

Supporting Information for
“Kinetic Gas-Water Transfer and Gas Accumulation in Porous Media during Pulsed
Oxygen Sparging”
Environmental Science & Technology

Gerd U. Balcke, Stefan Meenken, Carsten Hoefer, and Sascha E. Oswald

UFZ, Helmholtz Centre for Environmental Research, Department of Hydrogeology,
Permoserstr. 15, 04318 Leipzig, Germany

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This document provides additional technical information related to the laboratory column experiments and the numerical modeling. Also, some more results are presented and briefly discussed. It has 12 pages and includes two tables and six figures.

Additional Experimental Details. The column system with automatic sampler has been constructed with a modular design (Figure SI-1) using the compounds listed in Table SI-1. The influent solution could have adjustable dissolved oxygen levels. A new fiber-optic detection method to trace small oxygen concentrations was applied to measure effluent dissolved oxygen (DO) concentrations. Details about the detection principle are given in (1).

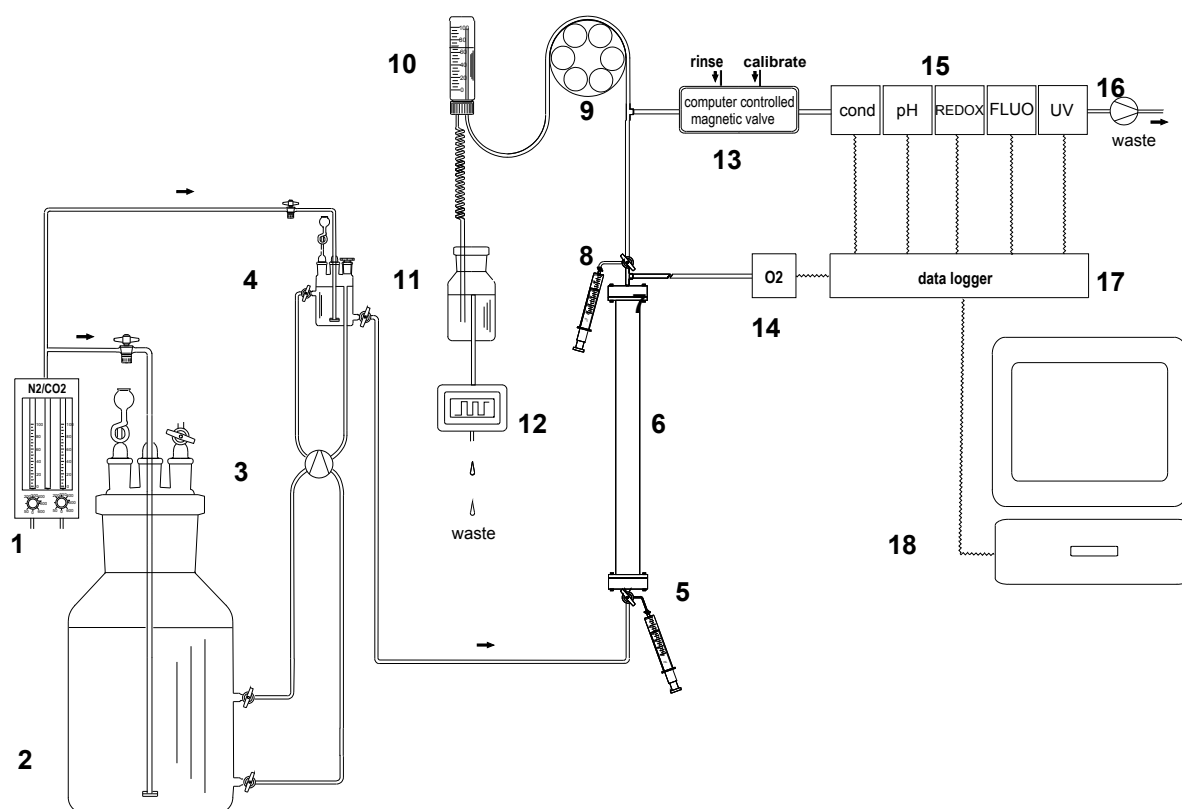


Figure SI-1. Bench-scale column setup used for pulsed gas injection experiments (for details and suppliers see Table SI-1).

