Using a Passive Multilayer Sampler for Measuring Detailed Profiles of Gas-Phase VOCs in the Unsaturated Zone

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The purpose of this study was to test in the laboratory the performance of a passive multilayer sampler (MLS) for obtaining detailed profiles of gas-phase volatile organic compounds (VOCs) in unsaturated sediments. The MLS is essentially a chain of isolated, cylindrical stainless steel dialysis cells filled with distilled water and closed with membranes at both ends. The sampling principle is based on passive equilibration of the unsaturated zone gas phase with water in the cells. Using trichloroethene (TCE) as a model VOC, and after testing the required equilibration time in the laboratory (about 50 h), results of a large container (210 L) experiment show that TCE concentrations obtained by the MLS deployed inside a well screen corresponded very well to the profile obtained by dialysis cells buried in the sediment. A field profile taken at the saturated–unsaturated interface region of a VOC-contaminated area using the MLS shows steep TCE concentration gradients (1119 ng TCE/L-saturated) in the gas phase of the unsaturated zone just above the water table.

Introduction

Volatile organic compounds (VOCs) introduced into the unsaturated zone of an aquifer via spills or by volatization from contaminated groundwater may be transported as vapors, creating widespread gas plumes (e.g., refs 1–6). In general, vapor phase transport may be an important cause of subsurface contamination for any VOC having a Henry's constant (KH) of at least 50 Pa·m³/mol and a vapor pressure ≥130 Pa at ambient temperature (7). Widespread and common VOC contaminants such as chlorinated solvents (e.g., trichloroethene, tetrachloroethene, trichloroethane) and liquid hydrocarbon components (e.g., benzene, toluene, xylene) fulfill these requirements. Many studies have shown gaseous diffusion to be a major mechanism in the transport of contaminant vapors through the unsaturated zone (1, 4, 5, 8, 9). Vapors can also be transported by advection due to density driven flow (2, 6, 10, 11), barometric pressure changes (12–14), fluctuations of the water table (4, 15, 16), and water infiltration (16). In all cases, the subsurface transport of VOC vapors is influenced by air–water partitioning (1, 17) and sorption to sediments (18–20).

To make correct estimates of fluxes across the soil/atmosphere and saturated zone/unsaturated zone interfaces, it is important to know the concentration distribution of VOC vapors in the unsaturated zone and to understand the mechanisms controlling vapor transport through it and across both interfaces. The unsaturated/saturated interface region (SUIR), which extends from an imaginary plane of 100% water saturation and positive water pressure (p = 0) to the surface of the capillary fringe, is generally characterized by high pore water content as compared with residual pore water in the unsaturated zone and by a relatively large gas-filled porosity as compared to that in the saturated zone proper (21, 22). Moreover, tortuosity and the area available for liquid and vapor mass fluxes at the SUIR are both highly variable since moisture content is also spatially and temporally variable. Mass transport of VOCs across the SUIR plays an important role in controlling contaminant fate in the subsurface. Transport of VOCs from the unsaturated zone to the saturated zone is a common mechanism of groundwater contamination, while volatilization of contaminants from groundwater through the SUIR and transport upward through the unsaturated zone to the atmosphere can provide a natural remediation pathway (4). For example, Smith et al. (12) found that annual TCE removal rates due to natural upward fluxes by diffusion were considerably lower than the removal rates by a subsurface pump-and-treat system at the Piscataway Arsenal in New Jersey.

Cases in the unsaturated zone are generally sampled by either active or passive methods (6, 23–26). In active sampling, a hollow pipe is commonly driven into the ground to a prescribed depth and a pump or vacuum canister is used to pull gas from the surface through the pipe. An alternative passive sampling method for obtaining gas samples involves use of packers and a sampling device inside an observation well screened along the unsaturated zone (26). In both techniques, the sample is collected into a sampling receptacle (e.g., syringe, Tedlar bag, or Summa canister) or the pipe can be directly connected to an off-site gas chromatograph. Active sampling requires specialized field equipment and a trained operator. Some common problems associated with this technique include leakage of samples from "gasight" receptacles, gas flow through preferential pathways (shunts) from different depths in the sediment, and technical limitations on the number of depths that can be sampled along a single profile. Moreover, dynamic pumping of vapors from the unsaturated zone may distort actual subsurface concentrations and misrepresent the vertical vapor distribution profile.

