Assessing Volatile Organic Chemicals in Soils via Passive Sampling

Raffaella Borrelli[1], Alessandro Oldani[1], Fabio Vago[1], John MacFarlane[2], Philip M. Gschwend[2], Luciano M. Zaninetta[3]

[1] CENTR- Renewable Energy and Environmental R&D - Istituto Eni Donegani, Novara, Italy; [2] Massachusetts Institute of Technology, Cambridge, Massachusetts, USA; [3] Syndial, San Donato Milanese, Italy

Group 2

Abstract

In order to advance soil/vadose zone site characterizations for VOCs, we have developed and field-tested a passive sampling approach (i.e., one in which no active gas pumping is used). We use low density polyethylene (LDPE) which can absorb nonionic organic compounds reaching equilibrium with the surroundings; knowing those chemicals' polyethylene-air partition coefficients, the resultant concentrations of the accumulated VOCs in the polyethylene can be used to quantify their corresponding soil gas concentrations. Deployment of these passive samplers at multiple depths below ground revealed soil gas concentration gradients indicative of transport potential both to groundwater below and people above.

## Methods

Low Density Polyethylene (PE)
LDPE sheet is cleaned by soaking in DCM, MeOH, and water. At MIT, the LDPE is formed into cylinders and impregnated with performance reference compound (1,4-bromofluorobenzene). At Eni, PE films are used without PRC; but the sampling technique was assessed by carrying out lab-scale batch tests. These were done using 70 μm thick PE films that were exposed in the headspace of 10 mL glass vials sealed with Teflon-faced butyl septa and aluminum caps and containing 100 μL of a standard solution of VOCs deposited on a filter. By analyzing the concentrations of the VOC absorbed within the PE (C_{PE}) at different exposure times (from 1 h to 264 h) we found that at 1 to 2 hours are required to reach equilibrium conditions between the PE and air.

