Terbuthylazine and Desethylterbutylazine:

Recent Occurrence, Mobility and Removal Techniques

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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.

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.

Keywords

Pesticide; Triazine; Emerging pollutants; Water treatment; Photocatalysis; Advanced oxidation

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-2,4diamine) 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, Brumovsky et al.

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 longterm 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 (HerreroHernandez 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.

Occurrence

Marine environment

There is significant evidence that numerous organics are transported beyond their source regions (Goolsby et al. 1997, van Pul et al. 1999, Asman et al. 2005, Scheyer et al. 2007, Yao et al. 2008) and their occurrence in coastal waters, shelf seas (Bester and Huhnerfuss 1993, Law et al. 1994, Alegria and Shaw 1999, Nodler et al. 2013, Brumovsky et al. 2016, Brumovsky et al. 2017) and in remote regions including the Arctic (Chernyak et al. 1996, Hoferkamp et al. 2010, Zhong et al. 2012) is well documented. However, their occurrence and behaviour in marine environments, fundamental to setting efficacious national and

international environmental regulations, have not been sufficiently studied and understood to date (Brumovsky et al. 2017).

TBA was detected in all 12 samples taken during a 2010 study, of the coastal waters of Italy and Spain, at concentrations between 13 and 84 ng L^{-1} (Nodler et al. 2013). There was also a 100% rate of detection of the herbicide, above the threshold of 10 ng L^{-1}, for 70 samples collected in ten offshore areas of the western basin of the Mediterranean Sea, in 2014. Diffuse coastal sources were suggested to be the cause, as no correlation was found between TBA levels and either sample distance from the coast, salinity, temperature or latitude (Brumovsky et al. 2017). Similar concentrations of TBA were detected in the North Sea in 2016 (Brumovsky et al. 2016), when this pesticide was already among those most frequently observed and was one of those with the highest reported concentrations (Mai et al. 2013) and 2014 (Brumovsky et al. 2016). The distribution pattern of TBA in the North Sea was found to be highly seasonally variable, and this is ascribed to the predominance of riverine inputs and transport by prevailing sea currents (Mai et al. 2013).

Surface waters

Seasonal variations in TBA concentration has been observed in surface waters, as a consequence of patterns in pesticide application and rainfall. In Greece, the highest concentrations, in the period autumn 2010 and winter 2011, were detected in spring in the Volvi, Doirani, and Kerkini lakes (Kalogridi et al. 2014), while a previous, earlier study of the same areas reported peak concentrations in winter (Koal et al. 2003). 2382 water samples were collected in the period August 2010 to December 2012 from 102 sampling sites located on rivers, streams and canals of the Pinios River Basin (Greece). TBA was among the most detected pesticides, posing a relevant risk for the environment, with 436 positive findings, 95 of which exceeded the 'predicted no effect concentration' (Tsaboula et al. 2016). In

Switzerland the highest levels of the herbicide were found in April during a 4-month monitoring study of the Sion-Riddes canal, which corresponded to the period of TBA application on crops (Schopfer et al. 2014), while maximum TBA and DET contamination levels were observed from April to August in surface waters of Croatia, shortly after field application of TBA (Fingler et al. 2017).

In 2008, Lombardy was the Italian region with the highest number of positive findings of TBA and DET in surface waters, detected from 89% of monitoring points; 59% (TBA) and 36% (DET) of the measured values where above 0.1 μg L^{-1} (Bottoni et al. 2013). Pollutant pathways of the Swist river basin (Germany) were investigated from 2012 to 2015; TBA and chloridazon were the two chemicals most often found in landscape runoff from cropland. TBA and DET were previously detected in effluent streams located immediately prior to the outlets of four waste water plants, as well as in water course discharges; 20% and 25% of readings were recorded as positive (above 0.2 μg L^{-1}) between July 2010 and August 2011, respectively (Christoffels et al. 2016). From April 2009 to November 2010, 83 of surface water samples collected in the south-eastern province of Jaen (Spain), a region with four natural parks, reservoirs, wetlands and a high olive oil production, showed TBA and DES to be two of the most detected chemicals (Robles-Molina et al. 2014). Nowadays, TBA is a ubiquitous compound in the natural waters of Spain, as a consequence of its increased use in recent years (Herrero-Hernandez et al. 2017), while TBA and DET concentrations over 0.1 μg L^{-1} have recently been reported for numerous river basins (Hermosin et al. 2013, Masia et al. 2015, Ccanccapa et al. 2016)**.**

Groundwater

Triazines and their metabolites are the most ubiquitous and abundant polar pesticides found in European ground waters (Loos et al. 2010), with TBA and DET often exceeding the

threshold of 0.1 µg L⁻¹ (Le Cunff et al. 2015). Groundwater contamination is more persistent than surface water pollution, biodegradation being slower in such systems, and this could have a continuous toxicological effect when groundwater is used for human consumption (Kim et al. 2017).

TBA and DET have frequently been detected in groundwaters around Zagreb in Croatia; during a monthly campaign conducted in 2014, TBA was detected in 26% of samples, up to 25 ng L⁻¹ (Fingler et al. 2017). The Vistrenque shallow alluvial aquifer (France) was tested between 2011 and 2013, where TBA was found in 59% of the 66 samples collected, up to 40 ng L⁻¹ (Sassine et al. 2017). DET was also the most frequently detected compound in Maribor groundwaters (Slovenia) collected in 2010, with 77% of the 56 samples analysed showing presence of the compound, with concentrations of DET higher than those of TBA. The highest levels of TBA (up to 25.7 ng L⁻¹) were observed during the spring campaign, and the DET/TBA ratio, calculated for 29 samples, ranged from 1.4 to 2.9 (Korosa et al. 2016), suggesting diffuse contamination. Indeed, in the case of a point source of pollution, the pesticide leaches directly into groundwaters without significant interaction with the soil, giving a DET/TBA ratio lower than unity. By contrast, when contamination is a diffusive phenomenon, biodegradation processes play a significant role, with formation of parental metabolites; these molecules are transported into groundwaters quicker than the generally less soluble parent compounds and the ratio is increased (Bozzo et al. 2013).