In commonly used passive sampling methods, an absorber is buried at a prescribed depth and allowed to collect VOCs from the unsaturated zone. After a predetermined time, the absorber is retrieved, sealed, and transported to the laboratory for VOC analysis. Disadvantages of this passive sampling method include delayed results, limited sampling depths, and limited number of sampling points along a single profile. Neither the active nor passive methods summarized above provide detailed vertical information (scale of centimeters) about VOC vapor phase distribution in the unsaturated zone. Therefore, they are not useful for exploring vapor behavior across the SUIR, where water content is highly...
The edges of two consecutive cells is 6 cm. Flexible Viton seals 0.3 mm thick made of Teflon-coated glass fibers that fit the inner diameter of the well screen separate between consecutive cells. For obtaining a groundwater profile or a profile of gases from the unsaturated zone, the cells are filled with distilled water and are closed at both ends with a dialysis membrane crimped in a PVC loop with Viton O-ring. The sampler is lowered into an observation well and retrieved from it after a given time interval (usually several weeks), and the chemical composition of the water in each dialysis cell is then determined.

In the unsaturated zone, gases will partition between the gas phase of the nearby sediment and water inside the dialysis cell. After equilibration, concentrations of VOCs measured in the water (Cw) of each dialysis cell are used to calculate concentrations in the gas phase of the unsaturated zone (Cg) according to:

\[ C_g = C_w \cdot k_P \]

where \( k_P \) is a dimensionless form of Henry's constant. The applicability of Henry's constant relies on the assumption that for slightly water-soluble compounds such as VOCs, the air-water partitioning ratio is negligibly affected by solute concentration or by the presence of VOC mixtures. Since Henry's constants vary with temperature (36, 37), in shallow aquifers where temperature is variable with time and depth, temperature of water in the dialysis cells should be measured upon retrieval, and then temperature-corrected constants should be applied. For deep aquifers where temperature is fairly constant, such corrections are minor.

**Experimental Setup — General**

The rate of attainment of equilibrium between TCE vapor and water in the dialysis cells was studied in closed glass jars. Two jar setups were used: (a) dialysis cells replaced in jars without any porous matrix and (b) dialysis cells embedded in air-dry packed sand. Gas-phase profiles of TCE in granular sediments were then obtained using dialysis cells embedded in open glass vessels packed with various porous media. All laboratory experiments were conducted at room temperature (23 ± 2 °C). A TCE gas-phase profile was also obtained inside a large container to test the performance of the MLS inside a screened pipe for obtaining vapor phase profiles that accurately represent the TCE gas-phase profile of the surrounding unsaturated porous media. After these laboratory tests, the MLS was deployed in a monitoring well to measure a TCE gas-phase profile in the region of the saturated—unsaturated interface at a site contaminated with chlorinated solvents.

**Materials.** Trichloroethylene (-99.5% pure, Aldrich Co., Milwaukee, WI) and naphthalene (Analyzed grade; Baker, Phillipsburg, NJ) were used for equilibration experiments in closed jars and open cylinders. Industrial Al grade TCE (+99.9% purity by weight), donated by Gadot Chemicals Israel, was used in the container experiment. All chemicals were used without further purification. Ultrapure (Milli-Q) water was used in all experiments. Versapor 0.2 µm hydrophilic membranes ( Pall Co., Ann Arbor, MI) were used throughout this study. Selected physical and chemical properties of TCE and naphthalene are presented in Table 1.

Three porous media were used in this study: (a) fine sand (<150 µm) collected from a coastal beach near Haifa, Israel; (b) commercial coarse sand (30% ov:wc dry-sieving between 1000 and 2000 µm, 60% between 500 and 1000 µm, and 10% < 500 µm); and (c) sandy-loam soil (20% clay, 5% silt, 75% sand) collected at Bet Dagan, Israel. All media were stored air-dry at room temperature. Crundor water content (εp) of the porous media was determined after drying overnight at 105 °C and is expressed as weight percent on a dry-weight basis. Field capacity was estimated after wetting the medium with excess water and allowing free drainage for 4 days.