Deployment Methods

Eni
LDPE sheet placed in compartment at end of probe…driven into soil up To 1 m and left 1 or 2 days
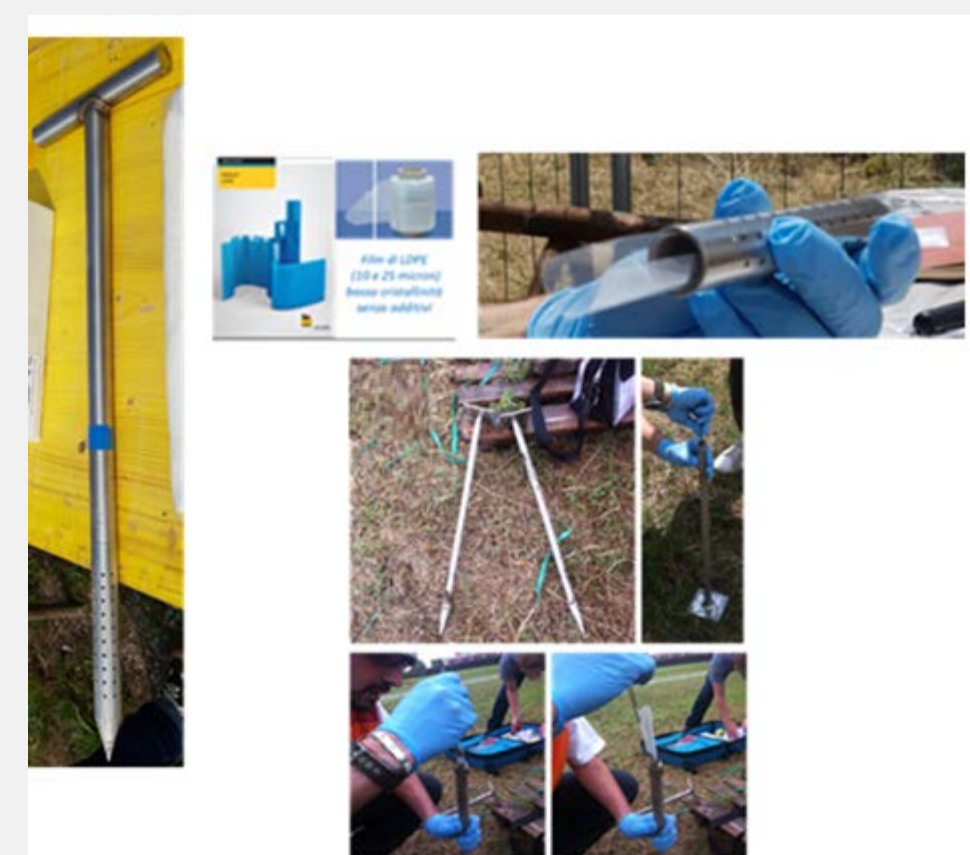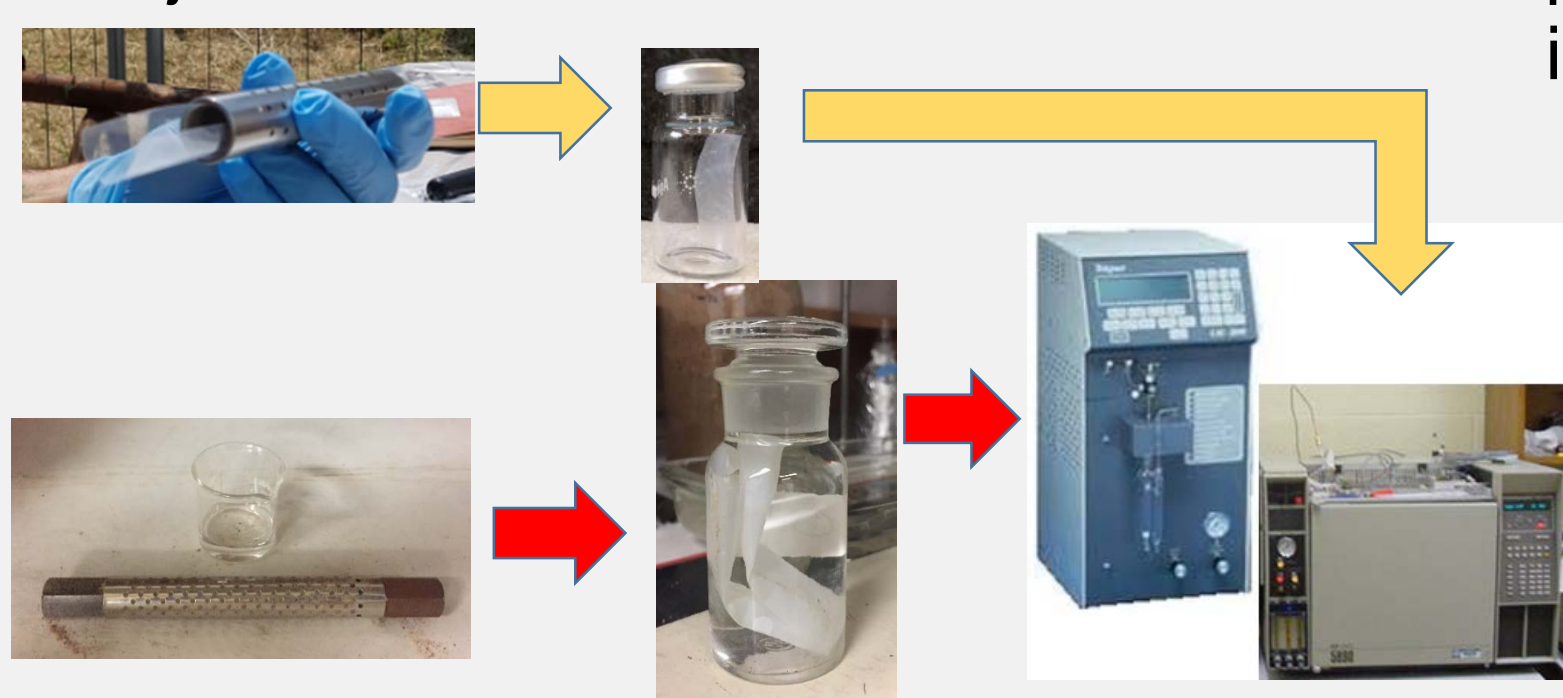
MIT
