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Microcosm experiments to control anaerobic redox conditions when studying the fate of organic micropollutants in aquifer material

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ABSTRACT

The natural processes occurring in subsurface environments have proven to effectively remove a number of organic pollutants from water. The predominant redox conditions revealed to be one of the controlling factors. However, in the case of organic micropollutants the knowledge on this potential redox-dependent behavior is still limited. Motivated by managed aquifer recharge practices microcosm experiments involving aquifer material, settings potentially feasible in field applications, and organic micropollutants at environmental concentrations were carried out. Different anaerobic redox conditions were promoted and sustained in each set of microcosms by adding adequate quantities of electron donors and acceptors. Whereas denitrification and sulfate-reducing conditions are easily achieved and maintained, Fe- and Mn-reduction are strongly constrained by the slower dissolution of the solid phases commonly present in aquifers. The thorough description and numerical modeling of the evolution of the experiments, including major and trace solutes and dissolution/precipitation of solid phases, have been proven necessary to the understanding of the processes and closing the mass balance. As an example of micropollutant results, the ubiquitous beta-blocker atenolol is completely removed in the experiments, the removal occurring faster under more advanced redox conditions. This suggests that aquifers constitute a potentially efficient alternative water treatment for atenolol, especially if adequate redox conditions are promoted during recharge and long enough residence times are ensured.

1. Introduction

The ultimate motivation of this work is artificial recharge of aquifers. Artificial recharge is beneficial both in quantitative (augmentation of groundwater resources, long term underground storage, etc.) and qualitative terms (overall improvement of water quality during aquifer passage: decreasing of suspended solids, pathogens, nitrogen, phosphates, metals and dissolved organic carbon). The interest in this technique is also related to the capability of subsoil processes to partially or totally remove organic contaminants from water (Aronson et al., 1999 and references therein; Christensen et al., 2001 and references therein; Neuhauser et al., 2009). Nowadays a great scientific effort is dedicated to assess whether organic micropollutants could also be effectively removed (Barber et al., 2009; Díaz-Cruz and Barceló, 2008 and references therein; Heberer, 2007 and references therein; Hoppe-Jones et al., 2010). A number of such compounds are not eliminated by conventional water treatments (Gros et al., 2010; Onesios

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et al., 2009 and references therein; Petrovic et al., 2009 and references therein; Stackelberg et al., 2007). The passage of water through the soil–aquifer system during artificial recharge may represent an alternative or complementary treatment for their removal.

As a general rule, the fate of organic pollutants within the aquifer depends on lithology, hydraulic and textural properties of the soil, temperature, physico-chemical properties of the specific compound, and microbial environment. Among all factors, the predominant redox state of the aquifer revealed to play a significant role (Aronson et al., 1999 and references therein; Bosma et al., 1996; Broholm and Arvin, 2000 and references therein; Christensen et al., 2001; Kao et al., 2003 and references therein). Since certain pollutants could be preferably removed under some particular redox conditions, such conditions could eventually be promoted in artificial recharge practices. Even more important, if different compounds are degraded under different redox environments, a water mass undergoing a sequence of redox states should have most of its initial contaminants eliminated.

Yet, in the case of organic micropollutants, the knowledge on a potential redox-dependent behavior is still limited. Beside field evidences (Drewes et al., 2003; Heberer et al., 2008; Montgomery-Brown et al., 2003; Pavelic et al., 2005; Tubau et al., 2010; and references therein), laboratory tests under specific and controlled simplified conditions have been carried out. However, many of the experiments reported in literature adopted settings that are not representative or directly applicable to aquifer systems.