**Analytical Measurements.** Aqueous TCE standards were prepared by injecting 100 µL amounts of TCE stock (1% TCE in
<table>
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<th>Property</th>
<th>TCE</th>
<th>Naphthalene</th>
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<td>Molecular weight (mg/L)</td>
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<td>128.18</td>
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<td>1100-1370</td>
<td>30-32</td>
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<tr>
<td>Vapor pressure (Pa)</td>
<td>13000</td>
<td>6.7 - 10.9</td>
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<td>6307-8000</td>
<td>[334-425]</td>
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<tr>
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<td>11.60</td>
</tr>
<tr>
<td>(dimensionless constant, Kₜ⁻¹)</td>
<td>99.00</td>
<td>4.39</td>
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<tr>
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<tr>
<td>log Kₜw</td>
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<td>3.36</td>
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* Calculated from PV = nRT, where P = vapor pressure, V = volume, n = number of moles, R = ideal gas constant, and T = absolute temperature.

** Calculated from Ac = (Ac/K), where Ac is a dimensionless Henry's constant, and K is Henry's constant in units of Pa·m³/mol.

**FIGURE 2.** Schematic representation of three experimental setups designed to test the suitability of the dialysis cells to sample TCE vapor and TCE vapor profiles. (a) TCE source and dialysis cell with distilled water in an air-filled jar; (b) TCE source and "double-cell" configuration (small vial with distilled water inside an empty dialysis cell, each covered with a membrane to prevent water losses by capillary suction) in a sand-filled jar; and (c) TCE source and four double-cells in a sand-filled open glass cylinder.

in methanol) into 10 mL of water in 22 mL headspace vials that were immediately capped with steel crimp top caps equipped with Teflon-lined silicone septa. Headspace headspace sampling was by automated injection (COMBI PAL CTC Analytics). Headspace samples were analyzed by gas chromatograph (Varian CP-3800) equipped with flame ionization detector. Linear external standard calibration curves were obtained by measuring TCE peak area in headspace over aqueous TCE standard solutions. Aqueous samples were prepared by transferring 200 mL of water sample using a Pipetman into 9.8 mL of water in 22 mL headspace vials, followed immediately by capping. Results obtained by this analytical procedure were highly reproducible (3.3% quiet). Quantification of VOC analyses in field samples was performed by PEI Laboratories, Florida by GC/MS according to EPA method 8260h.

Aqueous naphthalene standards were prepared from a concentrated stock solution of 0.1% naphthalene (w/v) in methanol with appropriate dilutions into water in glass volumetric flasks (maximum methanol content was 0.15%). Naphthalene was analyzed by spectrophotometric methods (Shimadzu, RF-5301PC) at 274 nm (excitation) and 330 nm (emission) wavelengths. A linear calibration curve was prepared from aqueous standards in the range of 0.1-1.65 mg/L, and samples were diluted as needed. To minimize loss of naphthalene due to adsorption to glassware, fluorescence measurements were performed immediately after preparation of standards and samples.

Electrical conductivity (EC) was measured in the field with a portable EC meter (Horiba, Twin Cond. B-173) with instrument reproducibility of ±1%.

**Dialysis Cell Equilibration Experiments.** To assess rates of achievement of equilibrium between VOC vapors and water inside the dialysis cells, a series of 20 mL dialysis cells filled with water and closed at both ends with Teflon-lined screw-caps. An open glass vial containing a VOC source (either liquid TCE or solid naphthalene) was placed in each jar (Figure 2a). The VOC source was in excess, i.e., an amount calculated to be much greater than that able to partition into the jar space and the cell water. The jars were closed for the desired time period and then sacrificed to determine the
concentration of TCE or naphthalene in the cell water. Equilibrium experiments were performed both in empty ("air-filled") jars and in jars filled with sand. The sand-filled jars required a slightly different dialysis cell setup, since direct contact between the sand and wet dialysis membranes resulted in capillary suction of the cell water. A "double-cell" was designed which consisted of a small glass vial (4 mL), closed with crimp-top Al seal and the same Versapor membrane, placed inside the 20 mL membrane-sealed dialysis cell (Figure 2b). It should be noted that the problem of direct contact between sand and wet cell membranes arises only in laboratory experimental setups since when the MLS is lowered into a well, the dialysis cells are protected inside the well screen. In sand-filled jars, the TCE source was also placed in a 4 mL vial closed with a membrane, to recreate the TCE source. The same double-cell arrangement was used in open cylinder experiments (Figure 2c; see below).

