Characterizing redox conditions and monitoring attenuation of selected pharmaceuticals during artificial recharge through a reactive layer

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HIGHLIGHTS

- We designed a reactive barrier to improve the PhAC removal during AR.
- The reactive barrier released DOC and increased the sorption surface.
- With the barrier, redox conditions beneath the basin became more reductive.
- The fate of atenolol, cetirizine, gemfibrozil, and carbamazepine was investigated.
- The barrier enhanced the removal of atenolol, cetirizine, and gemfibrozil.

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ABSTRACT

A permeable reactive layer was installed at the floor of an infiltration basin. The reactive layer comprised 1) vegetable compost to provide a sorption surface for neutral organic compounds and to release easily degradable organic matter, thus generating a sequence of redox states, and 2) minor amounts of clay and iron oxide to increase sorption of cationic and anionic species, respectively. Field application of this design was successful in generating denitrification, and manganese-, and iron-reducing conditions beneath the basin. This, together with the increase in types of sorption sites, may explain the improved removal of three of the four selected pharmaceuticals compared with their behavior prior to installation of the layer. After installation of the reactive layer, atenolol concentrations were below the detection limits in the vadose zone. Moreover, concentrations of gemfibrozil and cetirizine were reduced to 20% and 40% of their initial concentrations, respectively, after 200 h of residence time. In contrast, prior to installation of the reactive layer, the concentrations of these three pharmaceuticals in both the vadose zone and the aquifer were more than 60% of the initial concentration. Carbamazepine exhibited recalcitrant behavior both prior to and after the reactive barrier installation.

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1. Introduction

Demand for water increases in response to population growth, which leads to widespread aquifer over-exploitation and other detrimental effects (Konikow and Kendy, 2005; Wada et al., 2010). Artificial recharge of aquifers (AR) through infiltration basins may alleviate some of these effects because this technology contributes to water resources and enhances water quality during soil passage (Bouwer, 2002; Greskowiak et al., 2005). Numerous studies have demonstrated that

AR reduces the concentration of organic matter (Vanderzalm et al., 2006; Bekele et al., 2011), nutrients (Bekele et al., 2011), metals (Dillon et al., 2006; Bekele et al., 2011), pathogens (Dillon et al., 2006), and organic contaminants (Dillon et al., 2006; Hoppe-Jones et al., 2010; Patterson et al., 2011). The performance of AR, however, varies among pharmaceutically active compounds (PhACs), with some PhACs exhibiting site-specific removal efficiency. PhACs, which, by definition, are designed to have specific biologic effects, and are reported to be present in the water cycle (Heberer et al., 2004; Drewes, 2009; Kosonen and Kronberg, 2009; Onesios et al., 2009; Maeng et al., 2010; Rauch-Williams et al., 2010). "Many PhACs, such as carbamazepine, display recalcitrant behavior during conventional wastewater treatment (Carballa et al., 2004; Chefetz et al., 2008; Díaz-Cruz and Barceló,

2008; Maeng et al., 2011; Jelic et al., 2012) and in the aquatic environment" (Lim et al., 2008; Arye et al., 2011). Consequently, they are frequently detected in surface and ground waters and, in some cases, in drinking water (Heberer, 2002; Jones et al., 2004; Hoppe-Jones et al., 2010; Maeng et al., 2011; Dickenson et al., 2011; Lapworth et al., 2012).

Typical sources of water for AR include wastewater effluents (after different stages of treatment) and effluent-receiving rivers (Drewes, 2009; Maeng et al., 2011). Consequently, AR water often contains PhACs (Heberer, 2002; Heberer et al., 2004). The concentration of organic micro-contaminants is decreased during AR through infiltration basins due to various attenuation processes, such as biodegradation and adsorption (Maeng et al., 2011; Schaffer et al., 2012b). The type and bio-availability of organic matter affect PhAC degradation because the organic matter serves as a co-substrate in microbiologically-facilitated transformations (Rauch-Williams et al., 2010; Tran et al., 2013; Li et al., 2013; Alidina et al., 2014). The enzymes responsible for the biotransformation of different PhACs are produced by a range of microorganisms that are differentially affected by the composition and amount of organic matter (Li et al., 2013; Alidina et al., 2014). Electron acceptors are consumed during organic matter oxidation according to the energy released to the mediator microorganisms, which naturally leads to a sequence of redox states and different metabolic pathways. This is a well-established sequence described most recently by Farnsworth and Hering (2011). For bank filtration, reducing conditions occur near the bank and aerobic conditions occur near the production well. Nevertheless, Alewell et al. (2008) hypothesized that the theory of the sequential reduction chain does not always hold true under field conditions; they observed that sites with high dissolved organic carbon (DOC) concentrations may not follow the pattern of the sequential reduction chain because high electron donor availability does not trigger competition between processes attributed to different redox potentials. Some PhACs are preferentially removed under specific redox conditions (Patterson et al., 2011; Rauch-Williams et al., 2010; Barbieri et al., 2011; Maeng et al., 2011; Storck et al., 2012; Valhondo et al., 2014). Therefore, the passage of water through several redox environments should enhance the number and proportion of eliminated PhACs.

