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Soil gas transport above a jet fuel/solvent spill at Plattsburgh Air Force Base

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Abstract. We calibrate a stoichiometrically coupled soil gas diffusion model with spatially resolved observations of oxygen, carbon dioxide, total hydrocarbon, and trichloroethylene vapor concentrations in the unsaturated zone above a weathered jet fuel/solvent spill at Plattsburgh Air Force Base in upstate New York. The calibration suggests that aerobic microorganisms in the capillary fringe degrade jet fuel vapor at a steady rate of 9.5 μ g hydrocarbons (m⁻² s⁻¹). The solvent does not degrade in the fringe, however, and the model and data estimate a steady evaporation rate of $1.2 \times 10^{-2} \mu$ g TCE (m⁻² s⁻¹). Barometric pumping slightly alters the steady concentration profile at Plattsburgh, although the transient advective flux is the same order of magnitude as the steady diffusive flux. We derive a simple perturbation theory for the second-order transient concentration corrections and include it in the calibration. The perturbation theory is valid at Plattsburgh because the soil is uniform and permeable with a relatively deep capillary fringe.

1. Introduction

We use concentration data and a set of steady and transient, stoichiometrically coupled, one-dimensional, analytical transport models to estimate the flux of soil gas constituents through a uniform, permeable, unsaturated zone. We postulate aerobic biodegradation of hydrocarbons in the contaminated capillary fringe, so that, to leading order, oxygen diffuses steadily down from the atmospheric source at the ground surface, while carbon dioxide and hydrocarbon vapors diffuse steadily upward from a separate phase source at the edge of the fringe. The steady carbon dioxide and oxygen fluxes are evaluated above a jet fuel/solvent spill at Plattsburgh Air Force Base and found to be consistent with steady values found by *Lahvis and Baehr* [1996] and *Lahvis et al.* [1999] over automobile gasoline spills.

Wallach [1998] applies perturbation theory to the reactive term of a groundwater contaminant transport model. We compliment this approach by considering perturbations to the transport mechanisms of a soil gas constituent. Gaseous diffusion is assumed to dominate the steady profile and barometric pressure fluctuations drive the transient profile. The barometric pressure distribution is described by a diffusion equation [Shan, 1995] and induces a second-order, transient correction to the steady concentration profiles if the capillary fringe is uniform and relatively deep. The constraints validating the perturbation theory are easily satisfied at Plattsburgh.

2. Soil Gas Transport Theory

2.1. Steady and Transient Soil Gas Transport Equations

We assume that the advective, dispersive, and diffusive vertical flux of a dissolved and gaseous phase constituent through the unsaturated zone is balanced by a reaction and the temporal change of aqueous c and soil gas C concentrations

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Paper number 2000WR900128. 0043-1397/00/2000WR900128\$09.00

$$\frac{\partial}{\partial t} \left(\theta_{W}c + \theta C\right) + \frac{\partial}{\partial z} \left(v_{W}c + vC\right) \\ - \frac{\partial}{\partial z} \left[\theta_{W}\left(D_{W} + \alpha_{L} \frac{v_{W}}{\theta_{W}}\right) \frac{\partial c}{\partial z} + \theta\left(D + \alpha_{L} \frac{v}{\theta}\right) \frac{\partial C}{\partial z}\right] = \frac{\Lambda}{\zeta}$$
(1a)

$$\theta + \theta_W = n, \tag{1b}$$

with time t, distance z above the top of the capillary fringe, air porosity θ , water porosity θ_W , and total porosity n. The constituent phases diffuse down concentration gradients in accordance with the gaseous D and liquid D_W diffusivities and advect with specific discharge of water v_W and soil gas v in the vertical direction. A longitudinal dispersivity α_L characterizes dispersion as a property of the porous medium and not of the fluid. The depth integrated reaction rate Λ is assumed to be uniformly distributed over the thickness ζ of the unsaturated zone. We simplify (1) by incorporating separate conservation equations for water and soil gas and by assuming equilibrium partitioning between the phases