LDPE formed into cylinder and slid onto stainless steel rod. PE on rod combined into sampling string... driven into soil up to 2 m and left 1 or 2 days.
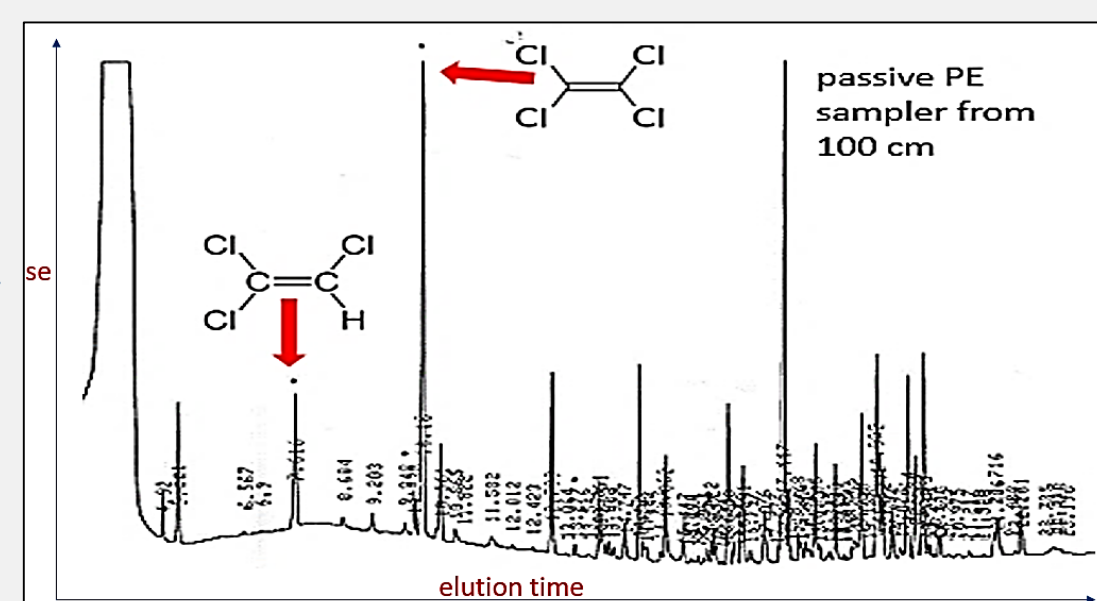
LDPE Analyses

