



Transport of Chemical Vapors from Subsurface Sources to Atmosphere as Affected by Shallow Subsurface and Atmospheric Conditions

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ABSTRACT

Understanding and modeling the movement of chemical vapor through unsaturated soil in the shallow subsurface when subjected to natural atmospheric thermal and mass flux boundary conditions at the land surface is of importance to applications such as landmine detection and vapor intrusion into subsurface structures. New, advanced technologies exist to sense chemical signatures at the land/atmosphere interface, but interpretation of sensor signals to assess source conditions remains a challenge. Chemical signatures are subject to numerous interactions while migrating through the unsaturated soil environment, attenuating signal strength and masking contaminant source conditions. The dominant process governing movement of gases through porous media is often assumed to be Fickian diffusion through the air phase with minimal quantification of other processes contributing to vapor migration, such as thermal diffusion, convective gas flow due to the displacement of air, expansion/contraction of air due to temperature changes, temporal and spatial variations of soil moisture and fluctuations in atmospheric pressure. Soil water evaporation and interfacial mass transfer add to the complexity of the system.

The goal of this work is to perform controlled experiments under transient conditions of soil moisture, temperature and wind at the land/atmosphere interface and use the resulting dataset to test existing theories on subsurface gas flow and iterate between numerical modeling efforts and experimental data. Ultimately, we aim to update conceptual models of shallow subsurface vapor transport to include conditionally significant transport processes and inform placement of mobile sensors and/or networks. We have developed a two-dimensional tank apparatus equipped with a network of sensors and a flow-through head space for simulation of the atmospheric interface. A detailed matrix of realistic atmospheric boundary conditions are applied in an on-going series of experiments. Water saturation, air pressure, air and soil temperature, and relative humidity are continuously monitored. Aqueous TCE is injected into the tank below the water table and allowed to volatilize. TCE concentration exiting the tank head space is measured through interval sampling by direct injection into a gas chromatograph. To quantify the transient concentration of TCE vapor in the soil pore space a novel use of Solid Phase Micro-Extraction (SPME) was developed. Results from our numerical simulations were compared with the experimental data, which demonstrated the importance of considering the interaction of the atmosphere with the subsurface in conceptualization and numerical model development. Follow-up tests and detailed analyses are still underway. Additional applications of this work include carbon sequestration leakage, methane contamination in the shallow subsurface and environmental impact of hydraulic fracturing.

1. AIMS AND SCOPE

Experiments:

- Develop a two-dimensional tank equipped with a network of recent sensor technologies for automated and continuous monitoring of moisture/temperature behavior
- Generate precision data under well-controlled transient wind and heat boundary conditions at the soil surface for a matrix of wind and heat values

Modeling:

- Develop and implement a numerical model to solve for transient air velocity and heat flux at the soil/atmospheric interface, using precisely determined unsaturated soil hydraulic/thermal properties
- Compare experimental data with numerical model results
- Design future laboratory experiments using systemic insights gained through modeling processes

2. EXPERIMENTAL METHODS (SPME)

Goal:

Measure transient vapor concentration in partially saturated soil

Theory:

Solid Phase Micro-Extraction (SPME) utilizes characteristic molecular attractions to remove analytes from a matrix. An inert rod is coated with a polymer appropriate for a given analyte, and the polymer is exposed to the analyte for a pre-determined amount of time to allow the analyte to adsorb or absorb onto the polymer surface or into the polymer matrix.

