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Removal of polar UV stabilizers in biological wastewater treatments and ecotoxicological implications

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HIGHLIGHTS

- The removal of two benzotriazoles (BZTs) was investigated in 20 WWTPs.
- Both BZTs were observed in all influent and effluent samples.
- MeBZT showed higher concentrations and lower removal rates than BZT.
- Larger hydraulic retention times do not guarantee higher removal rates.
- MeBZT may represent a hazard for different aquatic organisms.

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ABSTRACT

The present study describes the development, validation and application of a fully automated analytical method based on on-line solid-phase extraction–liquid chromatography–tandem mass spectrometry (on line SPE–HPLC–MS/MS) to assess the removal efficiency in water works and the ecotoxicological implications derived of the two most used benzotriazole-class UV stabilizers (BZTs), namely 1H-benzotriazole (BZT) and 5-methyl-1H-benzotriazole (MeBZT). Influent and effluent wastewater samples from 20 wastewater treatment plants (WWTPs) were analyzed. Removal rates (RE%) and half-lives ($t_{1/2}$) for each BZTs were calculated and correlated to the hydraulic retention time (HRT) of each plant. Both BZTs were detected in all influent and effluent samples (concentrations in the range 26.7 ng L^{-1}–42.9 μg L^{-1}), with the highest concentrations corresponding to MeBZT. Results indicated that both compounds were recalcitrant (RE% in the range 11.8–94.7%) and that no clear influence of HRT on removals could be drawn.

Finally, the potential environmental risk posed by the levels of BZTs detected was evaluated calculating the hazard quotients (HQs) MeBZT was the only BZTs posing a risk to *Vibrio fischeri*, *Daphnia galeata* and *Pimephales promelas*.

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1. Introduction

During the last decades, the constantly increasing concern on stability and conservation of goods has made the use of preservation compounds to increase. Compounds as UV stabilizers are used in many industrial processes and formulae to ensure the stability of products. Among these high production chemicals, 1H-benzotriazole (BZT) and 5-methyl-1H-benzotriazole (MeBZT) are widely used by their anticorrosive, antifreeze, coolant, vapor phase inhibitor, photographic developer, drug precursor and biocide properties (Weiss et al., 2006; Domínguez et al., 2012; Asimakopoulos et al., 2013,). Both compounds are fairly water-soluble, not readily biodegradable, and have a limited sorption tendency (Domínguez et al., 2012) that makes them potential candidates to pass water treatment processes.

Industrial wastewater, household sewage and surface run-off from roads and airports contain high levels of these compounds, which lead to highly contaminated wastewater (Weiss et al., 2006). Existing wastewater treatment plants (WWTPs) have proven to effectively accomplish carbon and nitrogen removal, as well as microbial pollution control. However, these installations receive also a large number of different trace organic contaminants, among them BZTs, for which conventional treatment technologies have

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not been specifically designed (Reemtsma et al., 2010). As a consequence, these compounds not efficiently removed ultimately may reach the drinking water supply (Weiss and Reemtsma, 2005).

Data on removal efficiencies (RE%) of BZTs during conventional wastewater treatment is still quite scarce, and elimination rates reported so far are quite different ranging from 0% to 74% (Voutsa et al., 2006; Reemtsma et al., 2010; Asimakopoulos et al., 2013). The hydraulic retention time (HRT, the time that a soluble compound remains inside a constructed bioreactor) could be a factor related to those highly variable removal rates.

So far, off-line methods involving gas chromatography (Voutsa et al., 2006; Domínguez et al., 2012) and liquid chromatography (Weiss et al., 2006; Asimakopoulos et al., 2013) coupled to mass spectrometry have been used for the analysis of BZTs. However, the need to minimize the sample preparation, to improve sample throughput and data integrity, and to reduce analysis cost is a relevant issue, which demands the development of automated multiresidue analytical methods based on on-line extraction, separation, and detection.

