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Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer

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ABSTRACT

The fate of nine trace organic compounds was evaluated during a 12 month large-scale laboratory column experiment. The columns were packed with aquifer sediment and evaluated under natural aerobic and artificial anaerobic geochemical conditions, to assess the potential for natural attenuation of these compounds during aquifer passage associated with managed aquifer recharge (MAR). The nine trace organic compounds were bisphenol A (BPA), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), *N*-nitrosodimethylamine (NDMA), *N*-nitrosomorpholine (NMOR), carbamazepine, oxazepam, iohexol and iodipamide. In the low organic carbon content Spearwood sediment, all trace organics were non-retarded with retardation coefficients between 1.0 and 1.2, indicating that these compounds would travel at near groundwater velocities within the aquifer. The natural aerobic geochemical conditions provided a suitable environment for the rapid degradation for BPA, E2, iohexol (half life < 1 day). Lag-times for the start of degradation of these compounds ranged from <15 to 30 days. While iodipamide was persistent under aerobic conditions, artificial reductive geochemical conditions promoted via the addition of ethanol, resulted in rapid degradation (half life < 1 days). Pharmaceuticals (carbamazepine and oxazepam) and disinfection by-products (NDMA and NMOR) did not degrade under either aerobic or anaerobic aquifer geochemical conditions (half life > 50 days). Field-based validation experiments with carbamazepine and oxazepam also showed no degradation. If persistent trace organics are present in recycled waters at concentrations in excess of their intended use, natural attenuation during aquifer passage alone may not result in extracted water meeting regulatory requirements. Additional pre treatment of the recycled water would therefore be required.

1. Introduction

One of the major health concerns associated with the use of recycled water is the potential presence of low concentrations of a range of trace organics (Díaz-Cruz and Barceló, 2008). These trace organics include endocrine-disrupting compounds, hormones, pharmaceuticals, pesticides and disinfection by-products. Recycled water can be used in many different ways but one mechanism gaining favour in many countries is recharging the recycled water to aquifers using Managed Aquifer Recharge (MAR) (Dillon et al., 2006). When recycled water is used for MAR, it may undergo biogeochemical changes during aquifer storage or aquifer passage resulting in the natural attenuation of some trace organics. MAR has been shown to reduce nutrient concentrations and microbial pathogen numbers in recharged water

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(Dillon et al., 2006; Toze and Hanna, 2002) but less is known about the potential removal of trace organics during recharge and storage. As the fate of trace organics are determined by aquifer biological and geochemical conditions (Barber et al., 2009; Carrara et al., 2008), fate assessment results from one aquifer system may not apply to other systems. To assess the transferability of results between different aquifer systems, fate assessment comparative data is required for different aquifer systems where MAR using recycled water is planned.

Knowledge of the fate of trace organic compounds in aquifers is essential to the assessment and design of proposed MAR recycled water treatment strategies. This fate data can be used to provide design criteria for (i) injection/extraction borehole spacing or extraction rate to ensure sufficient aquifer residence time for degrading compounds to be naturally attenuated so that the extraction water meets regulatory requirements, and (ii) identify if additional pre or post MAR treatment options such as reverse osmosis, advanced oxidation or UV radiation are required for persistent trace organic compounds, where sufficient natural attenuation is unlikely to be achieved during aquifer passage and where significant human exposure to the recovered water is considered likely.

This paper describes the findings of a 12 month large-scale column experiment investigating the fate of nine trace organics under natural aerobic aquifer geochemical conditions and under artificial anaerobic reducing conditions via ethanol addition. The fate of each trace organic was assessed based on their chemical retardation coefficient (*R*) and degradation rate, determined from the experimental data.

2. Materials and methods

Nine trace organics were investigated. Bisphenol A (BPA), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), carbamazepine (CARB), *N*-nitrosomorpholine (NMOR) and iohexol (IOX) were all obtained from Sigma-Aldrich (Sydney, Australia). *N*-nitrosodimethylamine (NDMA) was obtained from Chem Service (Perth, Australia), iodipamide (IDP) was obtained from Fluka (Sydney, Australia) and oxazepam (OXAZ) was obtained from the Chemistry Centre of Western Australia. These trace organics were selected, as all except for IDP have been detected in effluent water from local wastewater treatment plants (PCRP, 2009).