Specifically, aerobic/anoxic biodegradability and transformation mechanisms of organic micropollutants have been investigated in model systems for wastewater treatment. That is, laboratory experiments have been typically performed in wastewater matrices, and by using sludges from sewage treatment plants as adapted inocula (Clara et al., 2004; Quintana et al., 2005; Stasinakis et al., 2009; Zwiener et al., 2002). Their fate under aerobic/anaerobic or specific redox conditions have also been largely studied in aquatic environments. In these cases river-bed sediments rich in organic materials have been incubated with river water (Davis et al., 2006; Löffler et al., 2005; Radke et al., 2009) or with solutions/culture media containing specific electron acceptors (Bradley et al., 2001; Crawford et al., 1998; Lu et al., 2009; Somsamak et al., 2001). Some tests involved bacterial isolates, and have been carried out using standard silica sand or sintered materials as solid matrix for the colonization of the microorganisms (Crawford et al., 2000; Katz et al., 2001; Stucki et al., 1995). Finally, not only in the aforementioned studies but also when soil and aquifer material were included (Krueger et al., 1998; Schulz et al., 2008; Ying et al., 2008), the experiments have been often performed with concentrations of the target compounds from hundreds of $\mu g\ L^{-1}$ to tens of $mg\ L^{-1}$.

The above works are indeed useful to demonstrate the susceptibility of specific micropollutants to microbial or abiotic transformation, to understand degradation pathways, and to identify intermediate or stable metabolites. However, the organic content of aquifer materials, which may influence sorption and partitioning behavior of organic micropollutants, could be lower, the potential development of a sequence of redox states and the removal of micropollutants depends on the local native microorganisms, and target pollutants are found at concentrations some order of magnitudes lower.

Finally, quite limited laboratory experiments, a number of them related to managed aquifer recharge practices, resemble real subsurface environments (Baumgarten et al., 2011; Hua et al., 2003; Mansell and Drewes, 2004; Massmann et al., 2008; Rauch-Williams et al., 2010; Scheytt et al., 2004). In such experiments, the fate of organic micropollutants has been usually assessed within the range of redox conditions developing naturally in the system and being representative of those actually occurring at field site, namely aerobic, anoxic (prevailing denitrifying) and seldom unspecified anaerobic conditions. The identification of potential abiotic processes by performing analogous sterile experiments was not always included in such studies. Therefore, the potential effect of various redox states (especially the most reducing ones) on the fate of a wide range of organic micropollutants in subsurface environments still remains to be investigated.

In this context, the aim of our work was to create and sustain diverse anaerobic redox conditions in systems involving natural aquifer material and settings potentially feasible in artificial recharge sites, and to study in such environments the behavior of organic micropollutants at realistic concentrations.

The present paper describes thoroughly the experimental methodology and settings adopted. Details on the selection of the type/quantities of electron donors and acceptors used to stimulate the desired redox conditions have been integrated. Limited information on the design criteria is usually provided in studies on the fate of organic pollutants adopting this approach (Bosma et al., 1996; Bradley et al., 2001; van der Zaan et al., 2009; Weiner et al., 1998; Ying et al., 2008). This hinders running analogous studies with some different setting (substrates, electron acceptors, durations, etc.).

The description of the microcosms' hydrochemical evolution is also presented. Often this is not/poorly monitored or only incipiently reported in laboratory studies on the fate of organic contaminants, especially when focused on their transformation pathways, nor the actual occurrence of the expected/stimulated redox condition is verified (Baumgarten et al., 2011; Bosma et al., 1996; Bradley et al., 2001; Gröning et al., 2007; Krueger et al., 1998; Rauch-Williams et al., 2010; Schulz et al., 2008; van der Zaan et al., 2009; Weiner et al., 1998; Ying et al., 2008). We conjecture that the assessment of the geochemical state, which could be quite complex as in natural subsurface environments, and its quantitative numerical modeling has to be included in this type of studies for a more complete interpretation of the experimental results, and for the potential subsequent design of real field applications.

Finally, as example of application of the study to the fate of organic micropollutants in different redox environments, the results for the ubiquitous but still barely investigated β-blocker atenolol are presented in the paper.

2. Materials and methods

2.1. Sediments, water and micropollutants

The experimental set up included various sets of microcosms, each microcosm consisting of natural sediments and synthetic water spiked with a mixture of organic micropollutants.