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Removal mechanisms of benzotriazoles in duckweed *Lemna minor* wastewater treatment systems

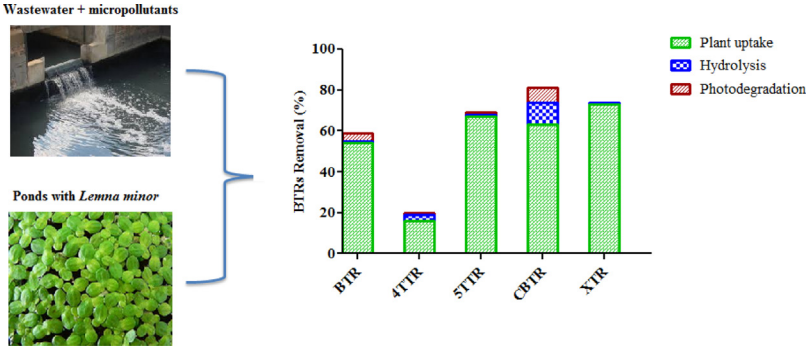
Georgia Gatidou, Maria Oursouzidou, Aimilia Stefanatou, Athanasios S. Stasinakis *

Water and Air Quality Laboratory, Department of Environment, University of the Aegean, University Hill, 81100 Mytilene, Greece

HIGHLIGHTS

- The fate of five benzotriazoles in *Lemna minor* systems was studied.
- The role of hydrolysis, photodegradation and plant uptake was investigated.
- Their removal in continuous flow system ranged between 26% (4TTR) and 72% (CBTR).
- The half-lives in presence of *Lemna* followed the order: CBTR < XTR < 5TTR < BTR < 4TTR.
- Plant uptake seems to be the major mechanism governing benzotriazoles' removal.

GRAPHICAL ABSTRACT



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ABSTRACT

The fate of five benzotriazoles (1H-benzotriazole, BTR; 4-methyl-1H-benzotriazole, 4TTR; 5-methyl-1H-benzotriazole, 5TTR; xylytriazole, XTR and 5-chlorobenzotriazole, CBTR) was studied in batch and continuous-flow *Lemna minor* systems and the role of different mechanisms on their removal was evaluated. Single and joint toxicity experiments were initially conducted using the Organization for Economic Co-operation and Development (OECD) protocol 221 and no inhibition on specific growth rate of *Lemna minor* was observed for concentrations up to 200 μg L^{-1}. All tested substances were significantly removed in batch experiments with *Lemna minor*. Excepting 4TTR, full elimination of CBTR, XTR, 5TTR and BTR was observed up to the end of these experiments (36 d), while the half-life values ranged between 1.6 ± 0.3 d (CBTR) and 25 ± 3.6 d (4-TTR). Calculation of kinetic constants for hydrolysis, photodegradation, and plant uptake revealed that for all BTRs the kinetic constants of plant uptake were by far higher comparing to those of the other mechanisms, reaching 0.394 ± 0.161 d^{-1} for CBTR. The operation of a continuous-flow *Lemna minor* system consisted of three mini ponds and a total hydraulic residence time of 8.3 d showed sufficient removal for most target substances, ranging between 26% (4TTR) and 72% (CBTR). Application of a model for describing micropollutants removal in the examined system showed that plant uptake was the major mechanism governing BTRs removal in *Lemna minor* systems.

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1. Introduction

Benzotriazoles (BTRs) are commonly used in corrosion-inhibiting products, cooling fluids, vulcanization accelerators and dishwashing detergents (Castro et al., 2005). They are highly soluble in water, highly polar and poorly volatile; they are commonly detected in the aquatic

* Corresponding author.
E-mail address: astas@env.aegean.gr (A.S. Stasinakis).

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environment (Nödler et al., 2016), while recent studies reported their endocrine disrupting effects in fish (Liang et al., 2014).

During the last decade, several articles have been published concerning the occurrence and fate of these compounds in Sewage Treatment Plants (STPs) and the mechanisms affecting their removal in biological wastewater treatment systems. According to the published studies, their concentrations in domestic wastewater vary from some hundreds ng L^{-1} to some tens μg L^{-1} (Reemtsma et al., 2010; Stasinakis et al., 2013; Molins-Delgado et al., 2015), while they are partially removed during biological wastewater treatment due to biotransformation processes (Mazioti et al., 2015a, 2017). Despite their frequent detection in water and wastewater, so far, there is only one study available concerning their removal in constructed wetland systems. Specifically, Matamoros et al. (2010) studied the removal efficiency of three BTRs in a surface flow constructed wetland planted with *Typha latifolia* and *Phragmites australis* and in a vertical flow constructed wetland and reported that their removal was affected by seasonality.

Among different plant-based systems, ponds with duckweed *Lemna minor* have been applied with success in different countries for the removal of nutrients and heavy metals, combining efficient wastewater treatment and important biomass production (Haarstad et al., 2012; Iatrou et al., 2015). Recent studies have also revealed the ability of such systems to remove organic micropollutants such as pharmaceuticals, personal care products and pesticides (Reinhold et al., 2010; Matamoros et al., 2012; Iatrou et al., 2015) via different mechanisms such as photodegradation, hydrolysis, plant uptake and biodegradation (Iatrou et al., 2017). To the best of our knowledge, so far, no information is available for the fate of BTRs in *Lemna minor* ponds and the contribution of different mechanisms on their removal.