As for surface waters, groundwater pollution is higher in those Mediterranean countries with a high prevalence of olive orchards (i.e. Italy, Greece, Spain and Turkey) (Hermosin et al. 2013). In 2008, TBA and DET levels were monitored in the regions of Italy most affected by their presence in aquifers (ISPRA 2011), with TBA detected in 36% of the monitoring points in Piedmont and 8% showing evidence of DET. This study also reported that of those

samples showing evidence of either chemical, 28% of samples showed TBA exceeding 0.1 µg L^{-1} and 14% exceed 0.1 µg L^{-1} for DET (Bottoni et al. 2013). Monitoring campaigns of groundwaters in the Lombardy region were carried out from 2005 to 2009; concentrations of TBA and DET exceeded the limit for drinking water in 9 and 11 sampling points of the Adda-Oglio basin, respectively. Analysis did not identify any seasonal trend for contamination, while the DET/TBA ratio was estimated as higher than 1, (Bozzo et al. 2013) suggesting deep interaction with the soil horizons (Guzzella et al. 2006).

High levels (> 5 µg L^{-1}) of TBA have recently been found in groundwater samples of La Rioja (Spain) (Herrero-Hernández et al. 2013), where TBA and DET were the most detected compounds in 12 surface waters monitored between September 2010 and September 2011. In September 2010, both the chemicals concentrations were found above 0.1 µg L^{-1} in 10 samples, at a time corresponding with the application period (Herrero-Hernandez et al. 2017). This threshold value was also exceeded for TBA levels, with 12 noncompliances during a 4 years monitoring program, conducted by the Catalan Water Agency on 29 aquifers of Catalonia (Kock-Schulmeyer et al. 2014). TBA concentrations several times higher than safe critical limits for water quality have been recorded in the Guadalquivir River Valley (Andalucia) during the winter season, simultaneous to principal application in olive orchards (Hermosin et al. 2013) and high rainfall, typical of the Mediterranean climate (Calderon et al. 2015). Herbicide runoff, and loss through soil particles, on which it is adsorbed, are favoured by low olive tree density and on slopes ranging from 10 to 30% in gradient (J.A. GómezCalero 2009). Groundwater analyses were performed on samples from the Jucar River Basin (Spain) during spring and fall campaigns from 2010 to 2013. TBA was the most frequently detected pesticide in the 314 samples analysed, exceeding 0.1 µg L^{-1} on 9 occasions (Menchen et al. 2017). The herbicide concentration in other Spanish river basins

was recently also found to be above 1.2 µg L^{-1} (Jurado et al. 2012), while values up to 0.62 µg L^{-1} were recorded during a two year monitoring programme (2009–2011) of reclaimed waters and a volcanic aquifer in Gran Canaria, with frequencies of detection of TBA reported at 90% and
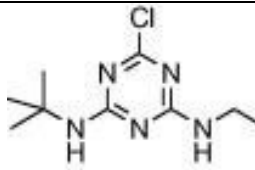
50%, respectively (Estevez et al. 2016).

Mobility and transformation

Physicochemical properties and degradation pathways

The persistence of pesticides in soil, and their transport from soil to groundwaters, is controlled by a number of factors, including the physicochemical properties of the substances (e.g. octanol/water partition coefficient, solubility in water, vapour pressure etc.) (Cheng and Koskinen 1986), their biotic (Caracciolo et al. 2010) and abiotic degradation rates (Zeng et al. 2012), the properties of the soil and the unsaturated zone, pH (Celis et al. 1998, Sannino et al. 1999), organic matter content (Barriuso et al. 1997, Beltran et al. 1998), clay content, soil moisture (Louchart et al. 2001), climate (Ulrich et al. 2013) and application techniques (Sadeghi et al. 2000, Fait et al. 2010).

TBA is weakly basic, and under circumneutral soil pH conditions, presents as neutral, moderately hydrophobic (log K_{ow} = 3.4, as shown in Table 1) compound (Scherr et al. 2017). It is relatively persistent in soils, with a half-life of up to four months (Stipicevic et al. 2015).

Table 1: Physicochemical properties and leaching potential index (GUS) of terbuthylazine

Molecular structure	Sol. (20 °C)[†] mg L^{-1}	Vapour Pressure[‡] mPa	pK$_a$ (25 °C)[‡]	Log Kow (20 °C, pH 7)[†]	K_{OC}[†] ml g^{-1}	GUS[‡]
	9	0.12	1.9	3.4	162-333	3.07

228   [†] (MacBean 2012); [‡] (Hertfordshire 2016)

229   TBA mineralization and transformation relies on two processes, mediated by common soil

230   microbes (Kontchou and Gschwind 1995, Mandelbaum et al. 1995, Satsuma 2010).

231   Chlorohydrolysis, with associated depletion of the chlorine atom in C2, is influenced by soil

232   pH and clay content (Horrobin 1963) and yields the hydroxylated product 2-OH-TBA

(Mandelbaum et al. 2008). This pathway is largely due to abiotic reactions, while Ndealkylation of the side chains of the *s*-triazine ring, which leads to deisopropylated (DIA) and deethylated (DET) metabolites (Nagy et al. 1995), depends mainly on microbiological activity (Bottoni et al. 2013). 2-Cl-4 hydroxyterbythylazine (2-Cl-4-OH-TBA) originates from DET deamination, while DET dehalogenation transforms the compound into 2-OHDET, which also derives from 2-OH-TBA desethylation. 2-OH-DET deamination then yields

2,4-dihydroxy –TBA (Di Corcia et al. 1999, Guzzella et al. 2003, Barra Caracciolo et al.