$$\frac{\partial \theta_W}{\partial t} + \frac{\partial v_W}{\partial z} = 0$$
 (2a)

$$\frac{\partial \theta}{\partial t} + \frac{\partial v}{\partial z} = 0$$
 (2b)

$$c = K_{W}C \tag{2c}$$

with Henry constant K_{W} . Equations (1) and (2) are combined with the result

$$(\theta + K_{W}\theta_{W})\frac{\partial C}{\partial t} + (v + K_{W}v_{W})\frac{\partial C}{\partial z}$$
$$-\frac{\partial}{\partial z}\left\{\left[\theta\left(D + \alpha_{L}\frac{v}{\theta}\right) + K_{W}\theta_{W}\left(D_{W} + \alpha_{L}\frac{v_{W}}{\theta_{W}}\right)\right]\frac{\partial C}{\partial z}\right\} = \frac{\Lambda}{\zeta}$$
(3a)



Figure 1. Empirical air porosity fraction characteristic curve.

$$D = D_{\text{REF}} \sqrt{\frac{m_{\text{REF}}}{m}} \left(\frac{T}{T_{\text{REF}}}\right)^{7/4} \frac{\theta^{7/3}}{n^2}.$$
 (3b)

Millington's [1959] classical soil gas diffusivity model expresses D in terms of a reference free air diffusivity D_{REF} , with adjustments for molar mass m and absolute temperature T summarized by *Reid et al.* [1987]. We note reference molar mass m_{REF} and reference temperature T_{REF} in (3b).

We partition this transport equation by assuming that the soil gas diffusivity, air porosity, water porosity, and concentration are comprised of steady (S subscript) and relatively small, transient (prime) components. The dissolved transport mechanisms are assumed to be much slower than their gaseous counterparts as well

$$C = C_{s}(z) + C'(z, t)$$
 ($C_{s} \gg C'$) (4a)

$$\theta = \theta_{S}(z) + \theta'(z, t) \qquad (\theta_{S} \gg \theta')$$
 (4b)

$$D = D_{\mathcal{S}}(z) + D'(z, t) \qquad (D_{\mathcal{S}} \gg D' \gg D_{\mathcal{W}}K_{\mathcal{W}}) \quad (4c)$$

$$v = v'(z, t) \qquad (v' \gg v_W K_W) \qquad (4d)$$

$$\theta_{W} = \theta_{WS}(z) + \theta'_{W}(z, t) \qquad (\theta_{WS} \gg \theta'_{W}) \qquad (4e)$$

$$\Lambda = \Lambda_{S} + \Lambda'(z, t) \qquad (\Lambda_{S} \gg \Lambda') \tag{4f}$$

We combine (3) and (4) and group steady and transient terms, assuming diffusion and advection to be of comparable importance. The first-order steady profile is a balance of diffusion and decay that supports a steady boundary concentration C_{SO} and flux J_{SO} at the top of the capillary fringe

$$-\frac{d}{dz}\left(\theta_{s}D_{s}\frac{dC_{s}}{dz}\right)=\frac{\Lambda_{s}}{\zeta}$$
(5a)

$$-\theta_s D_s \frac{dC_s}{dz} = J_{so} \qquad (z=0)$$
(5b)

$$C_s = C_{so} \qquad (z=0) \tag{5c}$$

We neglect (second-order) time averaged products of transient terms from (5). We combine (3) and (4) and retain the unsteady terms with the result

$$(\theta_{S} + K_{W}\theta_{WS}) \frac{\partial C'}{\partial t} - \frac{\partial}{\partial z} \left(\theta_{S}D_{S} \frac{\partial C'}{\partial z} \right) = \frac{\Lambda'}{\zeta} - \upsilon' \frac{dC_{S}}{dz} + \frac{\partial}{\partial z} \left\{ \left[\alpha_{L}\upsilon' + \theta_{S}D_{S} \left(\frac{D'}{D_{S}} + \frac{\theta'}{\theta_{S}} \right) \right] \frac{dC_{S}}{dz} \right\}$$
(6)

Transient dissolved transport terms are neglected in (6).