In this scenario, it is important to consider the potential ecotoxicological risk derived of the environmental presence of these contaminants. So far, data on BZTs toxicity is scarce and based on acute toxicity tests which hardly represent environmental real conditions (Pillard et al., 2001; Seeland et al., 2012). Due to this lack of information, the risk assessment guidelines set up by the European Medicines Agency (EMEA) for the marketing authorisation of new medicinal products are frequently used to evaluate environmental risk from drugs that are entering the aquatic environment (García-Galán et al., 2011; Santos et al., 2007; Park and Choi, 2008; Grung et al., 2008; Gros et al., 2010) could be applied to other type of organic contaminants also present in the aquatic environment. These guidelines consider that concentrations of the investigated substance higher than 10 ng L^{-1} in surface water should lead to a further toxicity evaluation in order to estimate their effects on different target organisms upon exposure (predicted no-effect concentration (PNEC) or non-observed effect concentration (NOEC). Risk evaluation is based on the calculation of hazard quotients (HQs), which estimate the potential adverse effects of the contaminant concentration detected in the studied environmental matrix, for aquatic organisms. This quotient is usually calculated as the ratio between the predicted environmental concentration (PEC) and PNEC. HQ above 1 imply a potential negative environmental impact which should be investigated in further detail.

In order to assess the removal rates in biological wastewater treatments of these two UV stabilizers jointly with a preliminary estimation of the annual mass loads (ML), half-life elimination times ($t_{1/2}$; time needed to eliminate half of the quantity of the compound) and HQs, we developed and validated a fully automated analytical method to analyze wastewater from the 20 most important municipal WWTPs in Catalonia (Spain). The method is based on on-line solid phase-high performance liquid chromatography–quadrupole-lineal ion trap mass spectrometry (SPE–HPLC–QqLIT–MS/MS). The performance of the validated analytical method and the discussion of the outcomes obtained, focusing on removal efficiency and the environmental risk posed by the target emerging contaminants are presented.

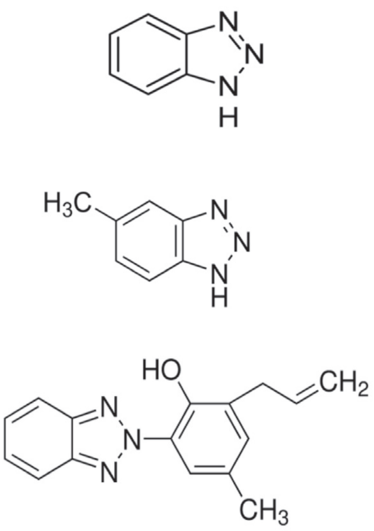
2. Experimental

2.1. Chemicals and materials

Chemical structure, CAS numbers, and other relevant physicochemical properties of the target compounds are summarized in Fig. 1.

Benzotriazole (purity >99%) and 2-(2H-benzotriazol-2yl)-4-methyl-6-(2-popenyl)phenol (AllylBZT) (purity >99%), used as internal standard (IS), were purchased from Sigma–Aldrich (Steinheim, Germany) and 5-methyl-1-H-benzotriazole (purity >99%) was supplied by TCI (Zwijndrecht, Belgium). HPLC-grade water, methanol (MeOH) and acetonitrile (ACN) were obtained from J.T. Backer (Deventer, The Netherlands). Formic acid (purity >99%) was provided by Merck (Darmstadt, Germany).

Stock standard solutions of each one of the analytes were prepared in MeOH at 100 mg L^{-1} and stored in the dark at −20 °C. Ten standard solutions of the mixtures of both benzotriazoles at concentrations ranging from 1 μg L^{-1} to 10 000 μg L^{-1} were prepared by appropriate dilutions of the stock solutions. These standard mixtures were used as spiking solutions for preparation of the HPLC-calibration standards and matrix matched calibration



1-H-benzotriazole (BZT)
CAS N#: 95-14-7
Solubility in water: 20 gL^{-1}
pKa = 8.2
Log K_{ow} = 1.23

5-Me-1-H-benzotriazole (MeBZT)
CAS N#: 136-85-6
Solubility in water: 5 gL^{-1}
pKa = 8.66
Log K_{ow} = 1.8

2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-propelyl)phenol (AllylBZT)
CAS N#: 2170-39-0
Solubility in water: 0.4gL^{-1}
pKa = 8.5
Log K_{ow} = 5.3
Internal standard (IS)

Fig. 1. Chemical structures, CAS N# and other relevant physicochemical properties (solubility in water, logK_{ow} and pK_a) of the target benzotriazoles and the internal standard (IS).

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