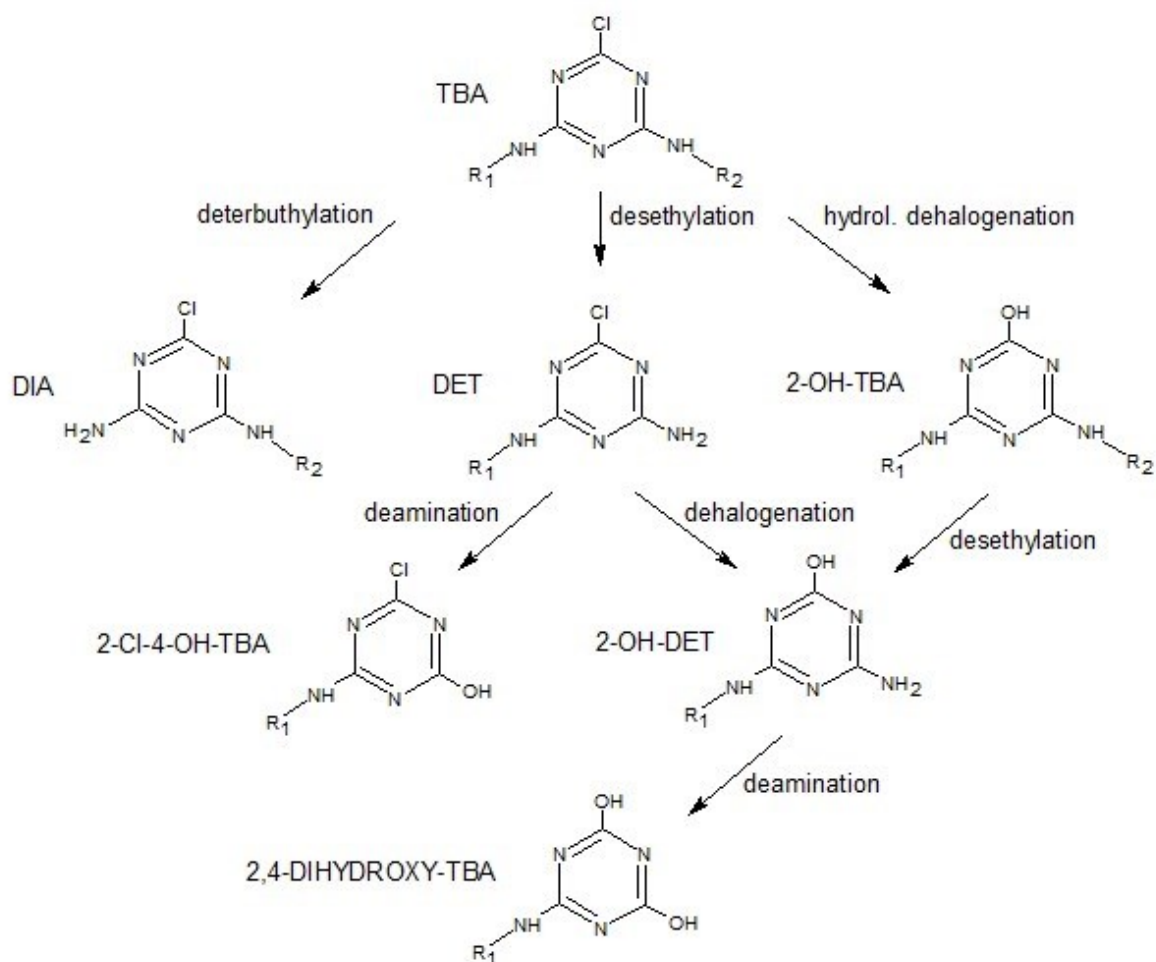2005). The pathways are summarised in Figure 1:

Figure 1: Main degradation pathways of TBA in soil and related intermediates (Di Corcia et al. 1999, Guzzella et al. 2003, Barra Caracciolo et al. 2005, Bottoni et al. 2013)

Mobility: leaching and adsorption

TBA is mainly used during the pre-emergence stage of plant growth (Milan et al. 2015), thereby reducing the possibility of plant interception; moreover, the risk of leaching is increased by the fact that application is generally made in periods during which heavy rainfall occurs (Bozzo et al. 2013). The water solubility of TBA is low (Table 1), but this compound has a significant potential for adsorption to soil and organic matter (Watt et al. 2010); hence, transport via sediment and organic matter, in waterways, is a relevant pathway (Kronvang 2003). While this pesticide exhibits a medium mobility, its metabolite DET is notably more mobile in soils than the parent compound (EFSA 2011).

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The GUS (Groundwater Ubiquity Score (Gustafson 1989)), also known as 'leaching potential index', of TBA and DET were estimated as 3.07 and 3.9, respectively (Hertfordshire 2016); these values denote the significant leaching potential of both compounds (Bozzo et al. 2013). The probability that the herbicides detected in sediments could pollute the groundwaters of the Alqueva reservoir (Portugal), if desorption processes were to occur, was recently evaluated using the GUS index. TBA was amongst the compounds with the highest probability of contamination (GUS > 2.8) (Palma et al. 2015). The potential of the herbicide, and its metabolite DET, for groundwater contamination was also proven by different lysimeter experimental studies (Guzzella et al. 2003, Milan et al. 2015). 70% of applied TBA was recovered from leachates during a leaching experiment conducted with hand packed soil columns (Calderon et al. 2016), while TBA and DET were often found in leached waters, at concentrations above 0.1 μg L^{-1}(up to 0.34 μg L^{-1} for DET), during a two-year study carried out with a battery of field lysimeters, filled with silty-loam soil and treated during preemergence with a mixture of commercial products (Milan et al. 2015). In a 17-month, fields under continental climate conditions study, TBA showed a similar leaching potential to atrazine, or even higher than the banned compound if the soil exhibited moderate TBA persistence (time needed for the disappearance of 50% of the initial compound mass DT_{50}: 30–100 days). Indeed, high persistence of TBA in soils may result in high transport in surface runoff and delayed leaching to the aquifer (Stipicevic et al. 2015).

TBA was monitored within the first 2 cm of soil in the Guadalquivir River Valley (Spain), after winter herbicide application. No herbicide residues were detected in the soil 107 days after application. The disappearance of TBA from the topsoil seemed to be mainly related to leaching processes, as only very low levels of both herbicides (TBA and DET) were recovered from runoff waters and sediment throughout the monitoring period (Calderon et al.