Aqueous samples equilibrated with the gas mixture to be injected were used as a basis for determining SF_6 recoveries. The integrated mass of SF_6 breakthrough curves was related to the injected mass of SF_6 calculated from aqueous saturation in equilibrium in the gas bottle wherein the gas mixture was prepared. According to GC-ECD measurements 81%, 83%, and

103% of the target value of 1.24 mg SF₆ were found to have been injected actually. Since optode measurements do not provide sensitive detection for very high DO concentrations an accurate determination of the oxygen gas-phase concentration could not be made. Therefore, the mass of oxygen injected could only be estimated using the ideal gas law and a constant value of 14.77 mg was taken for all injections.

Table SI-1. Details and suppliers related to the experimental setup (cf. Figure SI-1)

1	gas mixer (C73194, Novodirect, Kehl, Germany)
2	inflow reservoir with gas frit
3	peristaltic pump (C32067, ISMATEC, Novodirect, Kehl, Germany)
4	inflow potential bottle with gas frit
5	3-way valve with syringe adapter (Swagelok SS-42XS6MM, B.E.S.T., Schkeuditz, Germany)
6	glass column (alternative: drilling liners)
7	optode sensor flow-through cell with light conductor (FTCH with PST3 sensor, Presens, Regensburg, Germany)
8	3-way port with syringe adapter (Swagelok SS-42XS6MM, B.E.S.T., Schkeuditz, Germany)
9	peristaltic pump (C32089, ISMATEC, Novodirect, Kehl, Germany)
10	gas trap
11	outflow potential bottle
12	LED drop counter (DTZ, Windaus-Labortechnik, Clausthal-Zellerfeld, Germany)
13	multi channel magnetic valve (601100-A01, 2FFMSFK01-2-024/DC-04 core07, Buerckert, Kuenzelsau, Germany)
14	fiber optic device (Oxy4, Presens, Regensburg, Germany)
15	detector array (conductivity electrode Tetracon325, Novodirect, fluorescence detector FP-1520, UV absorption detector 1575-UV with preparative cell, Jasco, Gross-Umstadt, Germany, InlabLab 423, Inlab 501, Mettler-Toledo)
16	sampling pump (MCP MS4 12/00, Ismatec, Glatbrugg, Switzerland)
17	data logger (PC interface Almemo8990-6, Ahlborn, Holzkirchen, Germany)
18	computer (ADL-C271 PCI 8 channel card, PCJ-7250 8 channel digital I/O card, Software DASYPALAB 5.8, Datalog, Moenchengladbach, Germany)

Conceptual Framework for Gas Dissolution and Gas-Water Mass Transfer in Porous

Media. Our simulations were based on the model of Holocher et al. (2). This model considers multi-species, spherical gas bubbles trapped in a porous medium that kinetically exchange mass at the gas-water interface. Bubbles can therefore change size and completely dissolved.

This mass flux J of gaseous components i is driven by the following two equations

$$J_i = k_i \cdot \left(C_{wat,i} - \frac{p_i}{R \cdot T \cdot K_{H,i}} \right) \quad (1)$$

$$k_i \approx D_{mol,w,i} \left(\frac{1}{r_{bub}} + \sqrt{\frac{v}{2\pi \cdot r_{bub} \cdot D_{mol,w,i}}} \right) \quad (2)$$

where $D_{mol,w,i}$ is the aqueous diffusion coefficient for gas i [$\text{m}^2 \text{s}^{-1}$], r_{bub} is the bubble radius [m], v is the flow velocity [m/s], $C_{wat,i}$ is the actual aqueous phase concentration of gas i [mol m^{-3}], p_i is the partial pressure of gas i in the bubble [Pa], $K_{H,i}$ is the dimensionless Henry coefficient, R is universal gas constant [$\text{Nm mol}^{-1} \text{K}^{-1}$], and T is the water temperature [K]. The development of the gas bubble itself results from the behavior of all components (eqs. 3-4), i.e. here from N_2 , O_2 , SF_6 , but in turn affects the mass transfer of each component (cf. eq. 2).