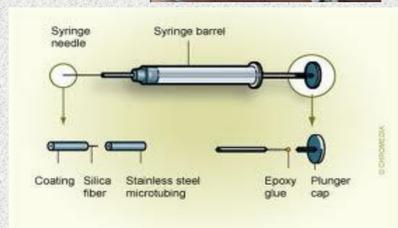
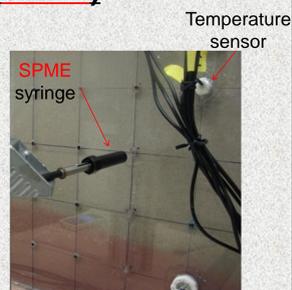
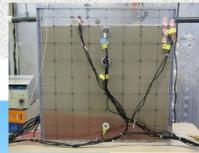
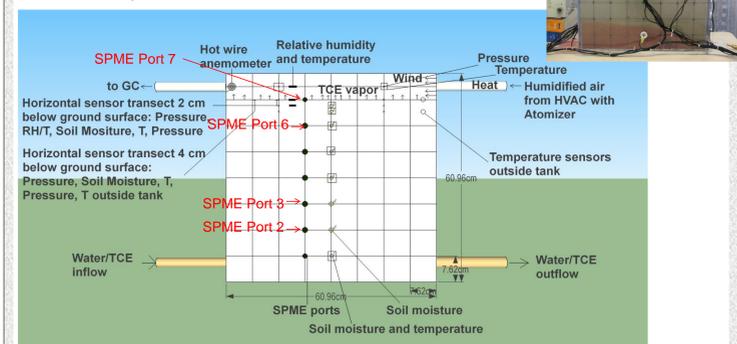


Diagram of SPME sampling process (overbooksscientific.com)

SPME sampler. (Photo: CESEP. Schematic: chromedia.org)

3. EXPERIMENTAL METHODS

Tank setup:



Test sand:

- Accusand #30/40
- 99.8% quartz
- $d_{50} = 0.53 \text{ mm}$
- Bulk density = 1.765 g/cm^3
- Porosity = 0.339
- $K_s = 0.104 \text{ cm/s}$

Continuously monitor:

- Soil Moisture
- Air Pressure (soil and head space)
- Temperature
- Relative Humidity
- Wind Speed
- Contaminant concentration (soil and head space)

Procedure:

- Water table initially at top surface of tank, then lowered to 8 cm above the bottom of the tank
- Water saturated with TCE pumped into tank through bottom port, displacing clean water
- TCE concentration sampling implemented along a vertical transect in the unsaturated zone using SPME
- Constant head space sampling carried out using Gas Chromatography (GC)
- For first test, ambient temperature and zero wind speed at the ground surface (slight wind variation to allow for GC sampling)

4. THEORY

Multiphase flow model

$$S_{w,e} = (S_w - S_{w,r}) / (1 - S_{w,r} - S_{g,r}) = (1 + (\alpha p_c)^n)^{-m}$$

$$S_w + S_g = 1$$

$$k_{rg} = (1 - S_{w,e})^2 \left(\frac{1 - (S_{w,e})^{\frac{1}{m}}}{1 - (S_{w,e})^{\frac{1}{m}}} \right)^2$$

$$k_{rw} = (S_{w,e})^{\frac{1}{2}} \left(\frac{1 - (S_{w,e})^{\frac{1}{m}}}{1 - (S_{w,e})^{\frac{1}{m}}} \right)^2$$

[Van Genuchten, 1980]

Gas transport equations

$$\mathbf{u}_g = -\frac{k_{rg}}{\mu_g} \mathbf{K}_1 (\nabla p_g - \rho_g \mathbf{g})$$

[Darcy, 1856]

$$\frac{\partial}{\partial t} (\theta \rho_g S_g) + \nabla \cdot (\rho_g \mathbf{u}_g) = 0$$

$$-\phi \rho_g \frac{dS_w}{dp_c} \frac{\partial p_c}{\partial t} + \phi S_g \frac{M_a}{RT} \frac{\partial p_g}{\partial t} + \phi S_g \left(1 - \frac{M_a}{M_n} \right) \frac{\partial C_g}{\partial t}$$

$$+ \nabla \cdot \left(-\frac{\rho_g k_{rg}}{\mu_g} \mathbf{K}_1 \nabla p_g + \frac{\rho_g k_{rg}}{\mu_g} \mathbf{K}_1 \mathbf{g} \right) = 0$$

[Bear, 1972]

Solute transport equations

$$\frac{\partial}{\partial t} (\theta S_g C_g) + \nabla \cdot (-D_g \nabla C_g + \mathbf{u}_g C_g) = (S_w/S_g) R_{stripping}$$

$$\frac{\partial}{\partial t} (\theta S_w C_w) + \nabla \cdot (-D_w \nabla C_w + \mathbf{u}_w C_w) = -R_{stripping}$$

$$R_{stripping} = k_s \left(C_w - \frac{C_g}{H_c} \right)$$

[Bear, 1972]