2016). Soil samples from two different layers (5–25 and 40–60 cm depth) were incubated

with TBA at two temperatures. DT_{50} values were found to be similar for the two layers at 15

°C, but a decrease was observed from 180 to 30 days, for the upper layer, at 22 °C. The

presence of urea appeared to slightly slow herbicide degradation, while the increase of DT_{50}

from 22 to 82 days, for sterilized soil, confirmed the role of microorganisms in the

desethylation process (Bottoni et al. 2013).

Table 2: DT_{50} of terbuthylazine and desethylterbuthylazine in different media and under different conditions.

Substance	Media and conditions	Value (days)	Reference
TBA	Lab topsoil (2 cm)	18 ± 2	(Calderon et al. 2016)
	Lab topsoil (5-25 cm), 15 °C	180	(Caracciolo et al. 2001)
	Lab topsoil (5-25 cm), 22 °C	30	(Caracciolo et al. 2001)
	Lab topsoil, 25 °C	13	(Bottoni et al. 1996)
	Lab soil (40-60 cm), 15 °C	200	(Caracciolo et al. 2001)
	Lab soil (40-60 cm), 22 °C	180	(Caracciolo et al. 2001)
	Lab soil	65–167	(EFSA 2011) [a]
	Field topsoil	44	(Funari et al. 1998)
	Field topsoil (silty loam)	20.1± 1.6	(Stipicevic et al. 2015)
	Field topsoil (silty clay loam)	86.6 ± 30.1	(Stipicevic et al. 2015)
	Field soil	10–48	(EFSA 2011) [a]
	Lab seawater (dark), 20 °C	184	(Navarro et al. 2004)
	Lab river water (dark) 20 °C	331	(Navarro et al. 2004)
	Lab groundwater (dark) 15 °C	151	(Caracciolo et al. 2013)
	Lab groundwater (dark) 20 °C	102	(Navarro et al. 2004)
	Lab seawater (light), 20 °C	76	(Navarro et al. 2004)
	Lab river water (light) 20 °C	196	(Navarro et al. 2004)

	Lab groundwater (light) 20 °C	102	(Navarro et al. 2004)
DET	Lab soil	27–113	(EFSA 2011) [a]
	Field soil	2–223	(EFSA 2011) [a]

[a] Data derived from different studies, considered from the European Food Safety Authority (EFSA) for regulatory purposes (EFSA 2011).

While binding to the dissolved organic matter increases mobility of organic pollutants through the soil column, their sorption in soil reduces transfer from the soil surface layers to the aquifer. When the persistence of herbicides in soil is high, their dissolution becomes a long-term source of groundwater pollution (Fingler et al. 2017).

TBA sorption intensity in two agricultural soils was evaluated in terms of the Freundlich sorption isotherm:

$$q_e = K_F C_e{}^n$$

Where q_e (nmol g^{-1}) is the amount of herbicide sorbed per unit mass of sorbent at equilibrium, C_e (nmol mL^{-1}) is the equilibrium herbicide concentration in the aqueous phase, K_F (nmol$^{(1-n)}$ mL^n g^{-1}) is the coefficient related to the sorption capacity and n is a dimensionless heterogeneity parameter (Goldberg 2005). The sorption coefficients (K_F) of TBA were found to be similar (1.5; 1.4), while the values of the coefficients obtained by normalising K_F to organic carbon content were 125 and 156, the latter related to a soil with higher clay content, which showed higher herbicide persistence (Stipicevic et al. 2015).

As in the case for soils, pesticides can be accumulated in sediments (Gong et al. 2007) and subsequently released to the water column. Therefore, sediments are a secondary source of contamination of the aquatic system (Wang et al. 2013, Yuan et al. 2013). In an attempt to

quantify and outline the fate of compounds in the environment, the pesticide distribution coefficient K_d can be calculated using the following equation:

$$K_d = C_s/C_r$$

Where C_s is the pesticide concentration in the sediment (g kg^{-1}) and C_r is the pesticide concentration in the runoff (g L^{-1}) (Calderon et al. 2016). A K_d of 5 L kg^{-1} was determined for TBA in sediments of the Alqueva reservoir (Palma et al. 2015); similar low K_d values were reported by other authors (Cabrera et al. 2008, Calderon et al. 2016), indicating that this compound is weakly sorbed on sediments. K_d values of TBA were found to increase with time (Calderon et al. 2016), probably due to aging effects (Regitano et al. 2006). Low adsorption of this herbicide to sediments is also confirmed by the soil organic carbon-water partitioning coefficient (K_{oc} = K_d/TOC, where TOC is the total organic carbon content), found to be 231 mL g^{-1} (Palma et al. 2015). K_{oc} values reported from by EFSA range from 191–318 and 44-122 for TBA and DET, respectively (EFSA 2011).

Removal technologies and mitigation techniques

Adsorption

Addition of biochar to agricultural soils is an in-situ technique capable of reducing the dissipation of organic pollutants; however, with time, mineral particles could cover the reactive surfaces of this carbon-rich material, masking its sorption capacity (Kookana 2010).

Biochar particles were separated from soil after one and two years after application as a soil amendment; sorption batch experiments with TBA were conducted to estimate the sorption coefficient K_s, defined as the ratio between C_s/C_e, where C_e is the equilibrium solution concentration and C_s is the difference between C_e and the initial concentration. K_s decreased from 595 (fresh biochar) to 312 and 221 for biochars aged at 1 and 2 years, respectively. Soil

mineral incorporation onto the surface of the aged biochar was investigated by Fourier transform infrared spectra (FTIR) analysis, which showed additional bands at 3695 and 1003 cm^{-1}, likely due to O–H stretching and Si–O vibrations of clay minerals. The decrease of the band around 1700 cm^{-1} (C–H bending) and the increase of the band at 1400 cm^{-1} (carboxylate anion stretching), comparing to the fresh biochar, have been linked to a partial elimination of the unsaturated fatty acid and to carboxylate anion interactions, respectively (Trigo et al. 2014).