$$\frac{dr_{bub}}{dt} = \frac{3RT}{4\pi r_{bub}} \cdot \left(\frac{1}{6\sigma + 3r_{bub}(p_{atm} - p_{vap} + \rho gh)} \right) \cdot \sum_i \frac{dn_i}{dt} \quad (3)$$

$$\frac{dn_i}{dt} = -4\pi r_{bub}^2 \cdot D_{mol,w,i} \left(\frac{1}{r_{bub}} + \sqrt{\frac{v}{2\pi r_{bub} D_{mol,w,i}}} \right) \cdot \left(C_{wat,i} - \frac{x_i}{S_i} \left(p_{atm} - p_{vap} + \rho gh + \frac{2\sigma}{r_{bub}} \right) \right) \quad (4)$$

where n_i is the number of moles of compound i in a single gas bubble, t is the time [s], x_i is the mol fraction of gas i , S_i is the solubility of gas i [$\text{Pa m}^3 \text{mol}^{-1}$], p_{atm} is the atmospheric pressure [Pa], p_{vap} is the partial pressure of water vapor in the bubble [Pa], ρgh is the hydrostatic pressure created by a water column of height h [Pa], $2\sigma/r_{bub}$ is the capillary pressure according to the curvature of the bubble surface [Pa] with the surface tension σ [Pa m]. Notably, a minor error in the mathematical development has been corrected and therefore eq. (3), used to calculate the temporal change of the bubble radius r_{bub} , is slightly different than the original one (cf. denominator in eq. 5, in Holocher et al. (2)).

Finally, the gas volume trapped, resulting from the particular gas water ratio r_{a-w} , defines the number of such identical gas bubbles. The mass fluxes of each gas component i from all bubbles into the water volume V_w at a position z determine the change of aqueous concentration of gas i by mass exchange at the aqueous-gas-phase interfaces,

$$\frac{dC_{wat,i}(z)}{dt} = \frac{N_{bubble} \cdot A_{int}(z)}{V_w} \cdot J_i = \frac{N_{bubble}}{V_{tot} \theta_{tot} / (1 + r_{a-w})} \cdot \frac{dn_i(z)}{dt} \quad (5)$$

where N_{bubble} is the number of bubbles, A_{int} is the surface area of each bubble, V_{tot} is the bulk control volume [m³], and θ_{tot} is the water-filled porosity. These mass fluxes create a source/sink term for the standard advection dispersion equation, representing the one-dimensional transport of dissolved gases through the column. Overall, at each location there is a unique value for bubble composition, bubble sizes and aqueous gas concentration, which undergoes a temporal evolution according to the coupled equations 3-5.

Differing discharge rates between experiments and gas-phase volume changes within each single experiment, change the column flow velocity. As calculated from eq. 2, using the experimental conditions, the velocity changes have only a moderate impact on gas-water mass transfer due to the square root dependence. In contrast, decreasing the gas bubble radii may increase the mass transfer coefficient k_i linearly, and thus can intensify the rate of bubble extinction (eqs. 1, 2).

Effective porosities n_{eff} and longitudinal dispersivities were derived from non-partitioning inert tracer breakthrough curves (BTCs) by fitting the solution of the 1-D advection-dispersion equation to the data. The mass recoveries of oxygen, non-partitioning tracer (KI), and gas-liquid partitioning tracer (SF₆) were obtained from integrated mass breakthrough curves. Integration results were related to the mass of the injected tracer.

The gas saturation S_g was estimated according to the equation

$$S_g(t) = \frac{\theta_{eff,tot} - \theta_{eff}(t)}{\theta_{eff,tot}}, \quad (6)$$

where $\theta_{eff}(t)$ is the effective water-filled porosity at an experimental time t , and $\theta_{eff,tot}$ the effective porosity under fully water saturated conditions.

Modifications of the Original KBD Model and Details on Model Parameters. While the set of processes already considered in *KBD* were sufficient to describe the column experiments, some operational specifics of the column experiments required additional implementations and modifications to the code.

