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Role of primary substrate composition and concentration on attenuation of trace organic chemicals in managed aquifer recharge systems

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ABSTRACT

This study was undertaken to investigate the role of primary substrate composition and concentration on the attenuation of biodegradable emerging trace organic chemicals (TOrCs) in simulated managed aquifer recharge (MAR) systems. Four sets of soil columns were established in the laboratory, each receiving synthetic feed solutions comprising different ratios and concentrations of peptone-yeast and humic acid as the primary substrate to investigate the effect on removal of six TOrCs (atenolol, caffeine, diclofenac, gemfibrozil, primidone, and trimethoprim). Based on abiotic control experiments, adsorption was not identified as a significant attenuation mechanism for primidone, gemfibrozil and diclofenac. Caffeine, atenolol and trimethoprim displayed initial adsorptive losses, however, adsorption coefficients derived from batch tests confirmed that adsorption was limited and in the long-term experiment, biodegradation was the dominant attenuation process. Within a travel time of 16 h, caffeine – an easily degradable compound exhibited removal exceeding 75% regardless of composition or concentration of the primary substrate. Primidone – a poorly degradable compound, showed no removal in any column regardless of the nature of the primary substrate. The composition and concentration of the primary substrate, however, had an effect on attenuation of moderately degradable TOrCs, such as atenolol, gemfibrozil and diclofenac, with the primary substrate composition seeming to have a larger impact on TOrC attenuation than its concentration. When the primary substrate consisted mainly of refractory substrate (humic acid), higher removal of the moderately degradable TOrCs was observed. The microbial communities in the columns receiving more refractory carbon, were noted to be more diverse and hence likely able to express a wider range of enzymes, which were more suitable for TOrC transformation. The effect of the primary substrate on microbial community composition, diversity and gene expression potential confirmed its influence on TOrC degradation.

1. Introduction

Reclaimed water is becoming an important source of alternate water supply, especially in regions where conventional freshwater resources are insufficient to meet growing water demands. Whether the reclaimed water is intended for direct or indirect potable reuse, it is necessary to select treatment processes capable of achieving drinking water quality goals, while being mindful of the overall carbon and energy footprint (National Research Council, 2012).

Riverbank filtration, soil aquifer treatment and artificial recharge and recovery, collectively referred to as managed aquifer recharge (MAR) systems, are soil-based natural treatment processes involving infiltration of water through vadose and saturated zones. Previous research has demonstrated that these systems are capable of attenuating total organic carbon and pathogens, as well as select trace organic chemicals (Maeng et al., 2010; Quanrud et al., 2003; Weiss et al., 2003), representing reliable natural water treatment systems with the advantage of little input of chemicals or residual generation and generally exhibiting a low energy and carbon footprint (Hoppe-Jones et al., 2010; Irmscher and Teermann,

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2002). These systems have been used in the US, Europe and other parts of the world to recharge groundwater using stormwater, impacted surface water and reclaimed water, with the aim of supplementing drinking water supplies (Drewes and Khan, 2011; Missimer et al., 2011; Ray et al., 2008).

Emerging trace organic chemicals (TOrCs), encompassing pharmaceuticals, personal care products, endocrine disrupting chemicals, household chemicals, and emerging disinfection by-products, are not completely removed by conventional wastewater treatment (Glassmeyer et al., 2005). Thus, many TOrCs have been detected in freshwater resources worldwide which are directly or indirectly impacted by wastewater discharge, combined sewer overflows or other non-point sources (Ashton et al., 2004; Focazio et al., 2008). Hence, the ability of treatment systems to attenuate TOrCs is important for water reuse schemes.

In order to utilize MAR systems effectively for the removal of TOrCs, a fundamental understanding of factors affecting TOrC attenuation is needed. Since TOrCs usually occur at ppt-levels in MAR systems, it is unlikely that these compounds provide the primary energy source for microbes present. We hypothesize that the primary substrate represented by the biodegradable portion of bulk organic carbon occurring in the mg/L range shapes the microbial community structure in MAR systems where TOrC degradation occurs. The role of the primary substrate in the attenuation of different TOrCs has been studied previously for riverbank filtration and aquifer recharge systems (Maeng et al., 2011; Nalinakumari et al., 2010; Onesios and Bouwer, 2012; Rauch-Williams et al., 2010), however, these findings were inconclusive as to the exact effect of the primary substrate on TOrC removal.

This study used controlled laboratory-scale column experiments to investigate the role of the primary substrate on TOrC attenuation. A group of six indicator TOrCs was selected to represent different degrees of biodegradability. Primary substrate solutions that differed in concentration and composition were fed to the columns along with TOrCs. In addition, the microbial communities established as a result of the different feed water compositions were characterized in a parallel study by phylogenetics and metagenomics (Li et al., 2014).

