

Stimulating, Sustaining and Assessing Diverse Anaerobic Redox Conditions in Batch Experiments Involving Aquifer Material

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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 and microcontaminants from water (Christensen et al., 2001; Díaz-Cruz and Barceló, 2008; Hoppe-Jones et al., 2010), representing thus an alternative or complementary treatment for their elimination.

As a general rule, the fate of organic pollutants within the aquifer depends on mineralogy, 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; Christensen et al., 2001; Rauch et al., 2009; Baumgarten et al., 2011). Yet, in the case of organic micropollutants, the knowledge on a potential redox-dependent behaviour is still limited.

In this context, the aim of our work was to create and sustain diverse anaerobic redox conditions in systems involving aquifer material and settings potentially feasible in artificial recharge sites. The experimental methodology consisted of

mixing a natural sediment with a finite amount of easily degradable organic matter and an excess of the target electron acceptor (NO_3 , Mn(IV) , Fe(III) , or SO_4 depending on the experiment), and was based on batch experiments.

MATERIALS AND METHODS.

Sediments, Water and Micropollutants.

The experimental set up included various sets of microcosms, each one consisting of a 0.3L glass bottle containing 120g of natural sediments and 0.24L of synthetic water spiked with a mixture of organic micropollutants.

Sediments were obtained from a test site for artificial recharge of groundwater located in Sant Vicenç dels Horts (Barcelona, Spain). The aquifer consists of quaternary alluvial sediments, mainly gravel and sand with a small fraction of lutites. Sediment samples were collected prior to the starting up of the facilities, from an oxic unsaturated horizon at about 1m depth under the bottom of the infiltration pond. They were sieved through a 1mm grid to remove the coarse fraction, which was expected to be less active for surface and microbially mediated reactions. Their mineralogical and chemical analysis revealed the presence of silicates, carbonates, and some Mn and Fe oxides and oxide-hydroxides. The organic carbon content was smaller than 0.2%.

Water used for the preparation of all the experiments was artificially prepared to mimic the recharge water at the test site (from the Llobregat river water) except for the organic carbon content, which at

a first stage was set equal to zero.

The mixture of organic micropollutants spiked in all experiments (initial concentration of each compound: $1\mu\text{g L}^{-1}$) included drugs, pesticides, estrogens, hydrocarbons, surfactant degradation products, apththalate and a biocide. The selection of the compounds was based on the micropollutants occurrence in the Llobregat river.

Creating Sustainable Redox Conditions.

A different anaerobic redox condition (nitrate-, manganese-, iron- or sulphate-reducing condition) was promoted in four different sets of batches by stimulating one specific step of the natural redox sequence for the microbially mediated organic matter degradation. To this end, easily degradable organic compounds (Sodium Acetate and the Methanol used as solvent in the micropollutants spiking solution) were provided as electron donors and, depending on the target redox condition, NO_3 , Mn(III/IV) , Fe(III) or SO_4 was added as specific electron acceptor.

The total amounts of organic substrate and controlling electron acceptor were selected so as to reach the desired redox state and to sustain it during a significant lapse of time. This implies on one hand that the total amount of organic substrate had to be large enough to consume electron acceptors with reactions energetically more favourable than the target one. On the other hand, for each potential selection of organic substrates the total amount of controlling electron acceptor initially available had to (slightly) exceed the

palabras clave: Redox, Recarga artificial, Experimentos batch, Modelación.

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stoichiometric quantity necessary for their complete mineralization.

Experimental Procedure.

The preparation of the batches was carried out inside a glovebox, under Ar atmosphere. The synthetic water was previously purged with Argon to remove all oxygen, except in the case of the "Natural Conditions" experiment. After assembling, each microcosm was incubated at controlled temperature (25°C). The total duration of the experiments ranged from 21 to 215 days. Duplicate bottles were sacrificed at each sampling time according to predefined sampling schedules. One at a time, the two bottles were opened under Ar atmosphere, chemical parameters (pH, Temperature, Dissolved Oxygen, Electrical Conductivity, Alkalinity) were measured, and aqueous samples for general chemistry (Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻, PO₄³⁻, F⁻, NH₄⁺, DOC, Fe and Mn, Ca, Mg, Na, K and minor elements) and micropollutants analysis were collected.