- (1) The flow of water in our experiments was vertically upwards, not downwards, which was accounted for in the model by inverting the direction of gravity. This causes the hydrostatic pressure to be larger at the inlet, in contrast to the original application of the *KBD* code. Gas bubble movement induced by the water flow was not observed.
- (2) Since we did not aim to simulate gas-phase flow as a two-phase flow process, two alternatives were implemented into the *KBD* code, to create initial conditions for each subsequent gas injection and dissolution event. In one approach we assumed that the newly injected gas mixes completely with the gas still present, forming gas bubbles of the same size as initially present, but with a new, averaged composition. In the other approach we assumed that existing gas bubbles are pushed upwards by, and do not mix with, the newly injected gas-phase. This approach results in two regions, the lower one identical to that created by the first injection, and the upper one retaining an averaged composition of the remaining gas-phase (Figure 1 in main article). In both cases it is assumed that gas-phase moving through the porous medium results in entrapped gas bubbles that always have the same typical bubble radius, while the new total injection height results from conservation of gas volume.

It is recognized that both types of processes will occur in the experiments, but assumed that the second approach (without mixing) is the more realistic approximation. During code modifications, both approaches were tested for some of the experiments, with the second approach (no mixing) giving better matches to observed BTCs.

(3) A one-time change in flow velocity was added to the code, because column experiments typically consisted of a first phase with higher average flow velocity due to tracer sampling and a second phase without tracer sampling with about 30% reduced flow velocity.

For a given Darcy flux the gas saturation determines the local pore water velocity, and there is no adjustment of relative permeability due to changing gas saturation. This effect appeared negligible, because the discharge measured during each operation phase of the experiments proved to be approximately constant.

(4) A number of additional output results, output files and run information have been included to allow direct plotting of various results, calculation of recovery rates, and identification of remaining gas-phase volume and composition. Related to the additional input features, several other input parameters were implemented, e.g., gas injection height z_{inj} , gas penetration height z_{gas} , gas-phase composition remaining from a previous injection experiment, and the time and extent of flow velocity change during the course of the experiment.

Impact of Gas Injection Height on Rising Flank of Oxygen BTC. A separate set of simulations was performed to fit the gas-water ratio to the rising flank of the first DO BTC, while calculating the corresponding gas injection height based on the known volume of O₂ gas injected (Figure SI-2). The best match to the initial DO concentration increase at the outlet, occurring after 6 to 8 h, was achieved by a gas-water ratio of 7.5%, which corresponds to an injection height of approximately 27.5 cm (rounded to the grid distances) (Figure SI-2).

