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Biotransformation of trace organic chemicals during groundwater recharge: How useful are first-order rate constants?

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ABSTRACT

This study developed relationships between the attenuation of emerging trace organic chemicals (TOrC) during managed aquifer recharge (MAR) as a function of retention time, system characteristics, and operating conditions using controlled laboratory-scale soil column experiments simulating MAR. The results revealed that MAR performance in terms of TOrC attenuation is primarily determined by key environmental parameters (i.e., redox, primary substrate). Soil columns with suboxic and anoxic conditions performed poorly (i.e., less than 30% attenuation of moderately degradable TOrC) in comparison to oxic conditions (on average between 70–100% attenuation for the same compounds) within a residence time of three days. Given this dependency on redox conditions, it was investigated if key parameter-dependent rate constants are more suitable for contaminant transport modeling to properly capture the dynamic TOrC attenuation under field-scale conditions. Laboratory-derived first-order removal kinetics were determined for 19 TOrC under three different redox conditions and rate constants were applied to MAR field data. Our findings suggest that simplified first-order rate constants will most likely not provide any meaningful results if the target compounds exhibit redox dependent biotransformation behavior or if the intention is to exactly capture the decline in concentration over time and distance at field-scale MAR. However, if the intention is to calculate the percent removal after an extended time period and subsurface travel distance, simplified first-order rate constants seem to be sufficient to provide a first estimate on TOrC attenuation during MAR.

1. Introduction

The increasing demand for drinking water supplies in recent years has resulted in steadily growing interest in using impaired water sources (i.e., recycled water, stormwater) for augmentation of potable aquifers via managed aquifer recharge (MAR). MAR systems, such as riverbank filtration and soil aquifer treatment, are natural water treatment processes with the goal to enhance groundwater quantity and quality by taking advantage of hydro-geochemical and biological processes. Since impaired water sources often contain a broad range of inorganic and organic contaminants, knowledge about their fate and transport during subsurface treatment in an aquifer leading to drinking water augmentation is essential for proper design and operation of MAR facilities. Attenuation of organic contaminants such as trace organic chemicals (TOrC) is mainly caused by microbial transformation, while sorption to soil components retards their transport. Modeling fate and transport of TOrC typically requires detailed numerical groundwater flow and multi-component reactive transport

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models (Greskowiak et al., 2006; Prommer and Stuyfzand, 2005; Sharma et al., 2012). However, studies that aim to quantify the attenuation of numerous TOrC characterized by different physicochemical properties often omit a detailed analysis of factors influencing contaminant transport behavior (Henzler et al., 2014). First-order rate constants and linear soil water distribution coefficients provide only a partial description of biodegradation and sorption processes since they neglect the temporal and spatial variabilities of key environmental parameters. Since the degree of TOrC biotransformation during MAR is determined by the composition of the source water (i.e., availability and make-up of organic carbon serving as primary substrate for microbial metabolism), predominant redox conditions, temperature, and residence time in the subsurface (Laws et al., 2011; Li et al., 2013; Massmann et al., 2006; Rauch-Williams et al., 2010), changes of these key environmental parameters may enhance, decelerate, and sometimes initiate biotransformation of TOrC.

Previous research revealed that the primary substrate, more specifically the bioavailability of biodegradable dissolved organic carbon (BDOC), directly affects the microbial community structure and function in soil–water systems and as a consequence also TOrC attenuation (Alidina et al., 2014a; Li et al., 2013, 2014). Although high BDOC availability usually results in a greater biomass production of biological active systems, the resulting microbial community usually is less diverse. Oligotrophic conditions, however, can result in an increase in diversity of the microbial community, which can feature the ability to better transform also moderately biodegradable TOrC (Alidina et al., 2014a,b; Li et al., 2013, 2014). Refractory dissolved organic carbon (DOC) is composed of a greater diversity of organic molecules creating a selective pressure for those microorganisms that can express different metabolic functions to utilize these carbon sources as primary substrate (Li et al., 2014). This overall increase in metabolic function (increase in enzymatic diversity) can provide a greater opportunity for co-metabolic transformation of TOrC. Since composition and availability of BDOC usually change with residence time and travel distance, TOrC attenuation is highly sensitive to changes in primary substrate composition.

