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Electronic Supplementary Material (ESI)

Oxygen profiling of the unsaturated zone using direct push drilling

A. Sopilniak,*[a] T. Elad, [a] R. Elkayam [a,b] and O. Lev*[a]

[a] The Casali Center of Applied Chemistry, The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel.

[b] Wastewater Treatment & Reclamation Plant, SHAFDAN, Mekorot Israel National Water CO.LTD., Israel.

CONTENT

1 Simulation of the oxygen diffusion through a liner equipped with an RTV septum

The primary goal of the simulation was to calculate the penetration time required for oxygen to transverse the septum and reach the measurement location. The concentration of oxygen at the measurement point was calculated 30 minutes after exposure of the outer section of the septum to ambient conditions. Simulations were carried out using COMSOL Multiphysics version 4.4.

The relevant geometry is depicted in Figure S1 frame A. A cylindrical septum with radius r=1 mm and thickness h=1.5 mm was set in the middle of the wall of a cylindrical liner with inner radius of r=17.5 mm and 50 mm length, L. A check point was set in the soil at a distance of 2 mm from the center of the septum, corresponding to the position of the miniature optode at the time of measurement.

The liner was impenetrable to oxygen at all sides, except for diffusion through the cylindrical septum. Diffusion coefficient of oxygen in silicone rubber at 25°C is $D_{septum} = 1.6*10^{-9}$ m^2/sec [1–3], the diffusion coefficients of oxygen in air is $D_0 = 2.3*10^{-5}$ m^2/sec [4], and the diffusion coefficient of O_2 in the soil was calculated by equation 2 in the text and equation S1 [5–8]. The various parameters are defined in Table 1. Effective diffusion for the cases of relative water saturation of 0%, 10%, 25%, 50%, 70% and 100% were used. For the case of 100% saturation, the diffusion was set to be the diffusion coefficient of oxygen in water D_o= $2.1*10^{-9}$ m^2/sec under 760 Torr, 25 °C [9]) multiplied by the void fraction [5].

$$D_{soil} = \frac{D_0 * \Phi^2 * \left(\frac{\varepsilon_g}{\Phi}\right)^{\tau}}{\varepsilon_g + B * \theta_V} \qquad (S1)$$

Fick's laws were assumed to describe the diffusion in the septum as well as in the soil phase. Convection was neglected, and we assumed instantaneous equilibrium at the solution - septum and at the septum – ambient air interfaces. Initial conditions were set as zero oxygen at all locations.

Boundary conditions were set as no-flux at the walls of the liner and in its upper and lower edges except for the outer section of the septum, where the oxygen concentration was set constant at 428 mg/L corresponding to the oxygen solubility in RTV, at 21% O_2/Air atmospheric pressure and 25 ^{0}C [1–3]. The corresponding oxygen solubility in water is 8.3 mg/L[9]. A constant solubility relationship $c_{soil} = K\ c_{septum}$ was set at the soil-septum interface with K =0.019.

The simulation results are depicted in Figures S1 frame B and in Figure S2. For convenience all the results are reported as the equilibrium aqueous phase concentrations corresponding to a solubility of 8.3 mg/L at 21% O_2 at 760 Torr in the gas phase.

Figure S1 frame B depicts the dependence of the time required to reach 0.1 mg/L at the check point as a function of the ratio between the soil and the septum diffusion coefficients. The diffusion coefficients that were checked range from that of silicone rubber, $1.6*10^{-9}$ m^2/sec to the diffusion coefficient of oxygen in air, $2.3*10^{-5}$ m^2/sec. The time required to reach 0.1 mg O_2/L at the check point for dry soil is *ca.* 55 hours.

Frame A of Figure S2 depicts the oxygen time trace at the check point for different levels of water saturation levels. The diffusion coefficients used were the same as those calculated in the article (Figure 4). After a short lag phase, which was required for oxygen to transverse the septum, the concentration of oxygen increased at a decreasing rate. In all cases the level of oxygen at the check point was far less than 0.1 mg/L after 30 minutes. The time required to reach 0.1 mg O_2/L at the check point for dry soil, 50% and 100% saturation marked in the figure by triangle, star and full circle symbols, respectively, are all around the 55 hours. Thus, the practical minimal detection limit of the method is not determined by diffusion through the septum and was set at 0.1 mg/L due to oxygen penetration through the edges of the liners as calculated in the text.