Hydrophobic interactions and π-π dispersive forces have been suggested as major mechanisms of TBA adsorption (Pan and Xing 2008) on activated carbon (AC). A removal efficiency of 60% was achieved by using 10 mg L^{-1} of powdered AC on natural water containing TBA at an initial concentration of 1.024 ug L^{-1} (Ormad et al. 2008). Testing the granular form of sorbents provides great insight into material performance within a filter configuration (Tasca et al. 2017); performances of AC granular samples (S$_{BET}$: 644 m^2 g^{-1}) were recently verified in batch and column tests. Granular AC exhibited a higher uptake in batch for TBA than multiwalled carbon nanotubes (MWCNT), probably due to the higher surface area of the AC used. However, adsorption was faster on MWCNT than on AC; this fact was attributed to the easier diffusion of TBA molecules into the more developed mesoporous structure of MWCNT materials, compared to AC. Experimental data of AC was described by a Freundlich adsorption isotherm model. Performance of AC samples was also studied in rapid small scale column tests (RSSCT), performed using a flowing aqueous solution of TBA at 5 mg L^{-1} through a glass column (internal diameter: 0.5 cm), with an empty bed contact time of 1.3 min. 40% breakthrough was achieved at the beginning of the run, while 50% breakthrough was achieved at ~10,000 bed volumes, and saturation was reached at ~30,000 bed volumes (Alvarez et al. 2016).

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TBA adsorption has been also studied on modified clay minerals. 20 mg each of Namontmorillonite (SWy-2) and Ca-montmorillonite (SAz-1), modified with organic cations, were tested in batch with a TBA concentration of 1 mg L^{-1}. TBA was reversibly sorbed, displaying high affinity for SWy-2 exchanged with l-carnitine; 95% removal was attained, attributed to acid−base interactions between the weakly basic herbicide and the carboxyl group of carnitine. TBA also displayed high affinity for SAz-1 exchanged with HDTMA cations; this fact may be attributed to the herbicidal affinity of the interlayer organic phase created by the paraffinic (d_{001} > 22 Å) structure, resulting from incorporation of HDTMA cations into the clay mineral (Celis et al. 2007).

Adsorption isotherms of atrazine, simazine and TBA on a poly 4-vinyl pyridine co styrenemontmorillonite (HPVP–CoS–MMT) composite were found to follow the Langmuir equation. The binding kinetics were in the order of simazine > atrazine > TBA, in the same order as their affinity at equilibrium, suggesting that binding rates increase with accessibility of the compound to the proton donor group of the composite. The removal of TBA (1 mg L^{-1}) was also conducted in 1.6 cm wide columns filled with 3.6 g of HPVP–CoS– MMT mixed with sand at weight ratio of 1:20. The pH of the aqueous solution of the herbicide was adjusted to 3.5. The adsorption and convection equation (Nir et al., 2012) was used to derive the adsorption and desorption coefficients, C_1 (M^{-1} min^{-1}) and D_1 (min^{-1}), respectively, for application in model simulations and predictions. The value estimated for C_1 was 24 M^{-1} min^{-1}, while D_1 was found to be 0.0013 min^{-1} (Gardi et al. 2015). Column test were also conducted with 50–400 μm polydivinylbenzene microspheres modified via a DielsAlder reaction. This porous material contains carboxyl groups able to form hydrogen bonds with triazines. In detail, interactions occur between the hydroxyl hydrogen atom of the carboxylic group from the polymer and the nitrogen atom containing a free electron pair of electrons on

triazine, as well as and between the carbonyl oxygen atom of the polymer and the hydrogen atom of the amino group of triazine. A neutral solution of 10 ppm TBA in ethanol:water (1:9 v/v) was passed down a microcolumn (0.9 cm wide) packed with the modified polydivinylbenzene microspheres, at a flow rate of 0.3 mL min^{-1}; a subsequent adsorption capacity of 66.2 mg g^{-1} was achieved (Ronka 2016).

Chlorination, sulfate radicals, ozone, peroxone and catalytic ozonation

Chlorination is commonly used in drinking water plants but, while its high effectiveness has been proven on widely used herbicides such as glyphosate (Jonsson et al. 2013), oxidation carried out with NaClO on natural water removed only 30% of TBA (initial concentration: 1.024 ug L^{-1}). No improvements have been observed with the additional use of $Al_2(SO_4)_3$ as a coagulating agent, while the combined treatment with chlorine and activated carbon reached 70% removal efficiency (Ormad et al. 2008).

The sulfate radical ($SO_4^{\bullet-}$) is another oxidizing agent effective on a wide number of contaminants. This compound degrades chlorotriazines more readily by electron transfer than $^{\bullet}OH$ radicals, but is slower than H-abstraction and addition (Neta et al. 1988, von Sonntag 2005). The high reactivity of chlorotriazines with $SO_4^{\bullet-}$ is mainly due to the ethyl or isopropyl group; however, dealkylated metabolites, such as DET, are less reactive toward sulfate radicals than the parent compounds (Lutze et al. 2015). Oxidation carried out with $SO_4^{\bullet-}$ is of increasing interest, but the energy demand in water purification plants needs to be estimated to allow meaningful comparison to other available techniques, such as ozonation (Lutze et al. 2015). The effectiveness of ozone oxidation was investigated on natural water containing TBA at a concentration of 1.024 ug L^{-1}. An ozone flow of 4.3 mg L^{-1} was applied by a corona discharge generator, obtaining a removal efficiency of 45%, increased to 90% if coupled with the use of activated carbon. The addition of $Al_2(SO_4)_3$ up to 40 mg Al L^{-1} did not enhance the

efficiency of the ozonation treatment (Ormad et al. 2008). Later ozone alone, and combined with hydrogen peroxide and titanium dioxide, was applied to pesticide removal from a sample of natural water from the River Ebro (Spain). 3 mg O_3 L^{-1} were applied by a corona discharge reactor obtaining only 15% TBA degradation. The dosage of 1.5 mg H_2O_2 L^{-1} did not modify the efficiency, and was slightly improved with catalytic treatment, using 1 g TiO_2 L^{-1} (Ormad et al. 2010). Another recent study achieved 99% of TBA and atrazine removal within one minute with applied doses of 1 and 4 mg L^{-1} of ozone, respectively. Intermediates detected for ozonation of TBA at pH 7 were: 2-chloro-4-acetamido-6terbutilamino-1,3,5-triazina (CDTT), DET, 2-chloro-4-etilamino-6-amino-1,3,5-triazina (DIA) and 2-chloro-4,6-amino-1,3,5-triazina (DEDIA). CDTT and DEDIA were not detected at pH 11 and 3, respectively, and DET was the most prolific by-product detected during the process (Pereira et al. 2015).