Water transport equations

$$\mathbf{u}_w = -\frac{k_{rw}}{\mu_w} \mathbf{K}_1 (\nabla p_w - \rho_w \mathbf{g}) = -\frac{k_{rw}}{\mu_w} \mathbf{K}_1 (\nabla p_g - \nabla p_c - \rho_w \mathbf{g})$$

[Darcy, 1856]

$$\frac{\partial}{\partial t} (\theta \rho_w S_w) + \nabla \cdot (\rho_w \mathbf{u}_w) = 0$$

$$\phi \rho_w \frac{dS_w}{dp_c} \frac{\partial p_c}{\partial t} + \nabla \cdot \left(-\frac{\rho_w k_{rw}}{\mu_w} \mathbf{K}_1 \nabla p_g + \frac{\rho_w k_{rw}}{\mu_w} \mathbf{K}_1 \nabla p_c + \frac{\rho_w^2 k_{rw}}{\mu_w} \mathbf{K}_1 \mathbf{g} \right)$$

$$= 0$$

[Bear, 1972]

Transport equations are coupled numerically using primary variables: p, p_c, C_w and C_n

Initial conditions

$$p(0, z) = p_0(z)$$

$$C(t=0, z) = 0$$

Boundary conditions

Air (no flow all boundaries except top boundary)

$$p(t, 0) = p_{atm}$$

$$p(t, z = \max(L)) = p_{atm} - \rho_{air} g h + A x$$

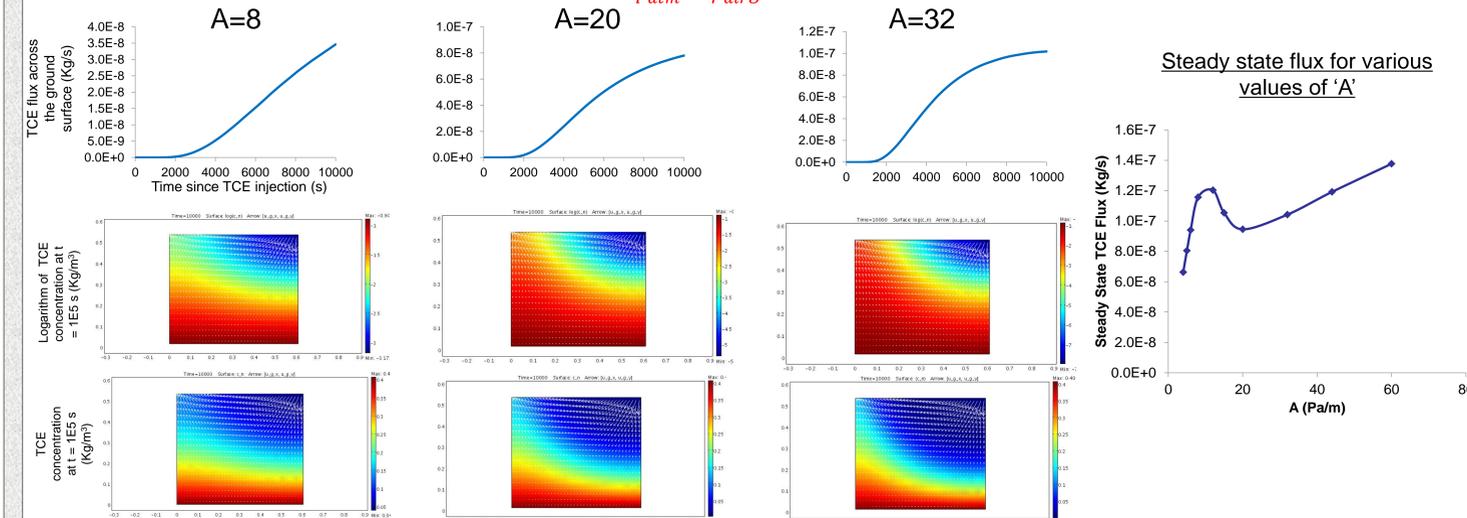
NAPL Vapor (zero concentration gradient boundary at the top, prescribed flow at bottom)