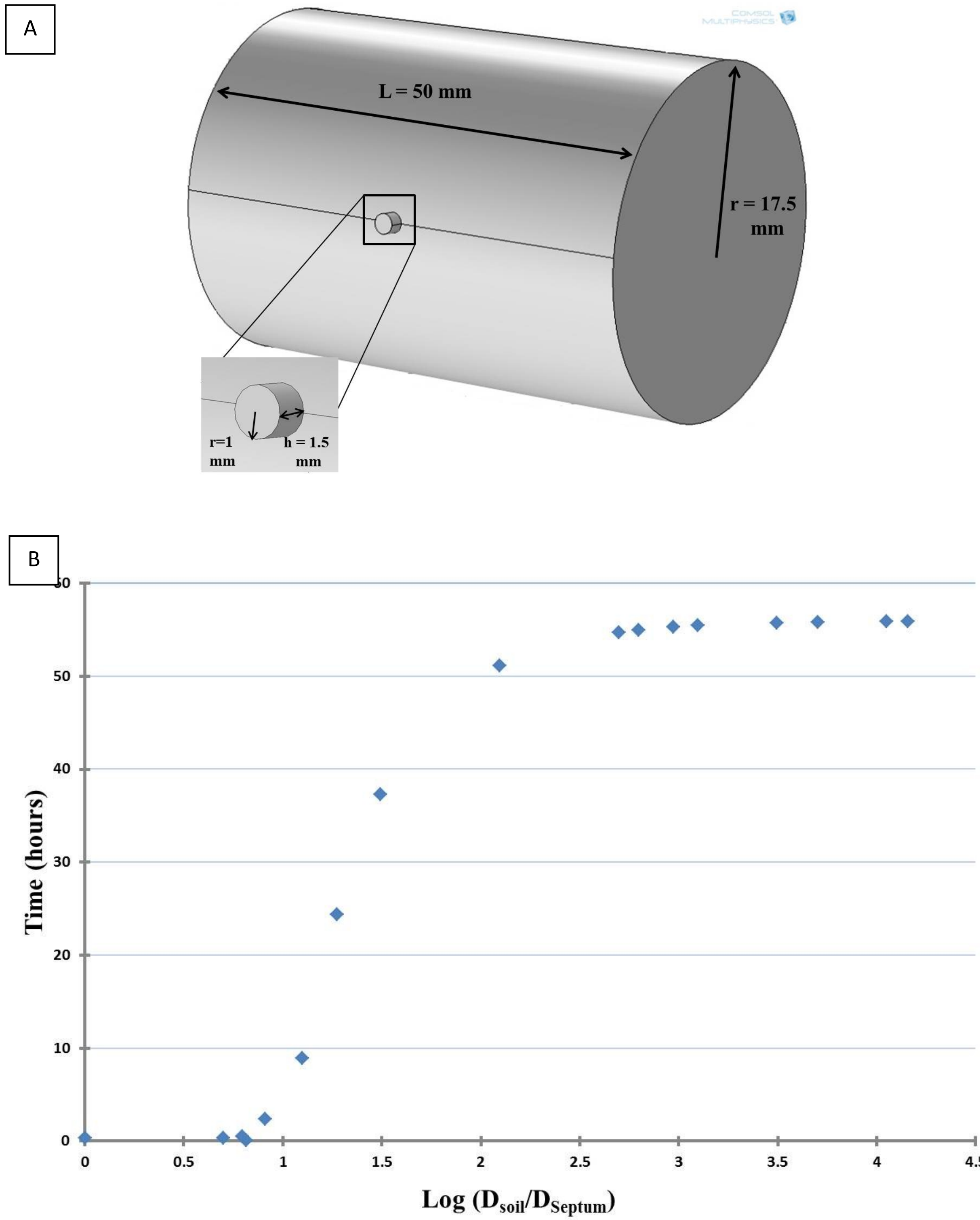

Figure S1 A) A scheme of the simulation set up with the experimental parameters. B) Time required to reach a concentration of 0.1 mg O_2/L in a set up with the geometrical parameters depicted in the text. The diffusion coefficients for silicone rubber and soil were $1.6*10^{-9}$ and $8.1*10^{-6}$ m^2/sec, respectively.