RESULTS AND DISCUSSION.

According to the reactions organic matter degradation, a general trend of decrease in DOC and increase in Alkalinity was expected in the experiments. A simultaneous decrease in the concentration of the target dissolved electron acceptors was expected for the NO₃- and SO₄-reducing experiments, whereas an increase in the concentration of Fe(II) and Mn(II), products of the reduction of the target solid electron acceptors was expected in the Mn- and Fe-reducing experiments. Details on the evolution of each experiment are presented (e.g., the case of the SO₄-reducing experiment is shown in Fig. 1), confirming the development of the expected trends. In fact, we found that the hydrochemistry was very complex. Numerous minerals (carbonates, iron sulphide) precipitated as a result of variations in alkalinity and pH, and of the simultaneous reduction of different electron acceptors (Fig. 2). The use of natural sources of Mn and Fe was realistic, but complicated the development of controlled redox conditions: natural sources are often quite crystalline, which slows down dissolution to the point of making it the rate limiting process. Moreover, biomass production had to be considered in the stoichiometries for a correct interpretation of DOC decreasing.

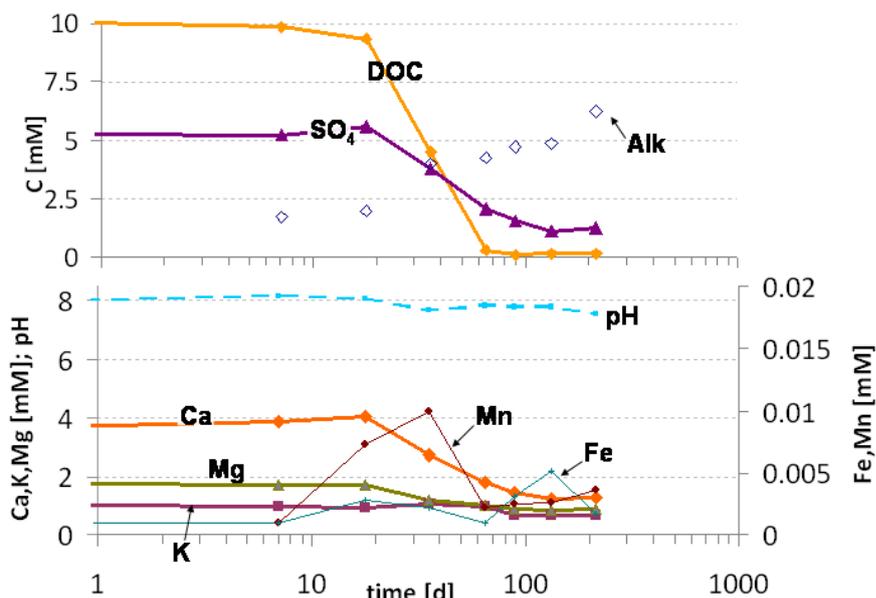


fig 1. Chemical evolution with time in the SO₄-reducing experiment.

Therefore, proper assessment required understanding not only the evolution of redox sensitive species, but major and minor ions too. Inspection of the sediments through SEM-EDS and the performing of numerical modeling (results of the simulations are also presented) proved useful in confirming the occurrence of the hypothesized processes. Improved characterization

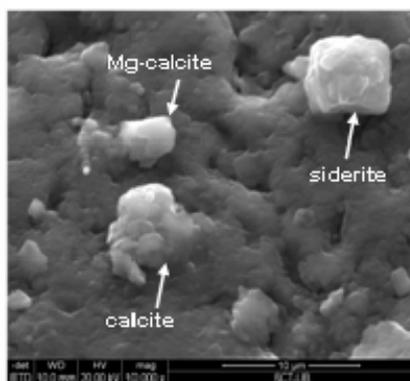


fig 2. Precipitates of Ca-, Mg-Ca- and Fe-carbonates in the experiments.

could have been achieved by the analysis of dissolved iron sulphide and methane, desorption experiments to verify the potential adsorption of reduced species (i.e., Mn²⁺ and Fe²⁺) onto clay surfaces, and by the evaluation of the microbial state during the experiments (e.g.: identification of microbial communities, measurements of Hydrogen, etc.).

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