2.2. Air Porosity Characteristic and the Steady Concentration Profile

We integrate (5a) from the top of the capillary fringe to any elevation in the unsaturated zone, invoke (5b) and so deduce

$$-\theta_s D_s \frac{dC_s}{dz} = J_{so} + \frac{\Lambda_s z}{\zeta}.$$
 (7)

Since *Millington* [1959] suggests that the soil gas diffusivity is sensitive to the air porosity, we continue the steady derivation by modeling θ_s . The air porosity increases with increasing elevation, and we postulate an empirical power law between the steady air porosity fraction θ^* and z, as a consequence

$$\boldsymbol{\theta}^* = \left(\frac{z}{\zeta}\right)^{\alpha} \tag{8a}$$

$$\theta^* = \frac{\theta_S}{n - \theta_F} \tag{8b}$$

with field capacity θ_F and uniformity exponent α . Figure 1 displays the air porosity characteristic curve; we note that θ^* vanishes at the capillary fringe and approaches unity at the ground surface. Uniform soils have exponents close to zero, with strong gradients of air porosity near the water table and essentially constant θ^* over most of the unsaturated zone.

The assumed air porosity characteristic (8) enables us to use the chain rule on (3b) and (7), with θ^* as the independent variable

$$-D_{S\zeta} \frac{\alpha(n-\theta_F)}{\zeta} \theta^{*13/3-(1/\alpha)} \frac{dC_S}{d\theta^*} = J_{SO} + \Lambda_S \theta^{*1/\alpha} \quad (9a)$$

$$C_s = C_{so} \qquad (\theta^* = 0) \tag{9b}$$

$$D_{S\zeta} = D_{\text{REF}} \sqrt{\frac{m_{\text{REF}}}{m}} \left(\frac{T_s}{T_{\text{REF}}}\right)^{7/4} \frac{(n-\theta_F)^{7/3}}{n^2}$$
 (9c)

with time averaged diffusivity at the ground surface $D_{S\zeta}$. We separate variables in (9a), integrate from the top of the capillary fringe to any elevation, and derive

$$C_{S} = C_{SO} - \frac{J_{SO}\zeta}{D_{S\zeta}(n - \theta_{F})\left(1 - \frac{10\alpha}{3}\right)} \theta^{*1/\alpha - 10/3} \cdot \left[1 + \frac{\Lambda_{S}\theta^{*1/\alpha}}{J_{SO}}\left(\frac{1 - \frac{10\alpha}{3}}{2 - \frac{10\alpha}{3}}\right)\right].$$
(10)

We recall (8) and write this solution in terms of elevation and a characteristic steady concentration C_{SC}

$$C_{s} = C_{so} - \left(\frac{C_{sc}}{1 - \frac{10\alpha}{3}}\right) \left(\frac{z}{\zeta}\right)^{1 - (10\alpha/3)} \left[1 + \frac{\Lambda_{s}z}{J_{so}\zeta} \left(\frac{1 - \frac{10\alpha}{3}}{2 - \frac{10\alpha}{3}}\right)\right]$$
(11a)

$$C_{SC} = \frac{J_{SO}\zeta}{D_{S\zeta}(n-\theta_F)}.$$
 (11b)

This nonlinear first-order profile extends from the top of the capillary fringe to the ground surface and is valid for a biologically active unsaturated zone regardless of uniformity.

2.3. Barometric Pumping for a Uniform, Abiotic Unsaturated Zone

Appendix 1 suggests that the transient soil gas equation is a balance of storage and pressure corrections when barometric advection is of first-order importance and the unsaturated zone is uniform and abiotic

$$R_D \frac{\partial C'}{\partial t} = \frac{v' C_{SC}}{\zeta (n - \theta_F)} \qquad \left(v' = O\left[\frac{D_{S\zeta}}{\zeta}\right] \right) \qquad (12a)$$

$$R_D = 1 + \frac{K_W \theta_F}{n - \theta_F} \qquad (\alpha \ll 1, \Lambda' \ll \Lambda_S \ll J_{SO}) \qquad (12b)$$