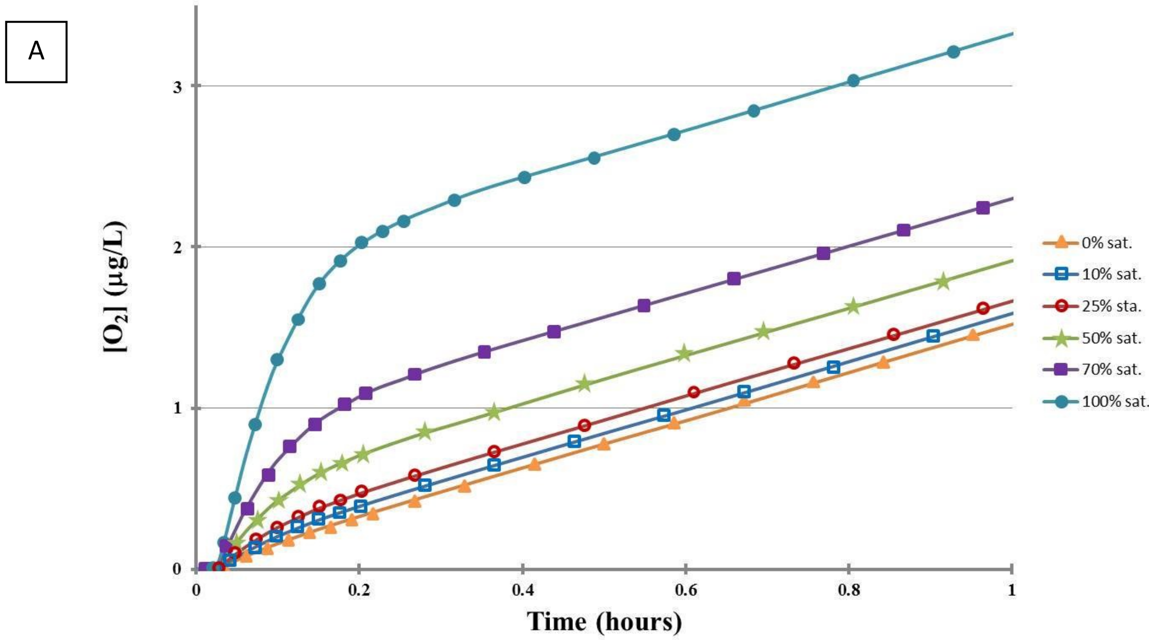

Figure S2 Simulated time trace of oxygen level at the check point as a function of soil wetting for our experimental setup.

2 Response time of the optode in dry and wet soils

The response time of the optode was evaluated by measurement of the oxygen level after the septum was punctured by the optode sleeve, until the signal levelled off. The tests were carried out under different soil wetting conditions and for various oxygen levels. In all cases the sensor response time was less than 6 seconds.

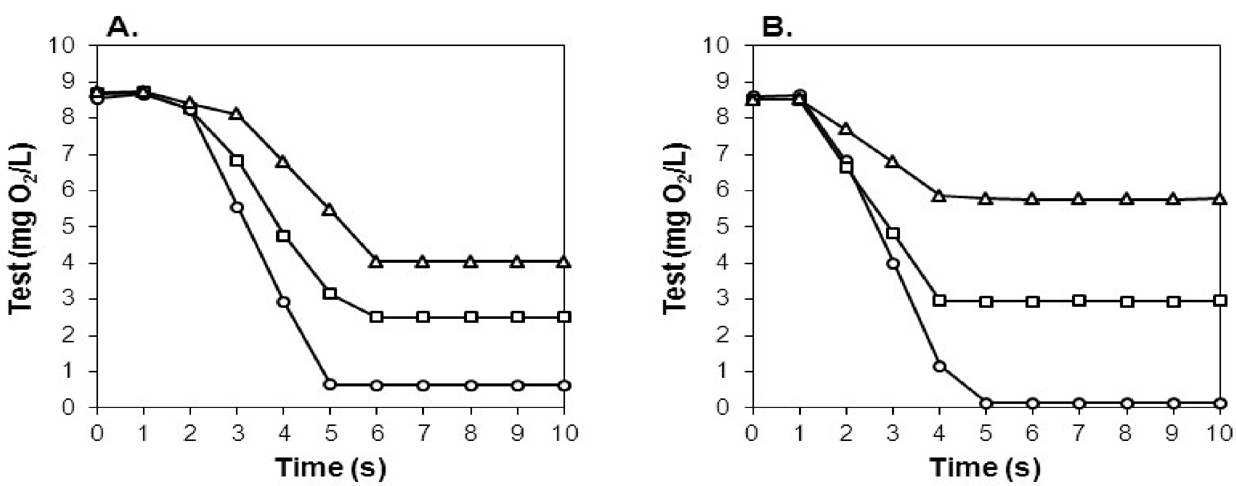

Figure S3 Representative response time curves for different oxygen levels in dry and partially saturated sands. (A) Dry sand (for equilibrium concentration, 0.6 (circle), 2.8 (square), and 4.0 (triangle) mg O_2/L; (B) Semi-saturated sand for 0.3 (circle), 2.8 (square), and 5.3 (triangle) mg O_2/L.

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