



Photolysis of the antidepressants amisulpride and desipramine in wastewaters: Identification of transformation products formed and their fate



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HIGHLIGHTS

- Photolysis of both compounds resulted in several transformation products, some of which were previously unknown.
- Short irradiation times may be adequate to degrade amisulpride whereas a longer exposure is required for desipramine.
- Transformation of desipramine was enhanced by about three times due to indirect photolysis in wastewaters.
- For desipramine, mixture acute toxicity increased after solar irradiation.
- Photolysis is unlikely to be the main removal pathway for the two antidepressants during wastewater treatment.

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ABSTRACT

Attenuation of pharmaceuticals due to natural sunlight is expected to be an important removal pathway in wastewater treatment plants using treatment lagoon systems. In this work, the photolysis of two antidepressants, amisulpride and desipramine, has been investigated in both ultrapure water and wastewater under simulated solar irradiation. Results showed that for amisulpride short irradiation times ($t_{1/2}$ approximately 3 h in pure water and 4 h in wastewater) were adequate to degrade the parent compound while a longer exposure period was required for desipramine ($t_{1/2}$ of approximately 36 h in pure water), although its degradation is enhanced almost three times by indirect photolysis in wastewaters. A significant number of transformation products (TPs) were identified for both pharmaceuticals by high-resolution mass spectrometry. In general, TPs formed are not persistent although acute toxicity tests for desipramine and its TPs showed an increase of the mixture toxicity after solar irradiation, suggesting that some TPs may be more toxic than the parent compound. In wastewaters collected from treatment lagoons, only amisulpride and one of its major TPs, TP 357, were detected. This indicates that long solar exposure times may be necessary for an effective elimination of these substances in lagoon systems or that photolysis may not be the main removal pathway for these particular compounds.

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1. Introduction

Discharges of effluents from municipal wastewater treatment plants (WWTPs) are an important pathway for pharmaceuticals to enter aquatic ecosystems. Several investigations have demonstrated that pharmaceuticals are only partially removed during conventional treatments applied in WWTPs (Jelic et al., 2011; Radjenovic et al., 2007; Gros et al., 2010). Some WWTPs also discharge effluents to lagoons for enhanced treatment, through settling and extended exposure to solar

irradiation and microbial activity (Li et al., 2013). Lagoon-based wastewater treatment consists of wastewater flowing through shallow, open ponds with extended hydraulic retention times, typically between 7 and 20 days (Hoque et al., 2014). As an enhanced treatment process, lagoon-based treatments are less expensive and may be as equally efficient as conventional wastewater treatments in removing organic contaminants.

Few studies, however, have evaluated the effectiveness of lagoons in removing organic pollutants and they only assess the removal of the parent compound (Hoque et al., 2014; Conkle et al., 2008; Lishman et al., 2006; MacLeod and Wong, 2010; Camacho-Muñoz et al., 2012; Carlson et al., 2013).

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Pharmaceuticals may undergo transformation during wastewater treatment, however, giving rise to transformation products (TPs) which can be more persistent and biologically active than the original compounds (Farre et al., 2008; Escher and Fenner, 2011). For example, following the UV degradation of carbamazepine the ecotoxicity of the irradiated samples increased in parallel with carbamazepine degradation (Donner et al., 2013). Also, Gomez et al. (2008) assessed the photodegradation of three dypirone metabolites, with acute toxicity tests showing an increase in toxicity following the degradation of the parent substances. Information about the occurrence, persistence and toxicity of these TPs is essential to understand the overall fate and behavior of pharmaceuticals as environmental pollutants.

The main goal of this study was to assess the fate of two selected antidepressants, amisulpride and desipramine, during exposure to solar irradiance. Amisulpride is an atypical antipsychotic used to treat psychosis in schizophrenia and episodes of mania in bipolar disorder while desipramine is a tricyclic antidepressant of the dibenzapine group, used to treat depression, and it is the active metabolite of imipramine. These two compounds were selected as model substances based on their susceptibility to photolysis from irradiation at a temperate latitude, their typical consumption patterns in high income nations and due to the lack of information relating to their fate and occurrence in WWTPs. The approach followed in this study to envisage the photolytic fate of amisulpride and desipramine in wastewater treatment lagoons consisted of four steps: (i) the determination of kinetic photolysis degradation rates of parent compounds in pure water (direct photolysis) and in lagoon wastewater (indirect photolysis) under simulated solar irradiation, (ii) the identification and structural elucidation of putative transformation products formed under simulated solar irradiation by means of liquid chromatography coupled to high-resolution mass spectrometry (iii) the monitoring of both parent compounds and the TPs identified under laboratory-based experiments in samples collected from an operational WWTP lagoon system, to assess if photolysis is an important removal pathway and (iv) a preliminary assessment of the toxicity of the TPs formed in laboratory-based experiments using a bioluminescence assay.