Open Cylinder Experiments. The utility of dialysis cells for determining vapor phase profiles in sediments was assessed using 1 L 30–40 cm long, open glass cylinders. A TCE source was placed at the bottom of the cylinders that were then packed with the desired porous medium to which 4–6 double-cells were buried at different depths (Figure 2c). The cylinders were left open in an operating fume hood. At a given time, the double-cells were retrieved and aqueous phase concentrations of TCE were determined. The cylinders were packed either homogeneously with fine or coarse air-dry sand (d50 = 0.15 cm) or with a layer of wet sand or sandy-loam soil between two layers of dry sand. Bulk densities of the packed media were determined from the mass of the porous medium packed in a defined volume of the glass cylinder. Total porosity (n) was determined by assuming average particle density of 2.65 g/cm³ (45). Air-filled porosity (nA) was determined by subtracting the volume occupied by water from total porosity.

Large Container Experiment. The suitability of the complete MLS setup for obtaining a gas-phase profile of unsaturated sediments was tested in a 210 L container in which a 10 cm ID screened PVC pipe was mounted in the center (Pumpenbrenne, Germany, slot size = 0.5 mm, open area = 6%). The container was designed to allow the addition of liquid TCE through an external inlet at the base (Figure 3). To support the porous media, a coarse steel grid on a 5 cm high platform was placed at the bottom of the container. The grid was covered by 2 layers of fine screens with a layer of Versapor membrane between them and a second coarse steel grid on top. The container was packed with air-dry coarse sand (d50 = 0.15 cm) and a 5 cm thick sandy-loam soil layer (d50 = 0.18 cm) in the middle (Figure 3). During packing, double-cells (in this case, 50 mL water-filled cells capped with Versapor membranes, inside empty 150 mL cells also capped with Versapor membranes were buried at six different depths. At each depth three double-cells were embedded in the sand; each of them was connected to the surface by a metal wire that enabled cell retrieval. After packing, the MLS (with the same double-cell arrangement) was lowered into the well screen. Four liters of Industrial Al-grade TCE was introduced into the bottom of the container. The MLS and buried cells were retrieved from the container after one week. The container was located in an open shaded area (daily temperature between 20 and 30 °C).

Field Profile. Study Site and Monitoring Well. The study area is located in the Tel Aviv metropolitan area in the sandy phreatic Coastal Plain aquifer of Israel. The average thickness of the unsaturated and saturated zones is about 60 and 150 m, respectively. An ongoing investigation has shown that bulk groundwater in this area is extensively contaminated.
with many VOCs including tetrachloroethene, trichloroethene, and 1,2-dichloroethenes along a swatch parallel to the coast stretching at least 20 km (44, 49). Concentrations in bulk groundwater of the most common contaminants reached levels to 100 ppb or more. At the heart of the contamination plume, below a former industrial site, an observation well was designed for studying the water table region and shallow groundwater was installed with a continuous 10 cm ID PVC screen from 13 m below the water table to 3 m above it. Along this 18 m interval the sediment in the aquifer is composed of medium size sand and sandstone. Below the water table the sediment collapsed onto the PVC screen. Above the water table, a sand pack was installed between the 10 cm ID PVC screen and the borehole wall (20 cm diameter).

MLS Installation and Retrieval. To obtain a profile of VOC vapor concentration in the unsaturated zone and VOC aqueous concentration in the saturated zone, the MLS was deployed in the well from ca. 1 m above the water table to 3 m below it. The exact position of the water table in relation to the MLS is evident from the electrical conductivity (EC) of the water in each dialysis cell upon retrieval above the water table EC ≤ 0.125 mS/cm; below the water table EC ≥ 1.34 mS/cm. The MLS was retrieved from the observation well 2 months after deployment. Immediately upon retrieval, the cells were closed with PVC caps until each cell was sampled by filling duplicate 40 mL VOC vials by pouring from the dialysis cells in a randomized order. EC was measured in the water remaining in each cell. Water samples for VOC analysis were stored on ice and transferred to the laboratory where they were held for same-day analysis air striping to the analytical laboratory in a refrigerated container guaranteed to maintain temperature between 2 and 8 °C. The samples were analyzed after 4 days by the analytical laboratory in good condition at 4 °C and were analyzed within one week of arrival.

