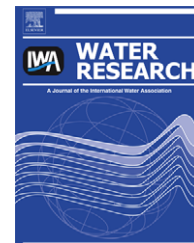


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# Interplay between oxygen demand reactions and kinetic gas–water transfer in porous media

Sascha E. Oswald, Marco Griepentrog, Mario Schirmer, Gerd U. Balcke\*

UFZ, Helmholtz Centre for Environmental Research – UFZ, Department of Hydrogeology, Permoserstrasse 15, 04318 Leipzig, Germany

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## ABSTRACT

Gas–water phase transfer associated with the dissolution of trapped gas in porous media is a key process that occurs during pulsed gas sparging operations in contaminated aquifers. Recently, we applied a numerical model that was experimentally validated for abiotic situations, where multi-species kinetic inter-phase mass transfer and dissolved gas transport occurred during pulsed gas penetration–dissolution events [Balcke, G.U., Meenken, S., Hofer, C. and Oswald, S.E., 2007. Kinetic gas–water transfer and gas accumulation in porous media during pulsed oxygen sparging. *Environmental Science & Technology* 41(12), 4428–4434]. Here we extend the model by using a reactive term to describe dissolved oxygen demand reactions via the formation of a reaction product, and to study the effects of such an aerobic degradation process on gas–water mass transfer and dissolution of trapped gas in porous media. As a surrogate for microbial oxygen reduction, first-order oxygen demand reactions were based on the measured oxidation of alkaline pyrogallol in column experiments. This reaction allows for adjusting the rate to values close to expected biodegradation rates and detection of the reaction product. The experiments and model consistently demonstrated accelerated oxygen gas–water mass transfer with increasing oxygen demand rates associated with an influence on the partitioning of other gases. Thus, as the oxygen demand accelerates, less gas phase residues, consisting mainly of nitrogen, are observed, which is in general beneficial to the performance of field biosparging operations. Model results additionally predict how oxygen demand influences oxygen mass transfer for a range of biodegradation rates. A typical field case scenario was simulated to illustrate the observed coupling of oxygen consumption and gas bubble dissolution. The model provides a tool to improve understanding of trapped gas behavior in porous media and contributes to a model-assisted biosparging.

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## 1. Introduction

Due to the limited availability of oxygen in contaminated groundwater, biodegradation of many hydrocarbons is often restricted. For this reason attempts are made to oxygenate zones of contaminated aquifers in order to stimulate aerobic biodegradation processes (Schirmer and Martienssen, 2007).

One in-situ method for achieving groundwater oxygenation relies on the dissolution of a ‘fence’ of trapped gas phase, established by direct sparging of air or pure oxygen gas into the aquifer, preferably in pulsed mode (e.g. Wilson and Norris, 1997; Yang et al., 2005). Although numerous field sparging operations are in place worldwide, the complex interplay between gas dissolution, microbial oxygen uptake, groundwater

\* Corresponding author. Metanomics GmbH, Tegeler Weg 33, 10589 Berlin, Germany. Tel.: +49 30 34 807 148; fax: +49 30 34 807 300.

E-mail address: [gerd.balcke@metanomics.de](mailto:gerd.balcke@metanomics.de) (G.U. Balcke).

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flow, and gas accumulation in the pore space is not yet fully understood. As dissolved oxygen levels are continuously depleted due to microbial activity, the dissolved oxygen concentration downstream of the sparging wells is often too low to be used to control the pulse frequency. Furthermore, oxygen gradients may induce large changes of microbial biomass and thus may affect oxygen demand rates even at small distances (Rees et al., 2007). Hence, field operations are still largely driven on an empirical basis, and thus often suffer from shortcomings such as clogging, uncontrolled oxygenation, or gas breakthrough (Islam and Singhal, 2004; Salanitro et al., 2000).

Gas–water inter-phase mass transfer in porous media is influenced by different partitioning kinetics of relevant gases, which, in turn, are driven by different aqueous diffusivity and partitioning constants (Cirpka and Kitanidis, 2001; Holocher et al., 2002, 2003). Consequently, incongruent dissolution of gas compounds and interactions between the injected, oxygen-containing gas phase with other naturally occurring dissolved gases such as nitrogen are observed (Geistlinger et al., 2005). Since dissolved nitrogen concentrations in natural groundwater are expected to be similar to the atmospheric saturation level, significant volume fractions of nitrogen may transfer out of the water phase and accumulate in a trapped gas phase as long as the partial pressure has not yet reached equilibrium with the surrounding groundwater. Increasing volume fractions of nitrogen also decrease the inter-phase mass transfer for oxygen (Holocher et al., 2003), retard the spreading of dissolved oxygen (Balcke et al., 2007), and possibly interfere with the goal of efficiently oxygenating the aquifer.