Eni
LDPE pieces put in crimp vial, heated to 85°C, and headspace Injected into GC-MS & GC-ECD

MIT
LDPE put into glass vessel filled with water. After 1 week, water subsample analyzed via purge and trap-GC or direct aqueous injection with FID or ECD.

### Calculation of Concentrations in Soil Gas

$$C_{soil\ gas}\ (\mu g/m^3) = C_{PE}(\mu g/g_{PE})\ /\ K_{PEgas}\ [(\mu g/g_{PE})/(\mu g/mL)]\ \times 10^6\ mL/m^3$$

where $C_{PE}(\mu g/g_{PE})$ is the measured VOC concentration in the PE, and K_{PEgas} is the polyethylene-gas equilibrium partition coefficient.

Results

K_{PEgas} values (where gas = air in soil) were measured in the lab for 15 hydrocarbons and chlorinated hydrocarbons. As expected, these values correlated very well with the octanol-air partition coefficients:

$$\log K_{PE/gas} = \log K_{PE/air} = 0.945 \pm 0.057 \log K_{octanol/air} - 0.377 \pm 0.189$$

y = 0.945x - 0.377
R^2 = 0.955, N=15
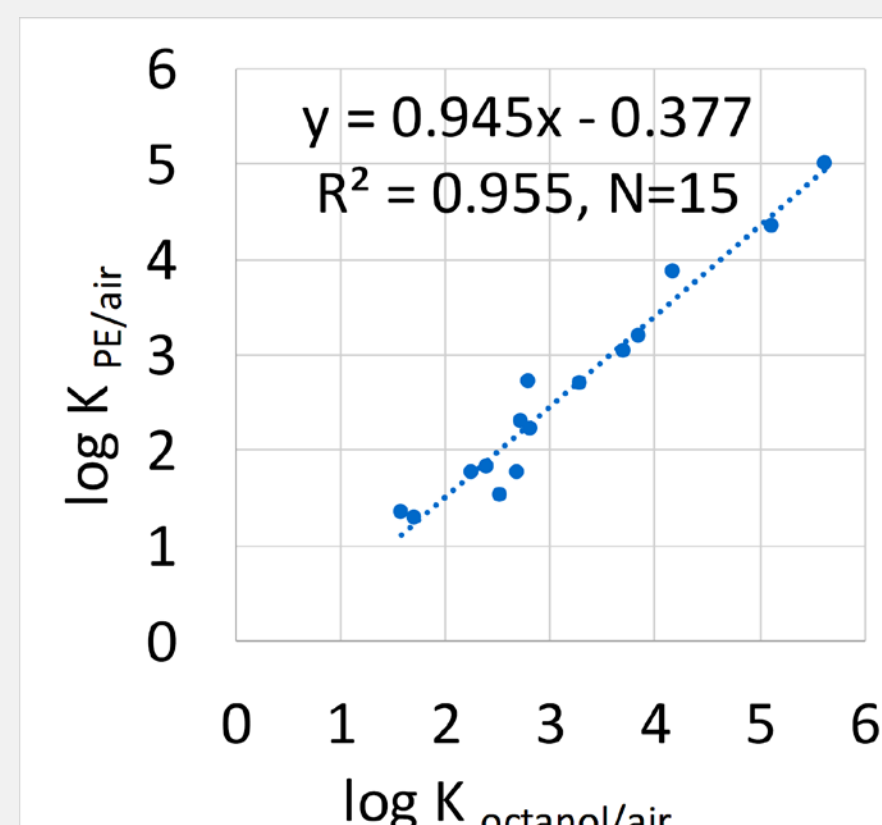
Repeatability Testing in Field
Passive samplers were deployed at alternating positions, 50 cm below the ground surface, for 46-47 hours.
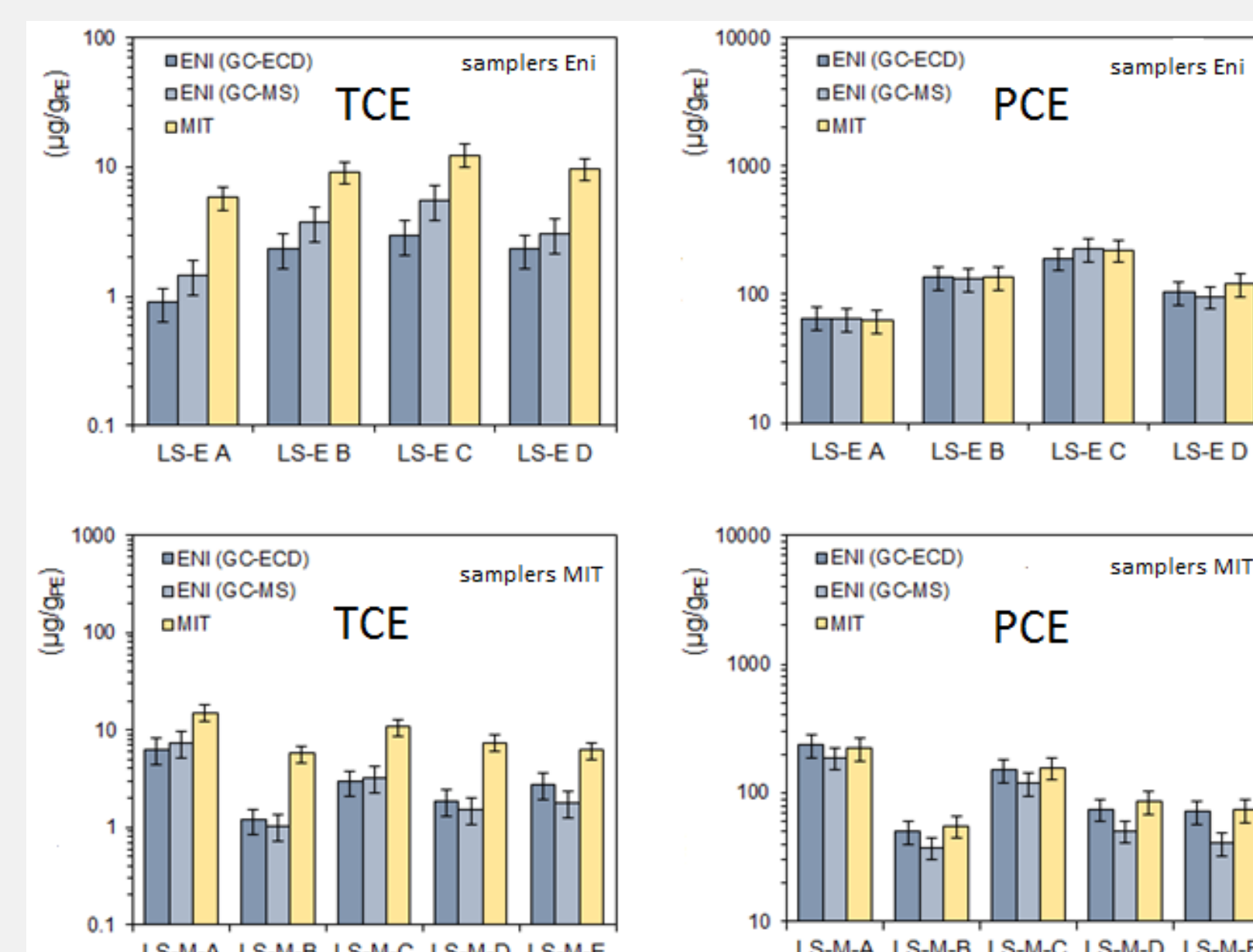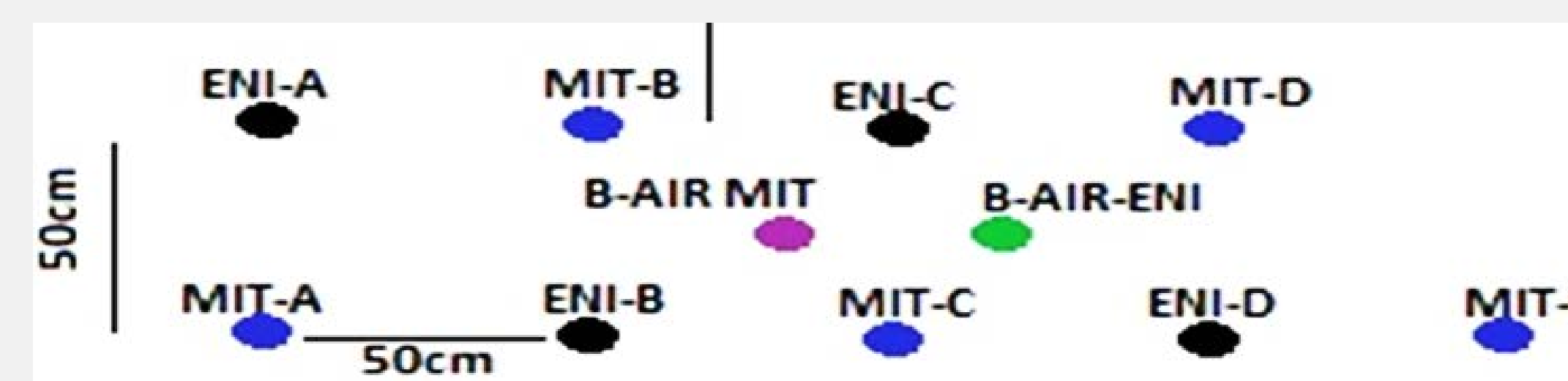
	average (mg/m³)	std dev	coeff var
TCE by MIT	32	14	43%
TCE by Eni	20	9	46%
PCE by MIT	79	46	58%
PCE by Eni	240	120	49%