Determination of Potential TCE Loss during MLS Retrieval. Retrieving the MLS from a depth of about 20 m below ground surface takes 5 to 10 min. Sampling 20–30 cells of the MLS typically takes between 0.5 and 1 h. During this time period, and although the cells are closed with PVC caps, there may be some losses of VOCs. To evaluate the extent of such losses, a series of dialysis cells was placed in glass jars with a TCE source, as in the equilibration experiments described above (Figure 2a). The cells were retrieved after 2h and were immediately closed with PVC caps as in the field protocol. Analytical TCE concentrations were determined as above from 0 and 60 min after retrieval.

Results and Discussion

Equilibration of Dialysis Cells with VOC Vapors in Jar Experiments. The results of equilibration experiments are presented in Figure 4. Since the liquid TCE source was placed in the jar in great excess, it is assumed that the vapor concentration in the jar space rapidly reached saturated TCE vapor concentration (in the range of 334–356 mg/L-air) (Table 1). It was also expected that partitioning between the gas and water phases will be according to Henry’s law, such that at equilibrium, the aqueous phase TCE concentration in the dialysis cells will be equal to TCE aqueous solubility (1000–1500 mg/L; Table 1). The applicability of Henry’s law over the full TCE solubility range in water is apparently well-founded based on results reported in the literature for chlorinated solvents (48) and benzene and toluene (47).

Average equilibrium concentration of TCE in the cells was 1349 mg/L-water (st.dev. = 43.8 mg/L-water for the last 4 data points in Figure 4a), corresponding to 540 (±17.5) mg/L-air, using an average K_a of 0.00 (Table 1). This value is well within the range of values reported in the literature (Table 1). According to Figure 4a, equilibrium between gas and water phase TCE ratio of concentration at time t (C_W /C_G) to concentration at equilibrium (C_EQ) was achieved after about 50 h, whereas a value of C_C /C_EQ = 0.95 was reached after 24 h (Figure 4a inset). Using double-cells (Figure 2b), a similar equilibration period for TCE vapors was observed in the dry sand-filled jar as compared with the air-filled jar (Figure 4b, note that in this case double-cells were also used in the air-filled jar experiment). Thus, for this specific experimental setup, TCE diffusion through the membranes and cell water determines the rate of attainment of equilibrium between the gas and water phases rather than diffusion through the dry porous medium.

Equilibration of water with naphthalene vapors in air-filled jars was reached only after about 70 h (Figure 4c). This could be the result of a much slower evaporation rate for solid naphthalene (melting point 55 °C) compared with 4.46 for liquid TCE; evaporation rate is a dimensionless parameter comparing compound evaporation rate to evaporation rate of n-butyl acetate defined as unity (38) and (b) presumably greater sorption of naphthalene to the cell membrane and glassware due to its higher hydrophobicity (higher K_a). The average concentration of naphthalene found in the dialysis cells at equilibrium was 25.2
mg/L-water (st. dev. = 2.81 mg/L-water based on last 8 points between 69 and 117 h; not shown), which is close to reported literature values (30-32 mg/L; Table I).

The results of these experiments suggest that the dialysis cells are suitable for evaluating gas-phase concentrations of VOCs, after an appropriate equilibration period is determined empirically in the laboratory.

**Diffusion Profiles in Sand-Pack Open Cylinders.** Data obtained in the experiments conducted in sand-packed open glass cylinders are presented in Figure 5 with aqueous TCE concentrations in the dialysis cells on the lower x-axis and gas-phase concentrations on the upper x-axis. To measure a steady state gas phase profile in these cylinders, a steady state profile needs to develop in the porous medium, followed by establishment of equilibrium between the gas phase and the water in the dialysis cells (about 50 h; Figure 3). As shown in Figure 5a, TCE gradients obtained between 47.5 and 117 h were quite similar. Since attainment of equilibrium between the gas phase and the water in the dialysis cell required about 50 h (Figure 4), we can assume that steady state gas profiles were developed in the cylinders relatively fast.

The profiles presented in Figure 5a are linear (r² = 0.99).

