WATER RESEARCH 45 (2011) 2550–2560

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Fate of N-nitrosomorpholine in an anaerobic aquifer used for managed aquifer recharge: A column study

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ARTICLE INFO

Article history:
Received 3 December 2010
Received in revised form
4 February 2011
Accepted 12 February 2011
Available online 19 February 2011

Keywords:
N-Nitrosomorpholine
Degradation
Recycled water
N-Nitrosamines
MAR

ABSTRACT

The fate of *N*-nitrosomorpholine (NMOR) was evaluated at microgram and nanogram per litre concentrations. Experiments were undertaken to simulate the passage of groundwater contaminants through a deep anaerobic pyritic aquifer system, as part of a managed aquifer recharge (MAR) strategy. Sorption studies demonstrated the high mobility of NMOR in the Leederville aquifer system, with retardation coefficients between 1.2 and 1.6. Degradation studies from a 351 day column experiment and a 506 day stop-flow column experiment showed an anaerobic biologically induced reductive degradation process which followed first order kinetics. A biological lag-time of less than 3 months and a transient accumulation of morpholine (MOR) were also noted during the degradation. Comparable half-life degradation rates of 40–45 days were observed over three orders of magnitude in concentration (200 ng L^{-1} to 650 μg L^{-1}). An inhibitory effect on microorganism responsible to the biodegradation of NMOR at 650 μg L^{-1} or a threshold effect at 200 ng L^{-1} was not observed during these experiments.

1. Introduction

The high demand for water of drinking quality and increasing wastewater flow, as the consequences of population growth, have resulted in investigations of Managed Aquifer Recharge (MAR) using recycled water. However, potential trace organic contaminants in recycled water, sourced from wastewater or produced during disinfection, present a risk to recycled water use for MAR. If these trace organics are not removed, they may contaminate the aquifer and subsequently be present in the groundwater extracted from the aquifer.

While reverse osmosis (RO) treatment removes many of the larger hydrophobic compounds from recycled water (Steinle-Darling et al., 2007), a number of disinfection by-products such as nitrosamines are poorly removed because these molecules are small, polar and uncharged (Mitch et al., 2003; Steinle-Darling et al., 2007). One of nitrosamines which has become a concern in recycled water is *N*-nitrosomorpholine (NMOR). NMOR contamination of recycled water is of concern due to health risks if the water is to be used for drinking. NMOR has been classified as a possible human carcinogen (IARC, 1987) and a drinking water guideline value of 10 ng L^{-1} has been recommended in Germany (Planas et al., 2008). Chemical and physical properties of NMOR are given in Table 1. NMOR has been detected in the human environment notably in association with the rubber industry (de Vocht et al., 2007; Fajen et al., 1979; Spiegelhalder and Preussmann, 1983). It has also been found in wastewater effluent (Krauss and Hollender, 2008; Krauss et al., 2009; Planas et al., 2008; Schreiber and Mitch, 2006b) with concentrations up to 12.7 μg L^{-1} (Krasner et al., 2009). Moreover, NMOR has been reported as one of the most abundant nitrosamines in primary

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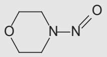
doi:10.1016/j.watres.2011.02.018

Table 1 – Properties of NMOR.

Chemical structure	
Molecular formula	$C_4H_8N_2O_2$
CAS number	59-89-2
Molecular weight	116.12
Colour/form	Yellow crystal
Boiling point	139–140 °C at 25 mmHg
Melting point	29 °C
Octanol/water partition coefficient	Log $K_{ow} = -0.44$
Density (specific gravity)	0.791 g cm^{-3}
Henry's law constant	2.45×10^{-8} atm m^3 mol^{-1} at 37 °C
Solubility	Miscible in water in all prop; soluble in organic solvent

All properties are taken from Hazardous Substance Data Bank (HSDB, 2003).

and secondary wastewater effluent (Krauss and Hollender, 2008; Krauss et al., 2009).