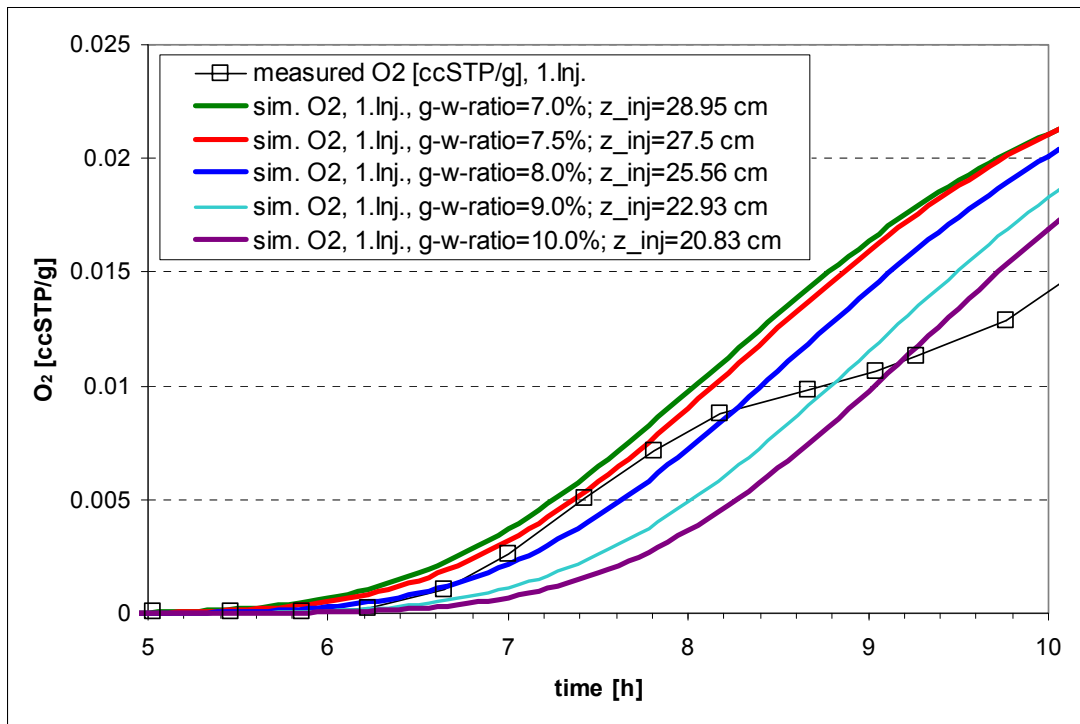


Figure SI-2. Parameter study on the oxygen BTCs for the first injection. The gas-water ratio was varied to obtain the best fit of the very first rise of dissolved oxygen concentrations at the outlet, originating from gas bubbles that penetrated farthest into the porous medium.

Impact of CO₂. Since the experiments presented were designed to resemble natural conditions as closely as possible, a hydrogen carbonate buffered liquid was used. This, however, required an elevated CO₂ partial pressure (about 5200 Pa) in the flushing gas in order to balance the pH to neutral conditions (for refs. see (3)). Since CO₂, due to its volatility, may also impact the gas-water transfer of other gases, additional simulations were carried out with and without CO₂ present in the recharging solution (Figure SI-3). The impact of CO₂ on the dissolution and transport of oxygen was negligible for the pH conditions chosen, based on nearly identical oxygen BTCs in both test cases.

Figure SI-3 also shows how the strong O₂ transfer out of the initially pure O₂ gas-phase quickly increases dissolved oxygen concentrations at the first bubble position (dotted line). This sums up to higher and higher DO concentrations in the water moving from the inlet along oxygen gas bubbles until the farthest bubble position is reached (hashed line). The

effect of advective/dispersive transport through the column can be observed by comparison of the DO BTC at this position and at the outlet.