According to Fick's first law (\( P = -D \frac{dC}{dx} \)), where \( P \) is the diffusive VOC flux (M L⁻¹ T⁻¹), \( D \) is the diffusion coefficient (L² T⁻¹), and \( \frac{dC}{dx} \) is the soil-gas vertical concentration gradient, a linear dependence of gas concentration on distance from the source (as in Figure 5a) could be expected in the homogeneously sand-packed open cylinder. In these experiments, where the top of the cylinder is open to the atmosphere (Figure 2c), it is expected that TCE gas-phase concentration will approach zero at the top of the sand pack and will approach the saturated vapor value of 540 mg TCE/L-air (according to our dialysis cell equilibration experiments; Figure 4) at the interface between the TCE source and the sand. The regression lines depicted in Figure 5a were extrapolated to zero concentration at the top of the sand column. Concentrations extrapolated to the liquid TCE interface were somewhat lower than expected (0.33 to 0.40 mg/L-air for the three lines depicted in Figure 5a). We postulate that this result is due to the point source nature of the TCE source which occupies only ~2% of the cross sectional area of the cylinder base. Diffusion from a point source is radially more horizontal, such that the concentration of TCE in a specific horizontal layer is not homogeneous. Thus the TCE content of the dialysis cells reflects the average gas-phase concentration in each horizontal layer along the profile. When two TCE sources were placed at the base of the cylinder (inset Figure 5a), geometric effects were minimized and the extrapolated concentrations were closer to the expected values (540 mg TCE/L-air, average of two profiles obtained after 48 and 71 h).

Figure 5b,c depicts TCE profiles obtained in open cylinders packed with heterogeneous porous media. The TCE concentration gradient was slightly changed when a 3.5 cm layer of wet coarse sand (\( \phi_w = 4.0\% \); 74% of field capacity) was located between two layers of dry coarse sand. In contrast, an abrupt change in the gas-phase TCE profile was observed when the cylinder was packed with a wet sandy-loam soil layer (\( \phi_w = 17.5\% \); 83.7% of field capacity) located between two dry coarse sand layers (Figure 5c). Considering a gas-phase tortuosity factor for porous media (\( \tau_g \)) and adopting the theoretical approach taken by Millington (48) for the relationship between \( \tau_g \), total porosity (\( \theta_t \)), average gas-filled porosity (\( \theta_f \)), \( \theta_f \) (where \( \theta_f = \theta_t / \tau_g \)), we computed the relative tortuosity factors on the subsampled media. The tortuosity factors are 0.73 for the wet coarse sand (\( \phi_w = 4.0\% \); 0.48 for the wet coarse sand (\( \phi_w = 0.33\% \); \( \phi_t = 0.40\% \)); and 0.037 for the wet sandy-loam (\( \phi_w = 0.11\% \); \( \phi_t = 0.41\% \)). As such, the effective diffusion coefficient (\( D_{eq} \)) of porous media, \( D_{eq} = D_{ref} \Sigma \theta_f \) (where \( D_{ref} \) is the free-air diffusion coefficient) for the dry coarse sand is calculated to be about 1.5 times greater than \( D_{ref} \) of wet sand and about 20 times greater than \( D_{ref} \) of the wet sandy-loam layer. The profile presented in Figure 5c is extrapolated to TCE vapor saturation concentration if the TCE gradient below the sandy-loam layer (Figure 5c) is extrapolated to the TCE source, a value of 513 mg/L-air is obtained, similar to the value obtained in the jar.
Figure 6. TCE profile obtained in the large container experiment. Bold squares denote results of double cells located inside the well screen (MLS). Empty squares and horizontal bars denote average concentration and standard deviation of three cells embedded at the same depth in the container. The regression lines depict concentration gradients calculated from cells embedded in the air-dry coarse sand below and above the wet sandy-loam layer ($\theta = 16.8\%$).

The profiles presented in Figure 5 clearly demonstrate the reliability of dialysis cells embedded in unsaturated porous media to capture abrupt changes in concentration gradients of VOC vapors on a scale of centimeters.

Large Container Experiment. The results of the container experiment are presented in Figure 6. Open squares represent average TCE concentrations in air obtained for replicate cells buried in the sediment at the same depth. The vapor phase TCE profile obtained with the MLS (filled squares) is seen to be in good agreement with the profile obtained from the buried dialysis cells. As in the open glass cylinder experiment depicted in Figure 5e, the wet sandy-loam layer in the middle of the container ($\theta = 16.8\%$; 80% of field capacity) created an abrupt change in the TCE gas phase concentration gradient. The variability in TCE concentration between cells located at the same depth in the sediment is considered to be related to heterogeneity in the packing of the 210 L container. This phenomenon is particularly noticeable below the sandy-loam layer in the proximity of the TCE source. Note that in the container experiment one of the MLS dialysis cells was located at the depth of the sandy-loam layer. TCE concentration in this cell reflects the expected TCE trend and clearly demonstrates the sensitivity and suitability of the MLS for obtaining detailed and accurate gas profiles. Results show that the gas profile obtained with the MLS inside the well reflects the gas profile in the surrounding porous media (Figure 6).