The redox environment of MAR systems has been identified as a primary driver for mobility, dissolution, transformation, and toxicity of most TOrC present in infiltrating water (Grützmacher and Reuleaux, 2011; Hoppe-Jones et al., 2010; Regnery et al., 2013; Wiese et al., 2011). Microorganisms are adapted to specific redox zones and microbial activity drives redox conditions in the subsurface besides hydro-geochemical reactions. Effluent-impacted waters usually contain high concentrations of BDOC, which serves as an electron donor for soil microorganisms. In a typical recharge situation, a sequence of reduction processes from highly oxidized conditions to reducing conditions will develop over time as a function of travel distance. Dissolved O_2, which usually is enriched in water applied to recharge basins, will be consumed in the initial zone of infiltration, followed by nitrate reduction and subsequent reduction of Mn(IV) and Fe(III) oxides, as well as sulfate providing electron donors are still present (McMahon and Chapelle, 2008). Where no particulate organic matter is deposited and the BDOC of the infiltrating water is characterized by limited bioavailability, less reduced redox conditions in the aquifer will establish.

Though several field studies from MAR sites investigated redox-dependent attenuation of certain TOrC (Drewes et al., 2003; Heberer et al., 2008; Massmann et al., 2006; Schmidt et al., 2004; Wiese et al., 2011), only limited knowledge is available from controlled laboratory-scale studies that systematically investigated and compared the influence of different redox conditions on biotransformation of TOrC in the subsurface (Baumgarten et al., 2011; Burke et al., 2014; Suarez et al., 2010). Burke et al. (2014) compiled the redox dependent degradation behavior of 27 wastewater-derived TOrC in groundwater based on several studies using tank aeration experiments with no soil present. Based on extensive field data from three MAR sites, Wiese et al. (2011) evaluated removal efficiencies for 29 TOrC under different redox conditions at a macro-scale. For TOrC exhibiting redox dependent degradation behavior, biotransformation rates can vary significantly (Greskowiak et al., 2006). Seasonal temperature changes also have an effect on the redox chemistry of groundwater and can lead to significant differences in TOrC removal efficiency (Massmann et al., 2006). Therefore, affecting redox conditions of MAR systems can change the removal performance of redox-sensitive TOrC (Grützmacher and Reuleaux, 2011; Müller et al., 2013; Regnery et al., 2013).

Rate constants are considered useful to provide first estimates of the fate of TOrC at field-scale, which is essential for the design and operation of MAR sites. Nevertheless, the question can be asked, how accurate rather simplified first-order rate constants are for model-based prediction of contaminant fate and transport considering the variability of environmental conditions. Thus, the objectives of this study were i) to develop relationships between the attenuation of representative TOrC as a function of retention time, system characteristics, and operating conditions using controlled laboratory-scale soil column experiments simulating MAR and ii) to evaluate if key parameter-dependent rate constants are needed in contaminant transport modeling to properly capture dynamic TOrC attenuation processes at field-scale.

2. Material and methods

2.1. Soil column experiments

Different 1D-soil column systems (PC, C1, C2) equipped with intermediate sampling ports were established and operated for more than five years to simulate prevailing biochemical conditions in MAR systems as described in Table 1. All soil column systems were operated at room temperature (20 °C) in top to bottom (one dimensional) flow at a hydraulic loading rate of 0.094 m d^{-1}. A detailed description of the soil column system's flow characterization and abiotic control experiments to assess whether physical retardation would be a contributing factor in the removal of select TOrC in the column experiments is provided elsewhere (Alidina et al., 2014b; Drewes et al., 2015; Hoppe-Jones et al., 2012; Rauch-Williams et al., 2010). The soil column feed water was either a dechlorinated tap water (City of Golden, Colorado) or a secondary treated wastewater effluent obtained from a local wastewater treatment plant employing nitrification and partial denitrification. To adjust the DOC level in the treated wastewater effluent, feed water was blended with nanofiltered (NF) permeate. NF permeate was produced from tap water