2011):

$$\phi_{ave} = \frac{C_0 k}{\sum I^0_{\lambda i} \times (1 - 10^{\varepsilon_{\lambda i} \times b \times C_0})} \quad (1)$$

where k is the apparent first order degradation constant (s^{-1}), C_0 is the initial concentration of ZEN in solution (mol L^{-1}), $I^0_{\lambda i}$ is the lamp emission intensity at the wavelength λ_i (Ein L^{-1} s^{-1}), ε is the molar absorbivity of ZEN at λ_i (L mol^{-1} cm^{-1}) and b is the path length inside the photoreactor (cm) (diameter of the cylindrical photoreactor, 1.5 cm). The lamp emission spectrum, as given by the manufacturer, is presented on Fig. S2 (Supplementary data).

An average quantum yield of 9.3×10^{-5}, 6.5×10^{-4} and 1.7×10^{-4} over the wavelength range of 290–800 nm, was obtained in pure, river and estuarine water, respectively, under simulated solar irradiation. No data for similar experimental conditions were published in the literature concerning ZEN phototransformation.

3.7. Environmental significance of the results

This research indicates that ZEN will be degraded significantly in the euphotic zone of surface waters. However, the phototransformation in the environment might be slower due to factors such as turbidity and coloring of the water (which would reduce the intensity of sunlight, an effect that is partially eliminated in laboratory experiments by water filtration) and also due to the height of the water column which also affects significantly the penetration of sunlight. The data presented here do not account for the light attenuation in the water column and other site-specific factors. However, the photodegradation of ZEN can be foreseen based on these data, especially in shallow, clear water (where less sunlight attenuation occurs) and under strong irradiation.

Under environmental conditions, direct photolysis is expected to be a minor pathway for ZEN degradation. On the other hand, indirect photolysis is likely to be the main phototransformation pathway. However, the persistence of ZEN depends greatly on the water constituents, such as dissolved organic matter, estuarine water salts or Fe(III)–oxalate complexes.

The half-lives measured in natural waters suggest that phototransformation is a potentially significant degradation process for ZEN. The phototransformation of ZEN was rapid in the natural waters (river and estuarine waters), with a half-life of less than one SSD. However, the high transformation rates might be compensated for by the continuous introduction of ZEN into the environment by release from infected plants, manure applications from exposed livestock, human waste via wastewater treatment plants and effluent from food-processing plants. This caveat is supported by the actual occurrence of ZEN in water bodies as shown in Section 1.

In a future work, we intend to identify the transformation products for ZEN and consider the potential ecotoxicological risks associated with their formation. Moreover, it is important to evaluate the degradation kinetics of *cis*-ZEN, which is unknown, since it appeared to be the main transformation product of *trans*-ZEN in environmental conditions. This study was not performed due to the lack commercially available *cis*-ZEN standards. Indeed, *cis*-ZEN is about as potent as *trans*-ZEN in terms of estrogenicity.

4. Conclusions

Environmental contamination by estrogenic mycotoxins has been detected in natural waters, mostly through wastewater facilities, agricultural applications of animal waste and runoff and drainage water from agricultural fields. The present study demonstrates that the phototransformation of ZEN in natural waters (river and estuarine water) by simulated sunlight is much faster than in deionized water (with half-life times ranging from 0.12 ± 0.02 to 8 ± 2 SSD, respectively), indicating that indirect photolysis is a major degradation pathway of this contaminant. The first step of the phototransformation is the fast conversion of *trans*-ZEN into *cis*-ZEN which occurs when *trans*-ZEN undergoes both direct and indirect photolysis. Apart from the photoisomerization, photodegradation of *trans*-ZEN also occurred but at a slower rate.

A tentative evaluation of the environmental water constituents which are mainly responsible for this acceleration of the ZEN phototransformation in river and estuarine waters revealed an appreciable synergistic effect between Fe(III) and oxalate (ratio 1:15). ZEN phototransformation is also significantly accelerated in the presence of seawater salts. However, this increase cannot be explained by the salinity alone. Additional studies are required to investigate the phototransformation products of ZEN and other metabolites, and to examine their effects on organisms living in contaminated aquatic environments.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.11.042.

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