PCE: Excellent agreement at each position.
TCE: Consistent trends from site to site.

Repeatability variation could well derive from spatial differences in TCE & PCE presence at the field site.

Approach to Equilibrium in 2 Days

Time Course Study : Exposure times: 2/4/23/27/47 h; MIT w/ 5 samplers @ 50 cm depth; Eni w/ 25 samplers @ 15, 30, 50, 70, 100 cm depths.
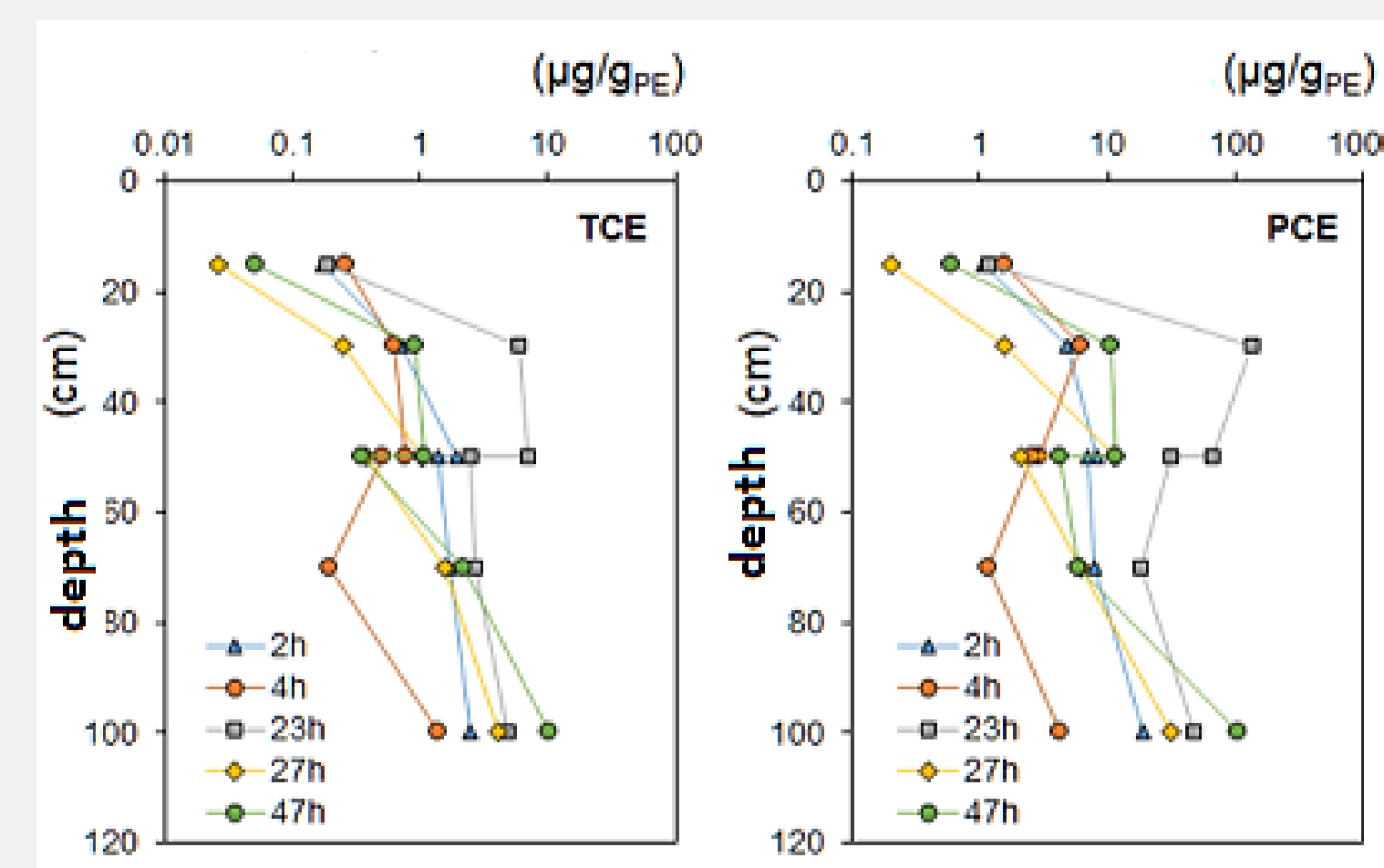