The role of AC in promoting ozone decomposition into hydroxyl radicals has been already confirmed (Alvarez et al. 2009). More recently, single ozonation, O_3/H_2O_2 process, and heterogeneous catalytic ozonation using AC, MWCNT and TiO_2 as catalysts, were investigated on an aqueous solution of 5.0 mg L^{-1} of TBA. The herbicide was entirely removed from the solution after 2 h using any of the treatments listed, with an applied flowrate of 20 L h^{-1} of O_3/O_2 mixture (▬10 mg L^{-1} O_3 concentration). The most efficient treatments in terms of O_3 consumption/TBA removed ratio were found to be the O_3/H_2O_2 (initial H_2O_2 concentration: 20 mg L^{-1}) and the O_3/AC processes. The MWCNT sample reduced the amounts of O_3 and hydroxyl radicals available to react with the herbicide, behaving as a scavenger of the radicals produced from ozone decomposition in solution and over its own surface (Alvarez et al. 2016).

UV and UV/H$_2$O$_2$ photodegradation

TBA does not react appreciably with H$_2$O$_2$ (Alvarez et al. 2016). Hydrogen peroxide alone (15 mg L^{-1}) was found to be ineffective in the oxidation of 10 μg L^{-1} of the herbicide contained in groundwater samples (Sorlini et al. 2014). In photolytic (UV) and UV/H$_2$O$_2$ treatments the abatement of TBA is due mainly to direct photolysis or oxidation by hydroxyl radicals, generated from the photolysis of H$_2$O$_2$ (Alvarez et al. 2016). Direct photolysis of 5 mg L^{-1} of TBA in a 250 mL reactor did not produce significant degradation (Quinones et al. 2015), while the removal rate increased significantly in the UV$_{254}$/H$_2$O$_2$ combined process. An average fluence rate of 2.9 mW cm^{-2} was applied to 400 mL of ultrapure water containing 5 mg L^{-1} of the herbicide. A fist-order kinetic law for TBA removal was suggested and the required doses for 90% TBA removal were1404 to 535 mJ cm^{-2}, with initial H$_2$O$_2$ concentration of 5 and 50 mg L^{-1}, respectively. The UV dose required to reach the same efficiency without H$_2$O$_2$ was 2002 mJ cm^{-2}. These doses are significantly higher than those commonly applied in drinking water disinfection (Alvarez et al. 2016). The enhanced efficiency due to increasing UV doses, as well as the main contribution of direct photolysis to the removal of TBA via the UV/H$_2$O$_2$ process, were recently confirmed by the oxidation of groundwater samples containing 10 μg L^{-1} of TBA. Up to 52% removal yield was obtained with a UV$_{254}$ dose of 1,200 mJ cm^{-2}; when H$_2$O$_2$ was added, the UV fluence increased from 1,200 to 2,000 mJ cm^{-2}, enhancing herbicide degradation by 10–30%, while an increase of H$_2$O$_2$ concentration from 5 to 10 mg L^{-1} at fixed UV doses did not affect the efficiency significantly (Sorlini et al. 2014).

Photocatalysis

Photocatalytic processes have been widely focused on the removal of many pesticides and endocrine disrupting chemicals not readily degraded by common treatments (Sirés et al.

2014, Le Cunff et al. 2015). These advanced oxidation processes (AOPs) are based on oxidation–reduction reactions involving excited electrons (e$^-$) and the generated holes (h$^+$) at the valence bands. Electrons are promoted from the valence to the conduction band by the excitation of a semiconductor through the absorption of photons, having energy greater than their band gap (Fujishima et al. 2000).

In a recent experiment it has been found that h$^+$ and other reactive species play a minor role in such processes, while 93% of removal efficiency is mostly as a result of interaction with hydroxyl radicals. The photocatalytic degradation of 100 µM each of TBA and two other *s*triazine herbicides over TiO$_2$ (1.0 g L^{-1}) was conducted in a 150 mL reactor; the suspension was stirred in the dark for 30 min, before illumination with a Xe lamp (350–780 nm, light intensity: 1.28 mW cm^{-2}). 92% of TBA was degraded within 90 min. H$_2$O$_2$ and NaBrO$_3$ improved the degradation rate by suppressing the recombination of h$^+$ and e$^-$; enhanced removal was found at low concentrations of H$_2$O$_2$. The pathway involved the cleavage of side chains, substitution of Cl atoms by hydroxyl radicals, hydroxylation and abstraction of H atoms (Yang et al. 2016). A simplified Langmuir–Hinshelhood (L–H) model was used to fit the kinetic data obtained:

$$-dc/dt = k_1C$$

Where k_1 is the pseudo-first order rate constant (Yang et al. 2010, Yang et al. 2010), equal to 0.0309 min^{-1} for TBA. The low value of k_1 was attributed to the weak polarity and steric effects of the tertiary butyl group. At the beginning of the photocatalytic process, the *s*triazine ring, rather than the side chain, was found to be in contact with the catalyst surface. Attack by ˙OH is likely to occur at the C atom of the *s*-triazine ring connected to the Cl atom. It was also observed that h$^+$ interaction starts with the *s*-triazine ring rather than the side chains;

adsorption and reaction of TBA with h^+ on the surface of TiO_2 particles are subject to the steric-hindrance effects of side chains (Yang et al. 2016).

