Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Fate of benzotriazole and 5-methylbenzotriazole in recycled water recharged into an anaerobic aquifer: Column studies

M.D. Alotaibi [a,b,c], B.M. Patterson [a,b,*], A.J. McKinley [a], A.Y. Reeder [d], A.J. Furness [b], M.J. Donn [b]

[a] School of Chemistry and Biochemistry, University of Western Australia, Crawley, Australia
[b] CSIRO Land and Water Flagship, Private Bag 5, Wembley, 6913, WA, Australia
[c] Department of Plant Protection, College of Food and Agricultural Sciences, King Saud University, Riyadh, Saudi Arabia
[d] Centre for Microscopy, Characterization and Analysis, University of Western Australia, Crawley, Australia

ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form
16 October 2014
Accepted 24 November 2014
Available online 4 December 2014

Keywords:
Benzotriazole
5-Methylbenzotriazole
Degradation
Recycled water
MAR

ABSTRACT

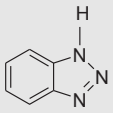
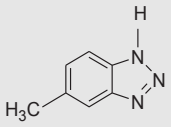
The fate of benzotriazole (BTri) and 5-methylbenzotriazole (5-MeBT) was investigated under anaerobic conditions at nano gram per litre concentrations in large-scale laboratory columns to mimic a managed aquifer recharge replenishment strategy in Western Australia. Investigations of BTri and 5-MeBT sorption behaviour demonstrated mobility of the compounds with retardation coefficients of 2.0 and 2.2, respectively. Degradation processes over a period of 220 days indicated first order biodegradation of the BTri and 5-MeBT under anaerobic aquifer conditions after a biological lag-time of approximately 30 −60 days. Biodegradation half-lives of 29 ± 2 and 26 ± 1 days for BTri and 5-MeBT were respectively observed, with no threshold effect to biodegradation observed at the 200 ng L^{-1}. The detection of degradation products provided further evidence of BTri and 5-MeBT biodegradation. These results suggested that if BTri and 5-MeBT were present in recycled water recharged to the Leederville aquifer, biodegradation during aquifer passage is likely given sufficient aquifer residence times or travel distances between recycled water injection and groundwater extraction.

1. Introduction

Managed aquifer recharge (MAR) using recycled water is becoming more attractive water management option due to the high demand for drinking quality water, combined with increasing volumes of wastewater produced as the consequences of population growth. However, using recycled water sourced from wastewater may pose a risk for MAR due to potential trace organic compounds contaminating aquifers. If trace organic compounds are not removed from recycled water prior to recharge into the aquifer, contamination of the aquifer may occur and subsequently be present in the groundwater extracted for drinking water purposes.

* *Corresponding author*. CSIRO Land and Water Flagship, Private Bag 5, Wembley, 6913, WA, Australia. Tel.: +61 8 9333 6276; fax: +61 8 9333 6211.
E-mail address: Bradley.Patterson@csiro.au (B.M. Patterson).
http://dx.doi.org/10.1016/j.watres.2014.11.040

Table 1 – Chemical structure and relevant properties of BTri and 5-MeBT.

Common name	Benzotriazole (BTri), 1H-Benzotriazole	5-Methylbenzotriazole (5-MeBT), 5-tolyitriazole (5-Trri)	References
Chemical structure			
CAS No.	95_14_7	136_85_6	
log K_{ow}	1.23	1.89	(Hart et al., 2004)
log K_{oc}	1.02	1.68	(Hart et al., 2004)
Melting point (°C)	98–99 °C	76–87 °C	(Castro et al., 2005)
pK_a (conjugated acid)	8.2	8.5	(Hart et al., 2004)
Vapour pressure (°C)	0.04 mmHg	0.03 mmHg	(Castro et al., 2005)
Solubility in water	28 g L^{-1}	7 g L^{-1}	(Giger et al., 2006)
Solubility in methanol	1.33 g L^{-1}	1.16 g L^{-1}	(Castro et al., 2005)
Refractive index	1.73	1.68	(Malhas et al., 2007)
Henry's low coefficient (at 25 °C)	3.17 × 10^{-7} m^3/mol	3.14 × 10^{-7} m^3/mol	(Castro et al., 2005)

While advanced wastewater treatment such as reverse osmosis removes many of the larger hydrophobic compounds from recycled water, a number of contaminant molecules that are small, polar and uncharged are poorly removed (Steinle-Darling et al., 2007).