$$dC/dt(t, z = \max(L)) = 0$$

$$C(t, z = 0) = u_c$$

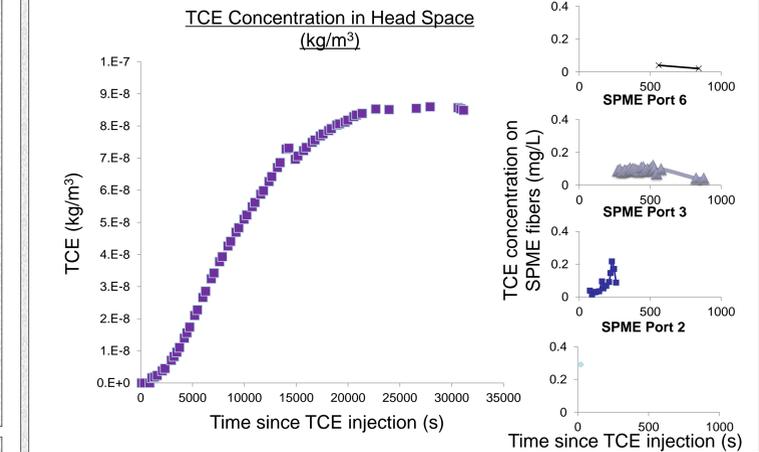
5. PRELIMINARY MODELING RESULTS

Varying top boundary horizontal pressure gradient $p_{atm} - p_{air} g h + A x$



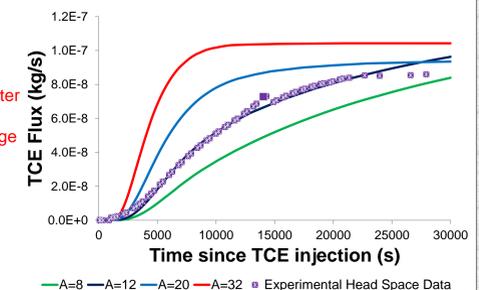
TCE flux as $L \int C_n u_{gy} \cdot n \, dl$ where L (m) is width of tank; C_n (kg/m³) is TCE concentration at top boundary; u_{gy} (kg/s) is gas flux in the y direction; n (--) is the unit normal vector; and l (m) is the length of the tank, against a range of horizontal pressure gradient values.

6. EXPERIMENTAL RESULTS



7. COMPARISON OF MODELING AND EXPERIMENTAL RESULTS

RESULTS: Preliminary results suggest that the shape of the TCE breakthrough curve is better approximated by parameter 'A' values in the range of 10 - 20 [Pa m⁻¹]. Best fit is at A=12.



8. PRELIMINARY FINDINGS & FUTURE WORK

- Varying horizontal pressure along the soil surface has a significant affect on the steady state magnitude of a contaminant concentration break-through curve. For a low pressure gradient, the shape of the curve can also vary.
- SPME is a valuable technique for sample collection, but work is necessary on sample port design and calibration.

Future work includes:

- Finding a more physically accurate method to simulate contaminant transport and variable wind speed at the subsurface/atmospheric interface.
- Completing a matrix of experimental runs with variable head space air velocity.
- Incorporating thermodynamic processes at the subsurface/atmospheric interface and non-equilibrium contaminant mass transfer between soil water and soil gas into numerical and experimental analysis.
- Continuing to validate use of SPME in porous media.

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REFERENCES

- Auer, L.H., N.D. Rosenberg, K.H. Birdsell, E.M. Whitney, 1996. The effects of barometric pumping on contaminant transport. *J. of Contaminant Hydrology*.
- Bear, J. A., 1972. Dynamics of Fluids in Porous Media.
- Pawliszyn, J., 1999. Applications of Solid Phase Microextraction.
- Smits, K. M., T. Sakaki, A. Limsuwat, and T. H. Illangasekare, 2010. Thermal conductivity of sands under varying moisture and porosity in drainage-wetting cycles. *Vadose Zone J.*
- van Genuchten, 1980. M.T. A closed form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*