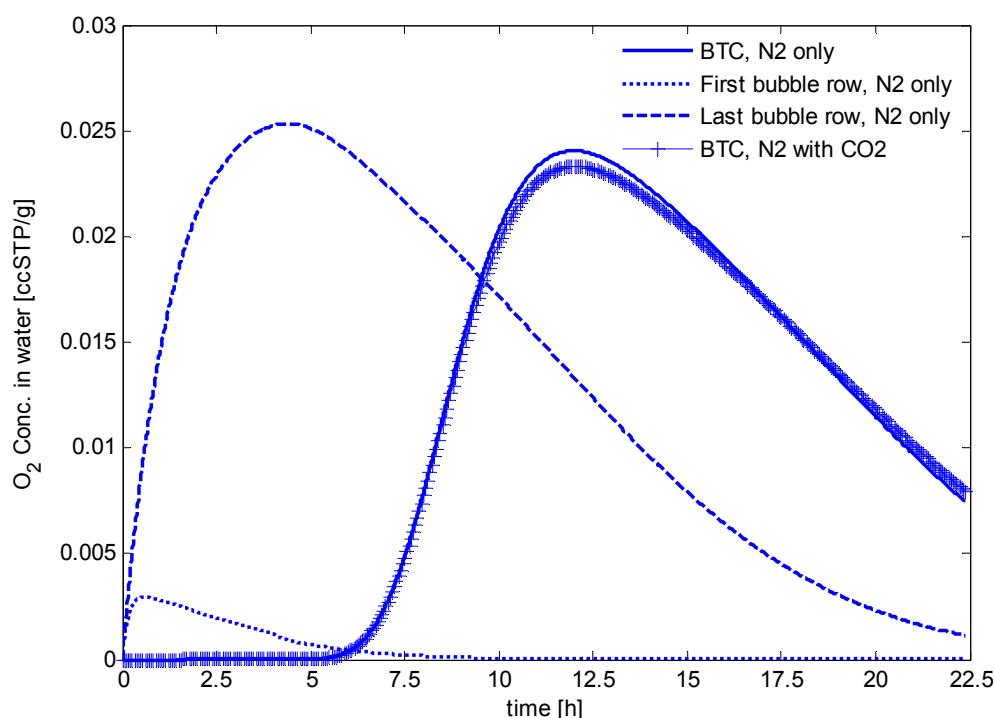


Figure SI-3. Simulation of dissolved O_2 concentration for first injection of pure O_2 gas when recharging with water equilibrated with pure N_2 versus the case with 95% N_2 and 5% CO_2 . Additionally shown are the BTCs at the first and at the farthest bubble location (for the pure N_2 case).

Oxygen Recovery. During the gas sparging experiments, less than 100% of the injected oxygen was recovered at the outlet. In order to identify the reasons, additional recovery tests were carried out on pulses of dissolved oxygen injected into similar columns with varying content of trapped nitrogen gas. In these tests 1.72 mg oxygen dissolved in 40 mL water were injected into a similar column as used for the main experiments and recharged with nitrogen-saturated solution for up to 67 h.

Table SI-2 Recovery of oxygen with different amounts of nitrogen gas present in an otherwise water-saturated column.

volume of nitrogen gas injected [mL]	0	12.5	30	50
recovery of O_2 [%]	96.1	88.2	85.5	71.7
Darcy flux [m/d]	2.1	2.3	2.3	2.3

The results clearly indicate a decrease in oxygen recovery, with increasing amounts of nitrogen gas in the porous medium (Table SI-2 and Figure SI-4). They also show that oxygen can be almost quantitatively recovered unless trapped gas is present. The trend of the BTCs, e.g. an increasing retardation of oxygen transport, with increasing gas saturations is very similar to the one observed (and simulated) for pulsed oxygen injections, demonstrating the impact of nitrogen gas remaining from previous oxygen injection. This is explored further in the following aided by simulated bubble evolution.