2. Materials and methods

2.1. Materials and reagents

All pharmaceutical standards were of high purity grade (>98%). Amisulpride and desipramine were purchased from Sigma Aldrich (St. Louis, USA). Solid phase extraction cartridges Oasis HLB (10 mg, 1 mL) and Oasis HLB (200 mg, 6 mL) were from Waters Corporation (Milford, USA). Glass fiber filters (0.6 μm and 0.3 μm) were purchased from Advantec (Japan). LiChrosolv grade methanol and HPLC water from Thermo Scientific (Sydney, Australia) were used for the chromatographic analysis. A Millipore system was used to obtain ultrapure (18.2 M Ω cm resistivity) grade water (Merck Millipore; Melbourne, Australia). Formic acid 98% was obtained from Scharlav.

2.2. Photolysis experiments

Photodegradation experiments were performed in an Atlas Suntest XLS+ solar simulator system (Chicago, USA), equipped with a Xenon arc lamp, at an irradiance of 500 W m⁻² to approximate average annual conditions in temperate zones (NASA, 2014). Glass filters were used to block transmission of irradiation wavelengths below 290 nm, giving a wavelength spectrum similar to that of natural sunlight. Ultrapure water and two wastewaters from a lagoon treatment system (collected from the initial and latter aerobic treatment stages) were used as media for the photolysis experiments. A chemical characterization of wastewaters is included in the supplementary material (Table S1). Water (50 mL) was spiked with amisulpride or desipramine, respectively, at 10 mg L⁻¹. The selected initial concentration of target compounds

was considerably higher than the levels that would be expected in the environment (between high ng L⁻¹ and low $\mu\text{g L}^{-1}$ level) in order to ensure the elucidation of the potential TPs formed. Solutions were transferred into borosilicate glass tubes sealed with polytetrafluoroethylene (PTFE) lined lids. Before irradiation, 1 mL aliquots of each sample were collected and placed in an amber 2 mL Eppendorf tube and stored at -20 °C until analysis. Samples were irradiated in the Suntest over a period of 72 h and were placed in a temperature-controlled water bath (~25 °C). At defined time intervals, 1 mL aliquots were withdrawn from the tubes and were stored in amber Eppendorf tubes at -20 °C until analysis. To evaluate that analyte degradation was actually due to photolysis, dark controls were performed, and were sampled at the same time periods as irradiation experiments. Temperature within the solar simulator system was assessed during the irradiation experiment using a HOBO (Onset; USA) temperature data logger.

The degradation rates of amisulpride and desipramine were studied in ultrapure water and in collected lagoon wastewater, with degradation in pure water representing direct photolysis and degradation in wastewater representing both direct and indirect photolysis. Direct photolysis occurs through a compound absorbing energy directly from solar radiation, while indirect photolysis takes place when matrix components absorb solar radiation and form reactive intermediates which subsequently interact with a compound (Tong et al., 2011; Garcia-Galan et al., 2012). The assessment of photolysis in environmental waters is critical, since indirect photolysis can lead to different photochemical pathways, compared with direct photolysis processes (Schwarzenbach et al., 2002a,b).

The degradation of both compounds was adjusted to a pseudo-first order kinetic model, following Eq. (1):

$$\frac{d[A]}{dt} = -k[A] \quad (1)$$

where A is the concentration of the target compound, t is the time of the experiment (h) and k is the rate constant (h⁻¹). Half-lives were calculated following Eq. (2):

$$t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

2.3. Analytical methods to evaluate photolysis kinetics and to identify TPs

Degradation kinetics were evaluated by liquid chromatography tandem mass spectrometry (HPLC-MS/MS) using a Thermo Finnigan TSQ Quantum Discovery Max (Thermo Electron Corporation, USA). The sample aliquots were appropriately diluted and analyzed by direct injection. On the other hand, TPs were identified by offline solid phase extraction (SPE), using Oasis HLB cartridges (10 mg, 1 mL) followed by ultrahigh-performance liquid chromatography (UHPLC) coupled to an Orbitrap Velos™ linear ion trap-orbitrap high-resolution mass spectrometer (HRMS) (Thermo Electron Corporation, USA). The SPE sample preparation step was used for sample clean-up, and not for sample pre-concentration, and only 0.5 mL of pure and wastewaters were used for the extraction. For more detailed information about the extraction and chromatographic methods used for the identification of TPs, see the supplementary material.

2.4. Toxicity evaluation by bioluminescent bacteria

Vibrio fischeri bioluminescent bacteria were used to perform toxicity tests of the irradiated samples (pure and wastewater samples) over time following the ISO 11348-3 protocol in a Microtox® bioassay (ISO, 1998). This method is based on the percent decrease in the amount of light emitted by the bioluminescent bacterium *V. fischeri* upon contact

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