Complete removal of TBA was achieved after 80 min of photocatalytic degradation (UV_{254} lamp intensity: 8 mW cm^{-2}) conducted with a TiO_2/chitosan thin layer immobilized on a glass fibre woven roving material, with cyanuric acid as the final product. Degradation of the herbicide started with N-dealkylation of the lateral chain and evolved with hydrolysis of the chlorine atom and the amino group. The main dealkylation product detected was DET. Without the presence of the photocatalyst (i.e. the absence of the hydroxyl radical source), the conversion to cyanuric acid was confirmed to be much lower (Le Cunff et al. 2015); this compound cannot be destroyed by either photolysis or photocatalytic degradation (Bozzi et al. 2004, Oh and Jenks 2004), but it can be removed through microbial processes.

Solar AOPs

Solar-driven advanced oxidation processes, in which solar energy is used to activate a semiconductor, have recently attracted growing attention in water treatment applications (Quinones et al. 2015). A 250 mL reactor was charged with an aqueous solution of TBA (5.0 mg L^{-1}) and irradiated by a solar simulator, providing an irradiance at the solution level of 581 W m^{-2}. A 20 L h^{-1} flowrate of a mixture ozone-oxygen (▬10 mg L^{-1} ozone concentration) did not produce appreciable degradation of the herbicide in about 2 h, but when TiO_2 was added as a catalyst, TBA was completely removed in 30 and 45 min, with UV-A exposure doses of 11.1 and 16.7 J cm^{-2}, respectively; moreover, the specific ozone consumption was below 5.5 mg O_3 mg^{-1} TBA. The greater TBA removal and better utilization of O_3 in catalytic solar photo-ozonation compared to single ozonation is in part explained by the decomposition of ozone into hydroxyl radicals (Rodríguez et al., 2013). When MWCNT-TiO_2 was used as a catalyst, 87% of TBA was removed during the 'dark'

stage (i.e. absence of radiation), through adsorption on the catalyst surface; hence, the photocatalytic effect does not play the main role in the process. Herbicidal degradation is due to O_3 and $^{\bullet}OH$ attacks on aminoalkyl substituents, with hydrogen abstraction or alkyl group cleavage, as suggested by the intermediates detected with HPLC-qTOF analysis. Hydroxyl substitution of the chlorine atom likely occurs during the oxidation phase (Alvarez et al. 2016).

The catalytic effect of TiO_2 was recently investigated in the solar-photodegradation of an aqueous mixture of TBA, diuron, o-phenylphenol and 2-methyl-4-chlorophenoxyacetic acid (5 mg L^{-1} each). The irradiation intensity of a 250 mL reactor was provided by a solar simulator and maintained at 550 W m^{-2} for 2 h. Boron-doped TiO_2 catalysts were found to be more effective than bare TiO_2, achieving 50% degradation compared to 35% obtained using TiO_2, which demonstrates stability for three consecutive runs. The adsorption capacity increased in the doped catalysts, and is probably due to their higher surface areas. The combination of ozonation and photocatalysis, obtained by a mixture of ozone–oxygen (5 mg L^{-1} ozone concentration), fed to the reactor at a flow rate of 10 L h^{-1}, led to 100% removal of the pesticides within 90 min, with 75% mineralization after 2 h (Quinones et al. 2015). The formation of H_2O_2 and its behaviour as an electron acceptor on the TiO_2 surface was experimentally confirmed, as O_3 is confirmed to be photolysed, giving rise to many other reactive oxygen species, which enhance the mineralization rate (Sanchez et al. 2003).

Biodegradation

The microbial potential to degrade TBA can be evaluated by comparing the disappearance time of 50% of the compound (DT_{50}) in microbiologically active microcosms with others that have previously been sterilized. The DT_{50} value of 1.5 mg TBA/kg soil decreased from 82 to 22 days when sterile and active soils were used, respectively. DT_{50} of TBA in sterile

groundwater was found to be 224 days, while this decreased to 151 days when active

groundwater (TBA: 0.1 mg L^{-1}) was used as a media. The degradation patterns were

confirmed to fit first-order kinetics (Caracciolo et al. 2013).

Biopurification systems can be used to reduce the contamination of soil and water sources;

these systems are based on biomixtures, with a composition depending on the local

availability of agro-industrial wastes. The effect of increasing microbial activity, due to

agricultural compost amendment, on TBA removal from soil was recently confirmed

(Kravvariti et al. 2010). Furthermore, the toxicity of herbicides to microorganisms can be

reduced via the adsorption capacity of natural substrates, especially in the early stages; the

removal rate of 65 mg kg^{-1} of TBA in pure soil was found to increase from 26% to 72%,

when cork was added as a substrate. Cork was also used as a substrate for the inoculum of the

white-rot fungus *Lentinula edodes,* obtaining up to 89.9% of TBA degradation after 4

months. The main metabolic pathway of the herbicide in biomixtures inoculated with *L.*

edodes proceeds mainly via hydroxylation, towards production of 2-OH-TBA, while DET

was observed to be the main metabolite in liquid cultures (Pinto et al. 2016). Degradation

does not always lead to detoxification; the metabolic pathways in biomixtures of soil, straw

and compost resulted in the formation of, completely degraded, DET, whereas a biomixture

of soil, straw and peat promoted the hydroxylation of TBA. Lower amounts of metabolites

were found to be accumulated in biomixtures compared to soil, and an acidic pH could

promote high formation of OH-TBA (Karanasios et al. 2013).

The potential of biomass to degrade xenobiotics was also tested in a laboratory bioreactor on

an aqueous solution of TBA, acetochlor, chlorpyrifos, and metalaxyl. The filtration column

(biofilter) was a mixture of 35% soil and 65% compost. After 35-40 days, the percentage of

TBA remaining was the highest between the pesticides analysed, greater than 26%. No

significant influence of the environmental temperature was observed, but practical issues

encountered when replacing the biomass need to be solved to promote the applicability of such systems (Suciu et al. 2013).

Wetlands and phytoremediation

Contaminants from agricultural drainage reach surface water bodies through shallow subsurface flow. Vegetation filter zones (i.e.: buffer strips) can considerably improve the stream water quality, through remediation of the contaminated runoff of agricultural catchments (Lowrance et al. 1984, Peterjohn and Correll 1984). Subsurface water entering and exiting a buffer composed of a 5 m wide grass strip and 1 m width of woodland was monitored. The vegetation filter zone was interposed between agricultural fields and a stream. The average abatement of TBA through the buffer was 81%. The concentration of the herbicide in the water table first decreased and then peaked after two months. The low solubility of TBA, as well its high K_{oc}, resulted in retention maintained of most of the chemical in the soil surface layer until frequent rainfall occurred, after which the TBA concentration reached 14.6 μg L^{-1} in the field groundwater (Borin et al. 2004).