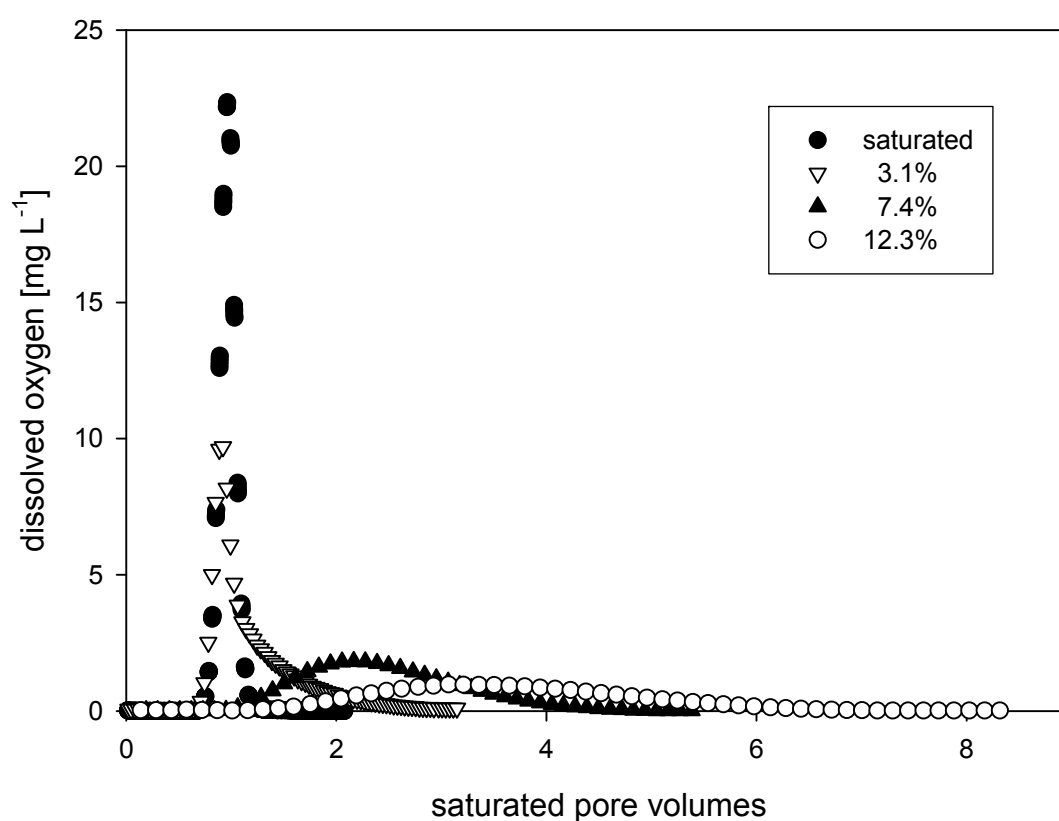


Figure SI-4. Breakthrough of dissolved oxygen, injected as pulse of nearly oxygen saturated water, in a sand column spiked with different amounts of nitrogen gas prior to injection. Percentages represent the mean effective gas saturation over the entire column.

Retardation of Oxygen Transport in the Aqueous Phase. Figure SI-5 illustrates the retardation of oxygen transport due to evolution of nitrogen-rich gas bubbles from previous gas injection-dissolution events. These bubbles initially contain minimal oxygen, but they pick up, store and later release substantial amounts of oxygen via exchange with the aqueous

phase. Near the inlet dissolved oxygen results from rapid partitioning out of the injected oxygen bubbles located there. Thus, the amount of oxygen stored in bubbles decreases quickly at the inlet, but drops more slowly further downstream (Fig. SI-5). Accordingly, this mutual gas-water transfer results in spatial and temporal zoning of oxygen supplying gas layers while water is passing through this fence of trapped gas bubbles.