Adsorption depends on both the surface type and the pollutant type. Neutral compounds tend to sorb onto solid organic matter, and cations and anions tend to sorb onto negatively- (e.g., clay) and positively- (e.g., iron oxide) charged surfaces, respectively (Schaffer et al., 2012b). Adsorption of PhACs is enhanced and hence the residence time prolonged, by increasing the diversity of sorption sites through the flow path. Thus, ideally, artificially recharged water should encounter neutral, positively-, and negatively-charged surfaces during infiltration.

We designed a layer acting as a reactive barrier to provide a broad range of redox states and a diverse set of sorption surfaces. We installed the layer in March 2011 in an infiltration basin that had been operating intermittently since 2009. The reactive barrier comprised 1) vegetable compost to release degradable organic matter, to promote microbial growth and generate diverse redox states, and to provide sorption surfaces for neutral organic compounds; 2) clay to increase sorption of cationic compounds; and 3) iron oxide to facilitate sorption of anionic compounds.

The aim of this paper is to report the practical application of this newly designed reactive layer and the field response. The effectiveness of the reactive layer to promote diverse redox conditions was verified by comparing DOC and redox indicators along the infiltration path prior to and after installation of the reactive layer. The behavior of four PhACs: atenolol, cetirizine, gemfibrozil and carbamazepine, was also studied during AR with the system operating prior to and after installation of the reactive barrier. The four PhACs were selected because of their respective charges (cation, zwitter-ion, anion, and neutral, respectively) at the experiment pH range (6.3–8.4), their different degradation behaviors and sorption properties, and their frequent detection in aquatic environments (Heberer, 2002; Schaffer et al., 2012b; Bahlmann et al., 2012; Grenni et al., 2013).

2. Materials and methods

2.1. Site description

The infiltration site is located in the Llobregat Lower Valley aquifer, 15 km inland from the Mediterranean coast. The aquifer beneath the basin comprises Quaternary alluvial sediments, mainly gravel and sand with a small fraction of clay (Barbieri et al., 2011). The minerals include quartz, calcite, and dolomite, and the solid phase fraction of organic carbon is less than 0.002 (g_{OC}/g_{Soil}). The regional groundwater flow direction is from NNW to SSE (Iribar et al., 1997) with a natural hydraulic gradient of 2.3‰ (Fig. 1B). Infiltration water is brought from the Llobregat River, which is impacted by numerous treatment plant effluents (Köck-Schulmeyer et al., 2011), to a settlement pond (≈ 5000 m^2), with a residence time of 2 to 4 days. Thereafter, the water is transferred to the infiltration pond (≈ 5000 m^2). This system has operated intermittently since February 2009 with a mean infiltration rate of 1 m/d.

The monitoring network comprised seven piezometers to sample aquifer water, and two suction cups to sample the vadose zone underneath the basin (Fig. 1A). The two suction cups, labeled cc1 and cc2, were installed at 1 and 2 m below the surface, respectively. One piezometer (P-1) was located upstream from the infiltration basin to monitor background concentrations of local groundwater, hereafter referred to as "Amb-GW" (ambient-groundwater). Three piezometers (P-8.3, P-8.2, and P-8.1) were located in the middle of the infiltration pond and screened at different depths (7–9 m, 10–12 m, and 13–15 m, respectively). Their placement allowed us to evaluate changes in the water quality at various depths within the saturated zone immediately upon entrance of the recharge water into the aquifer. Four completely screened piezometers (P-2, P-5, P-9, and P-10) were placed downstream along the flow path to assess the quality of the infiltrated water at increasing residence times. Most of the piezometers were equipped with CTD-Diver (Schlumberger water services, Delft, The Netherlands) sensors for continuous recording of electrical conductivity (EC), temperature, and water level.

2.2. Experimental procedure

To assess the effectiveness of the barrier, we performed three different infiltration tests: one prior to and two after installation of the reactive barrier. Infiltration rates were similar during the three tests (Fig. 2). The infiltration system was run continuously with occasional stops for maintenance operations or due to high turbidity levels in the source water. The sampling concentrated on three campaigns. The first campaign, referred to as the 'pre-L' test, lasted 29 days in early 2011 (Jan. 12th to Feb. 10th). Samples were collected from monitoring points and the infiltration pond after 20 days of continuous infiltration. The second campaign, referred to as the 'L-2011' test, was performed for 46 days in late 2011 (Sep. 8th to Oct. 24th), 4 months after installation of the reactive layer. The system operated intermittently during the previous 4 months (May–August), but was stopped whenever turbidity at the entrance of the infiltration basin was higher than 25 turbidity unit to avoid clogging the system. During this second campaign, monitoring points were sampled in six weekly events starting on Sep. 23rd. Water from the infiltration pond was sampled 14 times (at least twice a week). The third campaign, referred to as the 'L-2012' test, was performed for 50 days in the summer 2012 (Jun. 13th to Aug. 2nd), beginning 14 months after installation of the reactive layer. Water from the infiltration basin was sampled six times, suction cup CC2 was sampled once, and the monitoring points were sampled from two to six times. The first sample was collected 3 weeks after the infiltration was started. Mean infiltration rates were 1 m/d during the three tests. Fig. 2 shows