Wetlands can collect and retain many phytosanitary products, improving the sustainability of agricultural production (Pappalardo et al. 2016). Sedimentation, photolysis, hydrolysis and other degradation processes are strictly connected with the hydrochemistry and changes of runoff regime (Maillard et al. 2011). TBA concentrations were monitored to evaluate the efficiency of a 0.32 ha constructed surface flow wetland (CSFW), located at the outlet of a 6 ha agricultural basin. The wetland was flooded with 33 m^3 of water containing TBA (2.3 mg L^{-1}) and S-metolachlor (3.8 mg L$^{-1)}$) and with pure water after 21 days, and agin after 65 days. After the first initial flood, the reduction in TBA was more than 97%; likely due to reversible adsorption on plants, plant residues and soils; indeed, the second and third floods partially mobilized the herbicide. However, no hebicides by-passed the wetland and entered

the surface water outside the basin (Pappalardo et al. 2016). Complete TBA runoff mitigation was also demonstrated by samples collected from the inlet, the sediment deposition zone and the outlet of a 319 m^2 stormwater wetland, collecting the runoff of a vineyard catchment. The wetland consisted of a sediment deposition pond, collecting the suspended solids, and a gravel filter (saturated hydraulic conductivity: 10^{-3} m s^{-1}), which increased the hydraulic retention time. Results indicated 100% of TBA removal during the months of pesticide application, with no significant transfer of the herbicide from the water column to the bed sediments (Maillard et al. 2011). Biofilms, sediment, root complexes and electron donors, provided by roots and organic matter, likely contributed to the degradation of the herbicide via reductive dechlorination (Braeckevelt et al. 2007, Matamoros et al. 2007).

Phytoremediation can play an important role in pollutant abatement operated through constructed wetlands or buffer strips. This technique takes advantage of the ability of some plants to remove and/or metabolize pollutants. A plant-based biotest (RHIZOtest), conducted as described by Chaignon and Hinsinger (2003) and Bravin et al. (2010) (Chaignon and Hinsinger 2003, Bravin et al. 2010), was performed using *Lolium multiflorum* and TBA at aqueous concentrations of 0.5, 1.0 and 2.0 mg L^{-1}. The plant was able to remove 38%, 42% and 33% of the initial concentrations, respectively, in 240 h; over this period the capacity of plants to absorb the herbicide at 0.5 mg L^{-1} increased from 1.58 to 3.50 μg g^{-1} of fresh weight. Glutathione S-transferase activities increased in response to all treatments (Mimmo et al. 2015). This enzyme is involved in the response to the overproduction of reactive oxygen species (i.e. superoxide radicals [O^{-2}], hydroxyl radical [OH^-] and H_2O_2) caused by these herbicides (Del Buono et al. 2011, Skipsey et al. 2011).

Conclusions

Terbuthylazine (TBA) and its metabolite desethylterbuthylazine (DET) are two of the most frequently detected pesticides in surface waters, groundwaters and marine environments. The evidence discussed in this review summarises the current knowledge on the environmental fate, transfer and degradation of TBA and its metabolite DET. TBA is more persistent than atrazine in soil, however similar leaching potential has often been demonstrated (Stipicevic et al. 2015). Prolonged soil contamination is associated with the release of DET, and the related high risk of groundwater contamination (Scherr et al. 2017). Further studies are encouraged to evaluate the ecotoxicological risk of TBA and to estimate the risk posed to humans, due to its bioaccumulation potential (Palma et al. 2015), as well as the impact on human health, due to the intake of pesticide metabolites absorbed by crops, one of the most difficult aspects to account for in the impact assessment methods of agricultural systems (Tasca et al. 2017).

It appears critical to select herbicides with physical and chemical properties suitable to reduce losses due to high rainfall events after ground application, as well as the integration of specific soil management strategies. Real field data are needed to assess the risk of contamination of surface and ground-waters. The use of biosorbents, such as cork residues, in biomixtures enhances the biodegradation of herbicides and their metabolites (Pinto et al. 2016). Better knowledge on the interactions and aggregation of biochar and soil materials will facilitate the development of bioremediative materials to increase sorption and decrease dissipation of pesticides in soils (Trigo et al. 2014). *Phragmites australis and Lolium multiflorum* have shown potential in the decontamination of TBA (Mimmo et al. 2015), while constructed wetlands can protect downstream surface waters from contaminated agricultural runoff (Borin et al. 2004, Maillard et al. 2012, Pappalardo et al. 2016).

Techniques conventionally adopted in drinking water production do not lead to the complete removal of this herbicide and its metabolite, DET. Hydrogen peroxide alone is ineffective (Sorlini et al. 2014), chlorination is able to remove no more than 30% of TBA, while activated carbon provides higher efficiencies, up to 80% if combined with ozonation (Ormad et al. 2008). UV/H_2O_2 advanced oxidation and photocatalysis are the most promising techniques, with TBA removal above 90% (Le Cunff et al. 2015, Alvarez et al. 2016, Yang et al. 2016). The largest contribution to degradation efficiency during UV/H_2O_2 treatments is due to direct photolysis (Sorlini et al. 2014), while the large majority of photocatalytic degradation efficiency has been attributed to hydroxyl radicals (Yang et al. 2016). Almost complete TBA removal has been reached in ~30 min using TiO_2 solar-photocatalytic ozonation.

The range of emerging contaminants detected in drinking waters, and their seasonal and geographic variability, demands more accurate screening programs and greater attention has to be focused on the fate of herbicide metabolites (Tasca and Fletcher 2017). A cost-analysis of the treatments, together with careful evaluation of the toxicity of intermediates, would provide water quality managers with the information required to increase the quality of water supplies and mitigate for herbicidal contaminants.

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