No-trend of increasing PE concentrations with increasing exposure duration. Implies, in 2 hours the equilibrium between the sampler and the subsoil is achieved. Also, for all the MIT PE samplers, the PRC (BFB) was at least 90% lost implying equilibration.

Variability observed at different exposure times may be attributable to the spatial heterogeneity of the contamination.

Vertical Profiles of VOCs in Soil Gases
Concentrations of TCE and PCE (μg/m³) in overlying air and soil gas determined using PE samplers as a function of depth where depth = 0 is the ground surface.
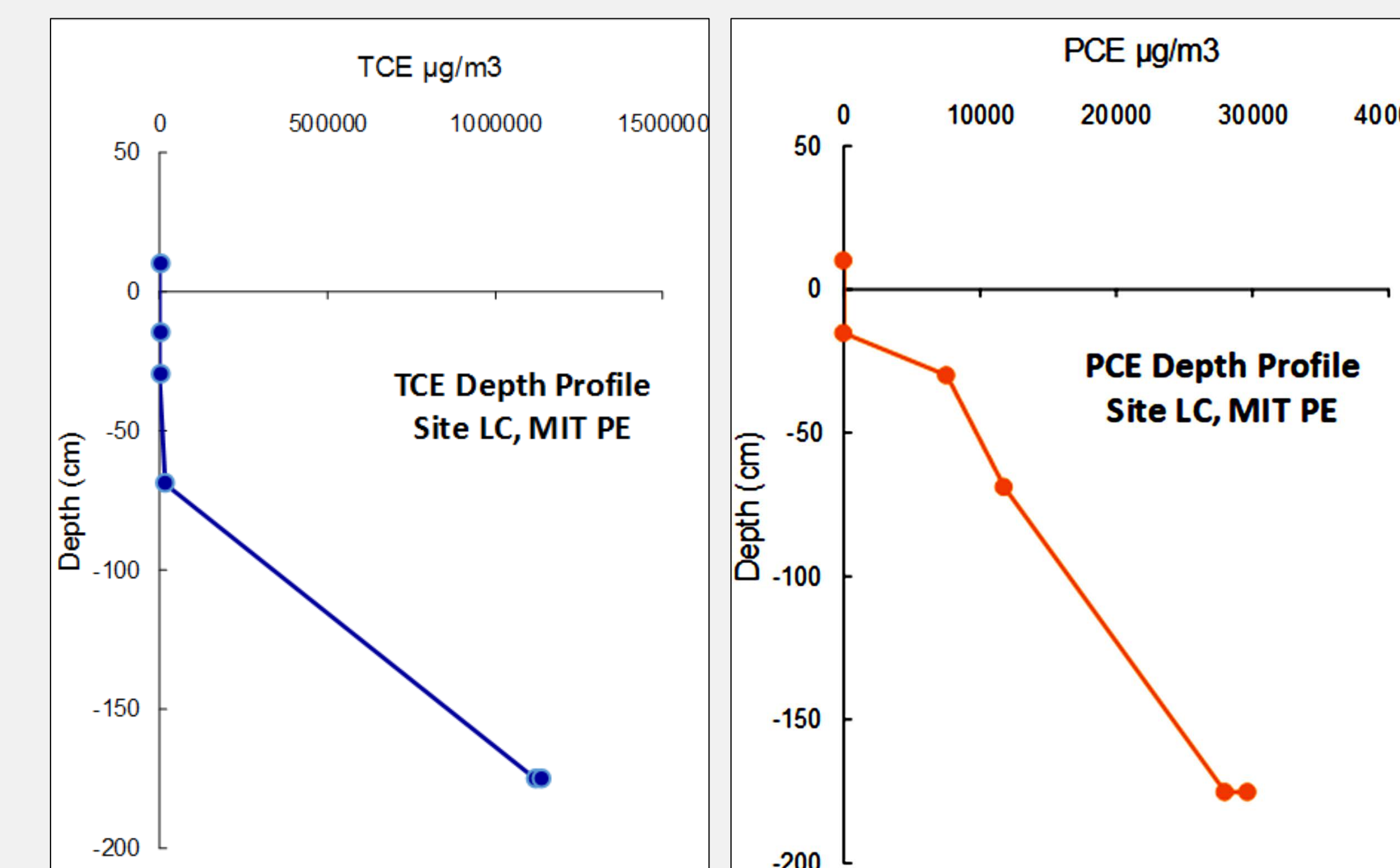
The PE deployed just above the ground surface had undetectable TCE and PCE (TCE <400 μg/m³; PCE< 60 μg/m³). In stark contrast, TCE and PCE at 170 cm depth were 1 g/m³ and 0.03 g/m³, respectively. These concentrations correspond to about 0.2% and 0.02% of the vapor pressures of TCE and PCE, respectively. Such profiles imply upward diffusive fluxes of TCE and PCE, which may well be overwhelmed by a soil gas pumping near the ground surface due to diurnal surface heating. The explanation could be that near-surface soil air is likely expanding and contracting throughout each day as the surface temperature varies. Hence, volatiles like TCE and PCE may well be "pumped" out of the ground each afternoon when the ground heats, sorption decreases and soil gases expand.

Other Features
Minimum detection limits proved to be about 0.1 mg PCE/m³ soil air, 1 mg TCE/m³ soil air (ECD or MS detection), and about 0.1 mg individual BTEX/m³ (FID or MS detection).

Comparisons of the passive sampling results with corresponding active sampling often did not yield good agreement. We suspect this may be due to the shallow location (only 70 cm below the ground surface) of the active sampling intake.

Conclusions
The polyethylene passive samplers allowed quantitation of VOCs in soil-gas with good repeatability. The technique can obtain vertical concentration profiles of VOCs in soil gas, even on a scale of centimeters. Traditional active sampling cannot do that. Unlike active sampling systems, PE films can also be installed at a few inches deep to more accurately assess the concentrations of vapors emitted into the atmosphere.
- The method overcomes most of the uncertainties of traditional methods.
- The approach provides faster, cheaper, and more scientifically-sound information.
- The method allows precise identification of the sources of contamination and helps the application of innovative remediation technologies (phytoremediation, in-situ bioremediation, natural recovery, etc.), with positive repercussions for technical and economical reliability of remedial activities.