NMOR can be formed during disinfection, particularly chloramination (Schreiber and Mitch, 2006a), and ozonation followed by chlorination (Zhao et al., 2008). However, the formation of NMOR during disinfection was usually lower compare to *N*-nitrosodimethylamine (NDMA), another nitrosamine which was detected frequently in disinfected wastewater (Krasner et al., 2009). Moreover, NMOR is less degradable in sewage treatment plants when compared to other nitrosamines such as NDMA, *N*-nitrosodiethylamine, *N*-nitroso-di-*n*-butylamine, and *N*-nitrosopiperidine (Hollender et al., 2009; Krauss et al., 2009). Activated sludge and sand filtration treatments have been reported to reduce NMOR concentrations in wastewater. However these methods are only partially effective. From 21 wastewater treatment plants in Switzerland, the average percent removal of NMOR by activated sludge treatment was 65% and by sand filtration was only 34% (Krauss et al., 2009).

The fate of NMOR at microgram per litre concentrations in aquifer have been previously assessed under anaerobic and aerobic conditions via column studies. These studies have shown limited degradation with degradation half-lives of >100 days compared to a sterile control under anaerobic condition (Patterson et al., 2010) and >50 days under aerobic condition (Patterson et al., 2011). Moreover, sorption studies of NMOR showed a low retardation coefficient of 1.0 for an aerobic soil with low organic carbon content of 0.02% (w/w) (Patterson et al., 2011) and 1.2 for an anaerobic soil with a higher organic carbon content of 0.32% (w/w) (Patterson et al., 2010). Low retardation coefficients suggest that NMOR is highly mobile in the different aquifer systems.

In this paper we report further experiments designed to mimic the injection of recycled water containing NMOR into an aquifer under anaerobic conditions. These experiments examine: (i) the degradation of NMOR in an aquifer at ng L^{-1} concentrations that are more typical of recycled water; (ii) the concentration effects on degradation rates and determine if higher concentrations (μg L^{-1} concentrations) provide comparable fate data; and (iii) changes in degradation rates during longer-term experiments and relate these data to degradation lag-times and bacterial acclimation.

2. Materials and methods

2.1. Chemicals

NMOR, morpholine (MOR) and sodium azide were sourced from Sigma–Aldrich (Sydney, Australia). d_8-NMOR was sourced from CDN isotopes (Honsby, Australia) and sodium bromide was sourced from Hayashi Pure Chemical Ind. Ltd. (Osaka, Japan).

2.2. Aquifer sediment

Anaerobic Leederville aquifer sediment used in the column experiments was collected from a trial MAR site in Perth, Western Australia. The sediment was collected via rotary auger and coring from the confined Leederville aquifer on the Swan Coastal Plain of Western Australia over the proposed MAR injection depth interval (between 120 m and 220 m below ground level). The sediment in this zone consisted of discontinuous interbedded sands, silts and clays (Playford et al., 1976). To prevent sediment oxidation, collected sediment was immediately stored in either sealed air-tight 4 L tins flushed with nitrogen or sealed air-tight 10 L buckets saturated with anaerobic groundwater and kept at 4 °C. The sediment mineralogy, based on X-ray defraction (XRD), was predominantly quartz (72%), and K-feldspar (24%), with minor quantities of pyrite (2%) and Na-feldspar (2%). All other minerals were below analytical detection (<1%) (Patterson et al., 2010). The sediment organic matter (SOM) content was 0.32% w/w and the chromium reducible sulphur (S_{Cr}) content of 0.71% w/w, which is consistent with the XRD pyrite content (Patterson et al., 2010). Particle size distribution of the sediment was >1 mm (10%); 1 mm to 500 μm (20%); 500–250 μm (50%); 250–125 μm (17%) and <125 μm (3%).

2.3. Column influent water

Column influent water was collected from the Beenyup microfiltration/RO pilot plant, located at the Beenyup Wastewater Treatment Plant, Perth Western Australia. A chemical analysis of the influent water is given in Table 2.

Table 2 – Chemical analysis of influent water.

Chloride	3.0 mg L^{-1}
Sulphate	0.38 mg L^{-1}
Nitrate-N	<1 mg L^{-1}
Sodium	5.0 mg L^{-1}
Potassium	0.55 mg L^{-1}
Magnesium	0.18 mg L^{-1}
Calcium	1.6 mg L^{-1}
Conductivity	34 μS cm^{-1}
Dissolved oxygen	8.5 mg L^{-1}
Dissolved organic carbon (DOC)	<1 mg L^{-1}