Benzotriazoles (BTs) which include benzotriazole (BTri) and 5-methylbenzotriazole (5-MeBT) are one group of compounds that have been detected in municipal wastewater and are not completely removed during wastewater treatment. BTs are classified as high volume production chemicals, with an estimated worldwide production in excess of 9000 tonnes/year (Hart et al., 2004; Weiss and Reemtsma, 2005). They are used as anticorrosive additives and can be found in dish-washing detergents. They are also used in antifreeze products, such as aircraft de-icing detergents (Castro et al., 2005; Giger et al., 2006; Janna et al., 2011; Liu et al., 2011b, 2012). The chemical properties of BTri and 5-MeBT are given in Table 1.

BTri and 5-MeBT have been identified in Australian wastewaters at concentrations of 5.7 μg L^{-1} and 6.8 μg L^{-1} (Liu et al., 2012). Likewise, they have been detected in wastewater collected from Denmark and Spain, with concentrations ranging from 0.2 to 2.2 μg L^{-1} (BTri) and 0.06 to 36.2 μg L^{-1} (5-MeBT) (Matamoros et al., 2010). Studies conducted across Western Europe found BTri in the effluents of wastewater treatment plants at concentrations up to 2.9 μg L^{-1} (Weiss et al., 2006). The removal efficiency from conventional wastewater treatment plants was found to be 20%–70% for BTri and 30%–55% for 5-MeBT (Reemtsma et al., 2010). Even with the use of advanced treatment such as ultra-filtration and reverse osmosis, removal of BTs from secondary treated wastewater was only 70% (Loi et al., 2013).

Evidence of BTri and 5-MeBT toxicity to terrestrial mammals such as rats has been demonstrated by several researchers (Hem et al., 2000; Sills et al., 1999; Weiss et al., 2006). A drinking water guideline value of 7 ng L^{-1} for 5-MeBT has been suggested by the Australian Guidelines for Water Recycling (AGWR) for drinking water supplies (NRMMC, 2008). While a health guideline of 20 μg L^{-1} for BTri has been suggested by the Department of Health in Western Australia and the Water Corporation of Western Australia (Loi et al., 2013).

Due to their occurrence in treated wastewater and their toxicity, the fate of BTs in aquifers used for MAR requires investigation. Natural attenuation of trace organic compounds during aquifer passage or storage as part of MAR has the potential to improve water quality (Dillon, 2005; Patterson et al., 2011). However, these improvements are generally compound and site specific.

Biodegradation of BTri and 5-MeBT have been previously investigated in microcosm experiments (Jia et al., 2006; Liu et al., 2011a; 2013), bioreactor experiments (Gruden et al., 2001; Hollingsworth et al., 2005; Weiss et al., 2006) and at field sites (Breedveld et al., 2003). The majority of the investigations were focused on assessing biodegradation within wastewater treatment systems. While some authors did observe biodegradation, others did not. Only a select number of investigations have focused on biodegradation of BTri and 5-MeBT in aquifers.

Typically, aquifers are less biologically active than wastewater treatment systems with more limited biologically-available carbon. Liu et al. (2013) conducted an aquifer-based investigation, observing biodegradation in microcosms using aquifer sediments and groundwater spiked with BTri and 5-MeBT to give a contaminant concentration of 1000 μg L^{-1}. Liu et al. (2013) found that BTri and 5-MeBT were degraded 65% and 61%, respectively. Breedveld et al. (2003) investigated groundwater contamination from de-icing fluids at an abandoned airport. They found BTri in groundwater two years after de-icing activities ceased at concentrations between 4.2 and 52 μg L^{-1} from an initial concentration of 1100 μg L^{-1}. The authors concluded that the reduction was due to dilution and no degradation of BTri had occurred. The persistence of low concentrations of BTri in the aquifer environment may be due to site specific or concentration effects. Threshold concentration effects could potentially explain why BTri persisted at low concentrations in the field, while biodegradation was observed in microcosm experiments at higher concentrations (Spain and Van Veld, 1983).