Based on the above, the main objectives of this study were to investigate the removal of five benzotriazoles; namely 1H–benzotriazole (BTR), 4-methyl-1H-benzotriazole (4TTR), 5-methyl-1H-benzotriazole (5TTR), xylytriazole (XTR) and 5-chlorobenzotriazole (CBTR) (Table S1), from water and treated wastewater using *Lemna minor* bioreactors and to identify plant and not plant-associated processes responsible for their elimination. The possible inhibition of target compounds in *Lemna minor* was initially checked in single and mixture toxicity experiments. Afterwards, batch experiments were carried out to study the role of photodegradation, hydrolysis and plant uptake on target compounds removal and their kinetics constants were calculated. A continuous flow lab-scale system planted with fresh duckweed was used to investigate the removal of target compounds from secondary treated wastewater in different ponds. Finally, a mass balance model was applied to describe the contribution of different mechanisms to target compounds removal.

2. Materials and methods

2.1. Chemicals and reagents

Analytical standards of XTR and CBTR were supplied by Sigma-Aldrich (USA). BTR was purchased from Merck (Germany), 4TTR by Fluka (Switzerland) and 5TTR by Acros Organics (Belgium). Stock and working solutions were prepared in pure water for both batch experiments and continuous-flow experiments. HPLC grade water was prepared in the laboratory using a MilliQ/MilliRO Millipore system (Bedford, USA), while MeOH (LC-MS grade) and acetonitrile (ACN, HPLC grade) were purchased from Merck (Germany) and Fisher (USA), respectively. Strata – X polymeric reversed phase SPE cartridges (200 mg/6 mL) and RC filters (0.2 μm, 4 mm) were supplied from Phenomenex (Torrance, CA, USA). Duckweed communities were donated from Federal Environment Agency (Berlin, Germany).

2.2. Toxicity experiments

The duckweed *Lemna minor* cultures were initially grown for 4 weeks in Swedish standard sterile growth medium (Medium SIS) in accordance with the conditions described by OECD Guideline 221 (OECD, 2006). Toxicity range finding tests were conducted to check the possible effects of the target compounds on *Lemna minor*, individually as well as in mixture. Single toxicity experiments were conducted in the presence of 20, 200, and 2000 μg L^{-1}, while for mixture toxicity 200 μg L^{-1} were applied. All toxicity experiments were performed in triplicates in glass petri dishes, containing 100 mL Medium SIS with 12 healthy fronds of *Lemna minor* per petri dish. Stock cultures and cultures of toxicity experiments were incubated in a temperature - controlled chamber at 24 ± 0.5 °C under continuous illumination with fluorescent lamps (OSRAM, FQ 39W/840 HO). The duration of each experiment was 7 d and the estimation of inhibition was based on the frond number calculation of specific growth rate (Gatidou et al., 2015).

2.3. Batch experiments

Three different batch reactor systems were used to investigate the aqueous removal of target compounds due to hydrolysis, photodegradation and plant uptake (Table S2, Experiments A to C). All experiments were performed in triplicate, in glass flasks that contained 100 mL SIS medium. Flasks were placed in an incubator chamber for a period of 36 d, under constant illumination with fluorescent lamps (OSRAM, FQ 39W/840 HO). The temperature was set at 24.0 ± 0.5 °C, the pH was 7.0 ± 0.2 and the initial concentration of target compounds was 150 μg L^{-1}. Samples were taken at different time intervals (0, 2, 5, 8, 12, 15, 19, 23, 29 and 36 d).

Experiment A was conducted in the absence of *Lemna minor* under dark conditions to investigate the hydrolysis of BTRs. Experiment B was conducted under light conditions and both hydrolysis and photodegradation accounted for the elimination of target compounds. In Experiment C, 2 g of *Lemna minor* were added in each flask to investigate the contribution of plant uptake on BTRs' removal. This plant density mimicked full surface coverage growth observed in natural and treatment wetlands (Tront and Saunders, 2006). It is worth mentioned that all three studied mechanisms are expected to contribute to the removal of target compounds in this set of experiments.

2.4. Continuous - flow system: set up and operation

The continuous flow set-up comprised from one treatment line with three duckweed mini ponds in series (Iatrou et al., 2017). Each pond had a working volume of 5 L and duckweed biomass was harvested every week in order to maintain a density of 600 g fresh weight per m^2 (Sekomo et al., 2012). The system operated with a total hydraulic retention time (HRT) of 8.3 days, under 16/8 h light/darkness, respectively. Evapotranspiration losses were counterbalanced daily by adding tap water.

The fed up of duckweed system was conducted using secondary biologically treated wastewater, originating from University Campus STP. The chemical characteristics of influent wastewater were Chemical Oxygen Demand (COD) 34 ± 6 mg L^{-1}, NH_4-N 4.8 ± 0.8 mg L^{-1}, NO_3-N 2.1 ± 0.3, Total Phosphorous (TP) 5.8 ± 0.7 mg L^{-1}, and pH 7.9 ± 0.1. The target compounds were also detected in collected wastewater at low concentrations that did not exceed 2 μg L^{-1}. After an initial start-up period of three months to stabilize flow rate and to allow duckweed acclimatization and growth onto wastewater, wastewater was spiked with target micropollutants in order to achieve a concentration of around 30 μg L^{-1} at the inlet of the lab-scale system. System was operated under these conditions for a period of 25 days. The sampling for the determination of micropollutants was started 16 days after the spiking with target compounds (time equal to two HRT) from four different sampling points (Fig. S1); namely, inlet of the system (Point A), outlet

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