Field Application. Possible TCE Loss upon MLS Retrieval. Figure 7 depicts the loss of TCE from dialysis cells over the course of an hour in the laboratory. Concentrations decrease gradually to about 90% of their initial value over a 60 min interval, which is about the maximum time required in the field to retrieve the MLS from a depth of about 20 m and sample about 55 dialysis cells. Thus, we estimate that in this study there is an average TCE loss of about 5%. Losses are randomly distributed along the profile as dialysis cells are sampled in a random order. For compounds having much higher vapor pressure or Henry's constant than TCE (for example, vinyl chloride with $K_{H}$ of 2.3 at 25 °C (98)), as compared with 0.4 for TCE) losses from the dialysis cells during MLS retrieval is expected to be higher than shown for TCE.

Field Profile. A field profile of the SUE obtained at the concentrations of coastal plain aquifer of Israel in the Tel-Aviv area is depicted in Figure 8 (water table at $-17.16$ m below ground surface). Above the water table, the concentrations...
of TCE are given both in water of the diaphysis cells and for the corresponding calculated gas-phase concentrations. The highest TCE concentrations (310 000 μg/L-water, corresponding to 124 000 μg/L-air) were detected 14 cm above the water table, decreasing with distance from the water table both in the unsaturated zone (to 150 000 μg/L-water, 60 000 μg/L-air) and the saturated zone (to 43 000 μg/L-water, 304 cm below the water table). Sharp gas-phase TCE gradients were also observed by McCarthy and Johnson (4) near the water table in a lab-scale aquifer model. They observed variation in TCE concentrations by 2–3 orders of magnitude across the capillary fringe and related it to the high variability in water content in this region. Figure 8 is shown as an example to illustrate the type of detailed information that might be obtained with the M.S. At this stage we do not know whether at this study site a TCE gas plume is causing groundwater contamination across the SUFR, or whether contaminated groundwater is degrading into the unsaturated zone through the SUFR.

The Potential of the M.S. for Studying VOCs in the Unsaturated Zone and at the SUFR. The exclusive feature of the M.S. for measuring vapor phase VOC concentrations relies on its suitability for measuring with great detail VOCs in the saturated and unsaturated zones simultaneously in one borehole. This requires the existence of a borehole and a well screen along the saturated and unsaturated zones, which may limit the accessibility of this method. Using the M.S., each diaphysis cell is a continuous passive sampling system where the concentration will change according to the concentration in both the gas and liquid phases in the cell vicinity. In the example presented in Figure 8 note the possibility of (1) detecting steep TCE concentration gradients in the gas phase of the unsaturated zone (119 μg TCE/L-air/cm) within a vertical distance of only 57 cm and (2) obtaining a continuous TCE profile across the SUFR and into both the unsaturated and saturated zones. Such details and gradients can only be detected under passive sampling conditions. This unique attribute makes the M.S. are especially useful tool for exploring vapor transport behavior during water table fluctuations and under the extremely variable conditions of water content prevailing in the SUFR (21, 22). It should be recognized that given the necessary equilibrium period, the M.S. collects time-averaged samples (maximum equilibrium time about 24 h for TCE).

Detailed M.S. profiles can also be useful for detecting VOCs below relatively impermeable barriers (such as clay or perched water), which could easily be missed in more traditional gas surveys. In fact, the profiles presented in Figures 5c and 6 underscore the limited information that may be obtained using shallow soil gas surveys, whereby very low or zero VOC concentrations may be obtained above geologic barriers, thus completely distorting the real picture of the gas phase plume in important regions of the unsaturated zone. Finally, the use of diaphysis cells instead of direct gas-phase measurements can increase the analytical sensitivity for organic contaminants with relatively low vapor pressure or low Henry’s constants. For example, upon equilibrium, naphthalene with K_H of 0.017–0.0197 (Table 1) will be found in concentrations about 50 times higher in the diaphysis cells than in the gas phase.

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