Finally, the oxygen demand kinetics may influence the inter-phase mass transfer. Maintaining sufficient enzyme activity for aerobic biodegradation is a function of oxygen availability and thus should be coupled to the inter-phase mass transfer. Hence, understanding the mutual interactions of oxygen demanding processes and gas–water inter-phase mass transfer in porous media is essential for better assessing the fate of trapped gas and to assist practitioners in optimizing intermittent gas sparging. In this context we applied a conceptual model, originating from air bubble entrapment at the water table (Holocher et al., 2003). Overall, this model incorporates mass transfer kinetics at gas–water interfaces of spherical gas bubbles, changes of gas phase volume, evolution of the gas phase composition, dissolved gas components, and 1D solute transport in the aqueous phase.

Previously, the original model code was adapted and further developed for cases of pulsed gas penetration–dissolution events (Balcke et al., 2007). Using this modified version, dissolution and transport of  $O_2$  and sulfur hexafluoride ( $SF_6$ ) were adequately predicted, excluding additional oxygen demanding reactions. In this study, we investigated oxygen gas–water mass transfer and gas dissolution in the presence of an oxygen demanding reaction in the aqueous phase. Experimentally, autoxidation of alkaline pyrogallol with a reaction rate set by the aqueous pH, was used to mimic microbial oxygen demand occurring simultaneously with water flow and inter-phase mass transfer. The assessment of oxygen transfer was enabled through detection of the oxidation product. The injected oxygen gas phase was spiked with traces of  $SF_6$  as a partitioning tracer to provide additional information on dissolution of trapped gas.

The numerical model for predicting kinetic gas–water mass transfer along a 1D flow path has been improved to include an oxidation product formed by first-order kinetics. The numerical simulations were evaluated for their ability to reproduce experimental measurements. For comparison, model predictions and experimental results omitting oxygen demand, (Balcke et al., 2007), were also included in the study.

## 2. Materials and methods

Experimental design of the column experiments, sampling procedures, and chemical analyses were similar to those described previously by Balcke et al. (2007) with the modifications specified below.

### 2.1. Solute tracers

Alkaline anoxic pyrogallol (1,2,3-trihydroxybenzene, Aldrich) served as an excess reagent to react with dissolved oxygen, and this choice will be discussed in Section 3. For preparation, aqueous TRIS buffers (trishydroxymethylaminomethane, 0.15 M) of pH 7.5 or 9.0, respectively, were purged with nitrogen (5.0 grade, Linde, Germany) until the dissolved oxygen concentration dropped below  $50 \mu\text{g L}^{-1}$ . Then, under continuous nitrogen flushing, a freshly prepared aqueous concentrate of pyrogallol was added to the buffer to give a final pyrogallol concentration of 4 mM. Throughout the tests this feed medium was kept anoxic by constant flushing with high-purity nitrogen (nitrogen 5.0 was passed through an oxytrap, RMSH-2, Agilent). Breakthrough of oxidation product was recorded by UV-absorbance at 320 nm using an HPLC detector with a preparative cell (0.5 mm light path). The time-stability of the absorbance signal over 15 h was confirmed in separate experiments. Inert tracer breakthrough curves (BTCs), using potassium iodide, were conducted for the water-saturated column before a gas injection and after complete breakthrough of  $SF_6$  ( $2\text{--}5 \mu\text{g L}^{-1}$  dissolved effluent concentration) only.

### 2.2. Gas tracer

Oxygen gas was blended with a volume fraction of 0.862%  $SF_6$  (both  $23^\circ\text{C}$ , 1 atm) where the  $SF_6$  acted as a partitioning gas tracer with a stronger tendency than oxygen to stay in the gas phase (Balcke et al., 2007). Using a gas-tight syringe, 11.5 mL of this  $O_2/SF_6$  gas blend was sparged as one injection pulse into the bottom of a water-saturated sand column. The gas injection height was observed directly after injection via the color change of the pyrogallol solution in the column from transparent to brown.

### 2.3. Calibration of product to molar oxygen demand

In order to relate the molar oxygen demand to the UV-absorbance signal at 320 nm at the column outlet, pyrogallol was allowed to react with different amounts of oxygen. For this purpose gas-tight syringes with stopcocks (Hamilton) were first completely filled with air-saturated solutions of 0.15 M TRIS buffer of pH 7.5 or 9.0, respectively, and balanced. Then,

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