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Review

Terbuthylazine and desethylterbuthylazine: Recent occurrence, mobility and removal techniques

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HIGHLIGHTS

- Contamination of water resources by pesticides is a serious environmental problem.
- Triazine and their metabolites are chemicals of emerging ecological concern.
- Desethylterbuthylazine poses a high risk for groundwater contamination.
- Occurrence and remediation technologies of terbuthylazine are discussed.
- Photocatalysis and UV/H_2O_2 processes are effective for oxidation of terbuthylazine.

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ABSTRACT

The herbicide terbuthylazine (TBA) has displaced atrazine in most of EU countries, becoming one of the most regularly used pesticides and, therefore, frequently detected in natural waters. The affinity of TBA for soil organic matter suggests prolonged contamination; degradation leads to the release of the metabolite desethylterbuthylazine (DET), which has higher water solubility and binds more weakly to organic matter compared to the parent compound, resulting in higher associated risk for contamination of groundwater resources. Additionally, TBA and DET are chemicals of emerging concern because of their persistence and toxicity towards aquatic organisms; moreover, they are known to have significant endocrine disruption capacity to wildlife and humans. Conventional treatments applied during drinking water production do not lead to the complete removal of these chemicals; activated carbon provides the greatest efficiency, whereas ozonation can generate by-products with comparable oestrogenic activity to atrazine. Hydrogen peroxide alone is ineffective to degrade TBA, while UV/H_2O_2 advanced oxidation and photocatalysis are the most effective processes for oxidation of TBA. It has been determined that direct photolysis gives the highest degradation efficiency of all UV/H_2O_2 treatments, while most of the photocatalytic degradation is attributed to OH radicals, and TiO_2 solar-photocatalytic ozonation can lead to almost complete TBA removal in ~30 min. Constructed wetlands provide a valuable buffer capacity, protecting downstream surface waters from contaminated runoff. TBA and DET occurrence are summarized and removal techniques are critically evaluated and compared, to provide the reader with a comprehensive guide to state-of-the-art TBA removal and potential future treatments.

Contents

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1. Introduction

Many biologically active xenobiotics enter the natural environment as a result of anthropogenic activities. The ubiquitous occurrence of herbicides and their metabolites in water resources poses a hazard for the environment, humans and wildlife in different parts of the world. Many of the them are classified as 'emerging pollutants'; however, despite the fact that their endocrine disruption activity has sometimes been recognized or the full impact is still unknown (Mai et al., 2013), they are often not included in drinking water monitoring programmes (Odendaal et al., 2015). The European Union has introduced the Water Framework Directive (WFD, 2000/60/EC) to protect water resources, and to reduce risks to animal and plant organisms, as well as risks to human health (Fingler et al., 2017). Annex II of the Directive 2008/105/EC (EC, 2008), establishes the environmental quality standards for substances in surface waters, providing a list of priority substances and related concentration limits. The Drinking Water Directive 98/83/EC states maximum admissible concentrations of 0.1 $\mu g\,L^{-1}$ for individual pesticides and 0.5 $\mu g\,L^{-1}$ for the collective sum of pesticide concentrations in drinking water supplies (EC, 1998).

European regulation, as well as the great debate raised in recent years, have led to routine screening of chlorotriazine herbicides in many environmental monitoring campaigns (Bozzo et al., 2013). Chlorotriazine herbicides include atrazine (ATR), simazine and terbuthylazine (TBA) (Scherr et al., 2017). TBA (*N*2-*tert*-butyl-6-chloro-*N*4-ethyl-1,3,5-triazine-2,4-diamine) is a pre- or post-emergence broad spectrum herbicide (Odendaal et al., 2015); chemically, compared with atrazine, it has a *tert*-butyl group in place of the isopropyl group. Due to the widespread contamination of ground and surface waters, as well as its associated endocrine disrupting activity (Sassine et al., 2017), atrazine was banned in Italy and Germany in 1991, and in the remaining countries of the European Union in 2004 (Fingler et al., 2017), and TBA has now replaced ATR in most EU countries, including Spain, Italy and Portugal (Alvarez et al., 2016). Notwithstanding the reduced mobility of TBA due to its lower water solubility and higher hydrophobicity than ATR (Stipicevic et al., 2015), TBA is presently one of the most frequently detected pesticides in the continental (Bottoni et al., 2013; Alvarez et al., 2016), and coastal and marine waters (Nodler et al., 2013; Brumovsky et al., 2016, 2017) of these countries. The high persistence of TBA in the surface soil layer is additionally associated with the release of the deethylated metabolite desethylterbuthylazine (DET), which is currently one of the most ubiquitous and abundant polar plant protection metabolites found in EU aquifers (Loos et al., 2010).

TBA is a chemical of emerging concern due to the combination of its persistence (Navarro et al., 2004), toxicity to living organisms at low doses (Brumovsky et al., 2017) and high long-term risks to aquatic organisms (Bottoni et al., 2013; Lopez-Roldan et al., 2013; Palma et al., 2014; Tsaboula et al., 2016), mammals, non-target plants and non-target soil macroinvertebrates (Bottoni et al., 2013). The high octanol–water partition coefficient of TBA poses a potential risk for bioaccumulation of this pesticide in animals and plants (Baillie, 2016), with bio-amplification in the food chain (Masia et al., 2013; Toan et al., 2013). Moreover, its ubiquitous presence in marine waters of the North Sea (Mai et al., 2013) and in the western Mediterranean basin deserve scientific attention about possible impacts on ecosystems in pristine areas (Brumovsky et al., 2017). It has been proposed that TBA be classified in the carcinogen category 3 by the European Food Safety Authority (EFSA) (Bottoni et al., 2013). Its by-product DET is more persistent and bioactive than the parent compound (Pereira et al., 2015); this chemical likely affects the endocrine systems of wildlife and humans, with potential inhibition or stimulation of hormonal metabolisms (Blair et al., 2000) and alteration of steroidogenesis (Taxvig et al., 2013). The triazine ring is the source of toxicity and oestrogenicity associated with chlorotriazine herbicides, suggesting that the replacement of ATR by TBA would be an inappropriate approach to the issues posed by ATR (Pereira et al., 2015). The oestrogenic activity of this compound has been linked to the presence of its phenolic ring, which is in a position similar to that in 17β-oestradiol, the hydrogen bonding ability of the phenolic ring, which mimics the 3-OH, the presence of electronegative compounds bound to the aromatic ring, and its hydrophobicity (Fang et al., 2001). The by-product structures of TBA inherently have these requisites and their oestrogenic activity has recently been confirmed within the first minutes of ozonation, using a yeast oestrogen screen test (Pereira et al., 2015).

Treatment technologies commonly applied in the process of drinking water production have been shown to result in only partial removal of TBA (Ormad et al., 2008). The herbicide and its metabolite DET have frequently been detected in tap water samples collected in France (Cotton et al., 2016), Croatia (Fingler et al., 2017) and other European countries (Herrero-Hernandez et al., 2017). Recent occurrence, and mobility, of TBA and DET in European waters are summarised in this review. Mitigation techniques are investigated and removal technologies are discussed, with the aim to provide water quality managers with the information required to enhance the quality of water supplies.

2. Occurrence

2.1. Marine environment

There is significant evidence that numerous organics are