2.1. Aquifer material

The sediment used in the column experiment was a calcareous medium grained Spearwood sand low in organic carbon and iron content (see Table 1), collected from the superficial Tamala aquifer, on the Swan Coastal Plain of Western Australia. The Spearwood sediment was collected from approximately 1 to 5 m below the water table (11 to 15 m below the ground surface) by installing a 80 mm temporary bore casing and using a 65 mm bailer to collect saturated sediment. The bailer, containing the sediment and groundwater, was repeatedly filled then opened inside the columns, displacing excess groundwater and gradually filling the columns on-site. Sediment porosities were determined using bromide tracer tests conducted during the column experiment (Stephens et al., 1998). Hydraulic conductivity (*K*) was determined based on the Darcy equation and the observed hydraulic head drop along the column. Other sediment properties were determined on a sediment sub-sample. Mineralogy of the sediment was determined by X-ray diffraction analysis (XRD) using a PANalytical X'Pert Pro Multi-purpose diffractometer and quantified using the commercial package SIROQUANT from Sietronics Pty Ltd. The results were normalised to 100%, and hence did not include estimates of unidentified or amorphous materials.

Table 1
Column sediment properties determined on a sediment sub-sample, and influent water chemistry. See text for methods used to determine column porosity and hydraulic conductivity.

Sediment		Influent water[a]	
Sediment Organic Matter (SOM)	0.02% w/w	pH	7.9
Iron content	0.13% w/w	Na	230 mg L^{-1}
Porosity	0.46	K	26 mg L^{-1}
Hydraulic conductivity	18 m d^{-1}	Mg	10 mg L^{-1}
Bulk density	1660 kg m^{-3}	Ca	27 mg L^{-1}
		Cl	180 mg L^{-1}
Mineralogy		HCO_3	180 mg L^{-1}
Quartz	75%	SO_4^-S	18 mg L^{-1}
Calcite	12%	NO_3^-N	30 mg L^{-1}
Microcline/orthoclase	11%	Dissolved organic carbon	6.6 mg L^{-1}
Albite/anorthite	2%	Dissolved oxygen	7.8 mg L^{-1}

[a] Control column influent water also contained 0.65 g L^{-1} sodium azide.

2.2. Column setup

Two stainless steel columns were constructed, an experimental column and a sterilized control column. Each column was 2.0 m in height and 145 mm internal diameter (i.d.). To avoid sediment migrating into the influent and effluent tubing, a stainless steel grate with holes 10 mm in diameter and stainless steel mesh was fixed at the bottom and the top of each column. Nineteen sampling ports were strategically placed along each column allowing for water samples to be collected from the columns. Each water sampling port consisted of a 4 mm i.d. stainless steel tube that protruded 60 mm from the wall of the column into the centre of the column. The inner end of the tube contained a stainless steel mesh (1 mm diameter) to prevent sediment entering, while the outer end contained a silicon septum allowing a hypodermic syringe needle to be inserted for the collection of water samples. The columns were operated in a saturated up flow mode. The effluent tubing from each column was passed through a peristaltic pump (ISMATEC Reglo) to regulate column flow at approximately 360 mL d^{-1}, giving a linear velocity of approximately 4.7 cm day^{-1}, based on an average porosity of 0.46 estimated from the bromide tracer test for the 2 columns. This gave a water residence time within the columns of 42 days. This linear velocity is within the range of typical groundwater velocities on the Swan Coastal Plain (Benker et al., 1997).

A silicone polymer mat for the diffusive delivery of ethanol to promote reducing conditions within the columns (Patterson et al., 2002, 2004; Grassi et al., 2007) was installed in each column. The polymer mat was placed horizontally within the circumference of the column, and orthogonal to the water flow direction to provide low concentration ethanol delivery via