



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-lives 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 ($t_{1/2} = 18 \pm 5$ min) and Fe(III)-oxalate complexes ($t_{1/2} = 61 \pm 9$ 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.

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1. Introduction

Mycotoxins 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 mycotoxins 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 C₁₁ and C₁₂ (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 (EC₅₀ = 0.41 nM) than *trans*-ZEN (EC₅₀ = 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 (¹O₂), 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: C₁₈H₂₂O₅, 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

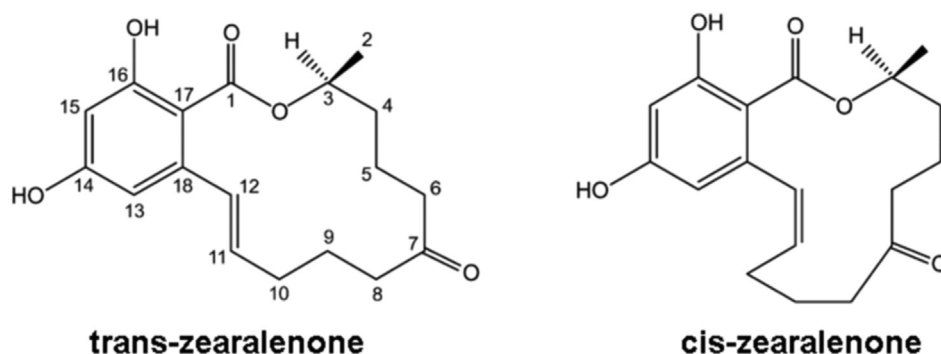


Fig. 1. Chemical structures of *trans*-zearalenone and *cis*-zearalenone.

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