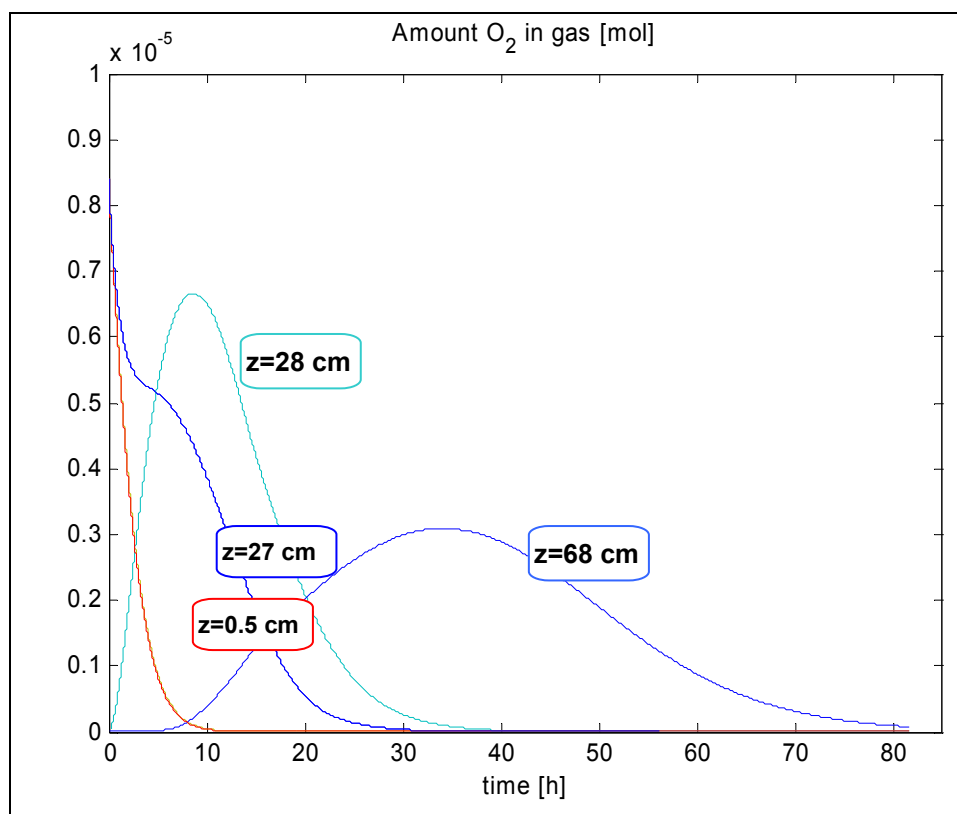


Figure SI-5. Simulated amount of oxygen present in the gas-phase at different distances from the inlet for the fifth oxygen injection. Each layer thickness, i.e. control volume, was 0.5 cm. The transition from freshly injected gas-phase to residual gas from the previous pulses is at $z_{inj}=27.5$ cm, the total gas penetration height is $z_{gas}=68$ cm.

Tailing of SF₆ breakthrough curves. Comparison of the three experimental and simulated SF₆ tailing flanks on a log scale revealed an excellent match, given the purely predictive approach of the simulations (Figure SI-6). However, these pulsed injection experiments had much less gas accumulation than the experiments using the oxygen-based trigger criterion. In this case one effect of the approximations applied in the conceptual model may be seen. The fitted gas bubble radius had been partially interpreted as an effective parameter representing

the real clusters and irregularly shaped gas bubbles. The higher surface area of such features, compared to spherical bubbles with the same gas volume, meant the latter have a relatively decreased gas-water transfer rate. Furthermore, the calculated mass-transfer coefficient in the model inversely depends on bubble radius, thus also lower for larger bubbles (cf. eq 2). Therefore, the conceptual simplification of bubbles and clusters as a single equivalent spherical gas bubble of somewhat larger radius can explain the tendency of the simulations to show a higher gas accumulation and longer tailing.

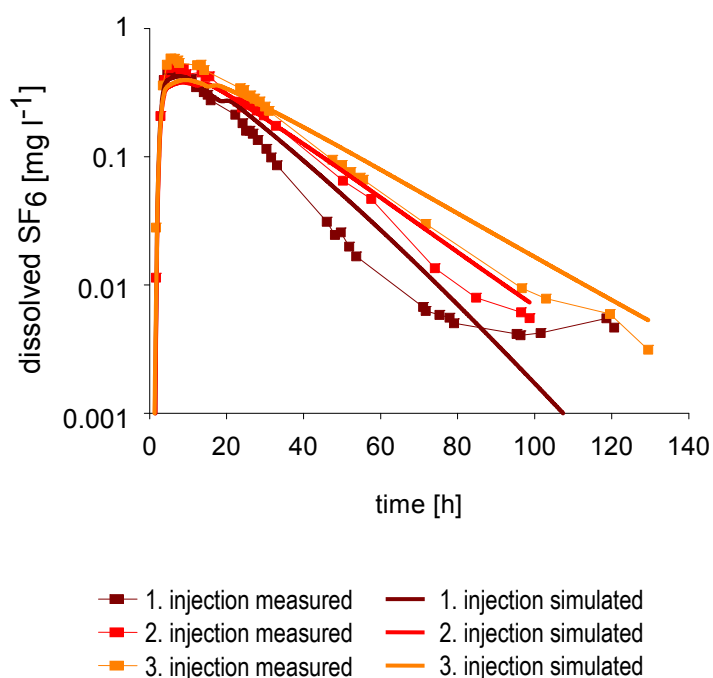


Figure SI-6. Comparison of predicted versus measured SF₆ BTCs for three subsequent gas injection pulses, shown on a log scale.

Literature cited

- (1) Klimant, I.; Kuhl, M.; Glud, R. N.; Holst, G. Optical measurement of oxygen and temperature in microscale: strategies and biological applications. *Sensors and Actuators B-Chemical* **1997**, 38, 29.
- (2) Holocher, J.; Peeters, F.; Aeschbach-Hertig, W.; Kinzelbach, W.; Kipfer, R. Kinetic model of gas bubble dissolution in groundwater and its implications for the dissolved gas composition. *Environmental Science & Technology* **2003**, 37, 1337.
- (3) Morel, F.M.M.; Hering, J.G. Principles and Applications of Aquatic Chemistry. John Wiley & Sons, N.Y. **1993**.