2. Materials and methods

2.1. Soil column setup

The laboratory-scale column set-ups consisted of four glass columns (length: 30 cm each, internal diameter: 5 cm) connected in series. Two column sets utilized GE Healthcare XK 50/30 glass columns (Sweden), while the other two utilized Spectrum Chromatography glass columns (Product 12403, Houston, TX). All columns were filled with native soil from Wadi Wajj – a wadi receiving urban run-off north of Taif, Saudi Arabia. Dry soil was collected from the wadi, sieved to retain the fraction between 0.2 mm and 2 mm (Retsch sieves) and rinsed with deionized water. Soil was transferred into the columns in a soil – water suspension to minimize introduction of air bubbles. The columns were operated fully saturated in up-flow mode with the hydraulic retention time for each column determined to be 4 h using potassium bromide (KBr) as a conservative tracer, providing a total hydraulic residence time of around 16 h for the series of four columns.

Grain size analysis of the native soil revealed that it was mainly sand (94.8%), with small fractions of gravel, silt, and clay. The soil was characterized as having low total organic carbon content (f_{oc} of 0.10 ± 0.01%). Hydraulic conductivity and porosity of the native wadi soil were determined separately under similar packing conditions to the columns, to be 41.2 m/day and 0.32, respectively as described in Rosas et al. (2013).

The feed solution to the soil columns consisted of synthetic wastewater comprising different ratios of the following organic carbon sources: peptone (BD Bacto™ Peptone; Becton, Dickenson & Co.), yeast (BD Bacto™ Yeast Extract; Becton, Dickenson & Co.) and humic substances (humic acid sodium salt; Sigma Aldrich). Peptone and yeast (mixed in a ratio of 2:1 and referred to hereafter as peptone-yeast) mimic the easily degradable organic matter (Zimbro et al., 2009) present in treated wastewater effluents, while the humic substances represent the more refractory carbon fraction (Filip and Tesarova, 2004). The composition of the primary substrate was varied by providing four different ratios of peptone-yeast and humic acid to the columns (Table 1). The synthetic wastewater also contained the following mix of salts at concentrations ranging between 3.5 mg/L and 50 mg/L, representing levels found in a typical secondary treated effluent: $CaCl_2 \cdot 2H_2O$, NaCl, $MgSO_4$, KNO_3, K_2HPO_4, and $ZnSO_4 \cdot 7H_2O$. In addition, small quantities (1 mg/L or less) of the following micronutrients were added: KH_2PO_4, $FeCl_3$, $MnCl_2 \cdot 4H_2O$, H_3BO_3, $Na_2MoO_4 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$ and KI, as described in Dantas et al. (2008).

Primary substrate feed stock solutions were prepared weekly at a 10× concentration and stored at 4 °C to minimize degradation in the feed container. The columns were also fed with a mix of selected TOrCs at environmentally relevant concentrations of 300–500 ng/L each. To achieve this target concentration, a stock solution of 50 mg/L TOrC mixture in methanol was used to prepare a 1 mg/L aqueous stock of TOrCs which was further diluted into separate feed tanks (kept at room temperature) containing the mixture of salts.

The primary substrate feed solution was delivered using an IPC 8-channel Ismatec pump (ISM 936, IDES Health & Science, Wertheim, Germany). A second IPC 8-channel Ismatec pump drew the salt buffer solution containing the TOrCs. Tubes from the two pumps were joined using a 3-way connector to achieve in-line mixing of the dissolved organic carbon (DOC) feed solution and salt buffer plus TOrC mixture, as illustrated in Fig. 1. The flow rates were controlled to provide a 10× in-line dilution of the DOC solution prior to delivery to the columns, achieving a loading rate of 1.44 m/d. Influent samples to the columns were collected from a

Table 1
Properties of feed composition to the columns.

	Label	100:0 peptone/humic acid	60:40 peptone/humic acid	40:60 peptone/humic acid	0:100 peptone/humic acid
	Peptone-yeast content	100%	60%	40%	0%
	Humic Acid Content	0%	40%	60%	100%
Period 1	Influent DOC	1.21 ± 0.42	1.80 ± 0.36	1.54 ± 0.68	3.91 ± 0.81
	Effluent DOC	0.66 ± 0.39	0.64 ± 0.12	0.92 ± 0.18	3.15 ± 0.53
	Degraded DOC (BDOC)	0.55 ± 0.15	1.16 ± 0.37	0.69 ± 0.60	0.67 ± 0.16
Period 2	Influent DOC	2.81 ± 0.68	2.56 ± 0.69	3.06 ± 0.73	3.49 ± 0.68
	Effluent DOC	1.14 ± 0.43	1.20 ± 0.43	2.06 ± 0.78	2.05 ± 0.61
	Degraded DOC (BDOC)	1.67 ± 0.44	1.54 ± 0.64	1.56 ± 0.52	1.53 ± 0.44
	Influent NO_3^-–N	0.77 ± 0.07	0.88 ± 0.05	0.95 ± 0.04	1.09 ± 0.14
	Effluent NO_3^-–N	ND	1.32 ± 0.80	1.09 ± 0.37	0.96 ± 0.19
	Redox condition	Oxic-anoxic	Oxic	Oxic	Oxic