$$v' \ll \frac{\zeta}{t_P}$$
 (C' \ll C_S) (12c)

with retardation factor R_D reflecting dissolution of gaseous constituents into the soil moisture. The constraint cited in (12a) ensures that transient advection and steady diffusion are of comparable importance. Constraint (12c) ensures the second-order importance of transient concentrations: the timescale of the barometric disturbance t_P is insufficient for the specific discharge to advect contamination far into the unsaturated zone. Our transport equations contrast with those examined by Massman and Farrier [1992], who model the response of an initially pure unsaturated zone to a contaminated atmosphere with a sinusoidally varying atmospheric pressure variation. Massman and Farrier [1992] demonstrate that the resulting periodic concentrations are of first-order importance in the absence of a steady state diffusive concentration profile. This is not the case at Plattsburgh: the soil gas concentrations have equilibrated to longstanding contamination in the capillary fringe, subject to aperiodic perturbation by atmospheric pressure.

The air specific discharge completes our transient model. We follow *Shan* [1995] and consider the case of transient barometric surface pressure, with a horizontal no-flow boundary condition at the water table. *Kidder* [1957] and *Massman* [1989] note that the pneumatics are described by a classical diffusion equation for small pressure disturbances

$$\frac{\partial p}{\partial t} - D_P \frac{\partial^2 p}{\partial z^2} = 0$$
 (13a)

$$D_P = \frac{k_{\text{AIR}} p_S}{\mu (n - \theta_F)} \tag{13b}$$

with constant D_p , air permeability k_{AIR} , atmospheric pressure p, and air dynamic viscosity μ . Darcy's law relates p to v' in the absence of gravity

$$v' = -\frac{k_{\rm AIR}}{\mu} \frac{\partial p}{\partial z}.$$
 (14)

The no-flow bottom and unsteady atmospheric boundary condition $\rho(t)$ are responsible for barometric pumping

$$p = p_{\mathcal{S}}(1+\rho) \qquad (z = \zeta) \tag{15a}$$

$$\frac{\partial p}{\partial z} = 0 \qquad (z = 0) \tag{15b}$$

$$p = p_s \qquad (t = 0) \tag{15c}$$

with assumed zero initial fluctuation.

We take the LaPlace transform [Rainville and Bedient, 1969] of (13) and (15) with the result

$$-D_P \frac{d^2 p^*}{dz^2} + sp^* = p_s$$
 (16a)

$$p^* = p_s \left(\frac{1}{s} + \rho^*\right) \qquad (z = \zeta) \tag{16b}$$

$$\frac{dp^*}{dz} = 0 \qquad (z=0) \tag{16c}$$

with transformed pressure p^* , time s, and surface disturbance ρ^* . A hyperbolic cosine satisfies (16)

$$p^* = p_s \left[\frac{1}{s} + \frac{\rho^* \cosh\left(z \sqrt{\frac{s}{D_P}}\right)}{\cosh\left(\zeta \sqrt{\frac{s}{D_P}}\right)} \right].$$
(17)

The pressure is the inverse transform of (17), which may be expressed as

$$p = p_{s}\{1 + L^{-1}[s\rho^{*}F(s)]\}$$
(18a)

$$F(s) = \frac{\cosh\left(z\sqrt{\frac{s}{D_P}}\right)}{s\cosh\left(\zeta\sqrt{\frac{s}{D_P}}\right)}$$
(18b)

$$L^{-1}\{s\rho^*\} = \frac{d\rho}{dt}.$$
 (18c)

Spiegel and Liu [1999] invert the transform F(s) with a convergent Fourier cosine series f(t)

$$f(t) = 1 + \frac{4}{\pi} \sum_{J=1}^{\infty} \left[\frac{(-1)^J}{2J - 1} \exp\left(-A_J^2 D_P t\right) \cos\left(A_J z\right) \right] \quad (19a)$$

$$A_J = \frac{(2J-1)\pi}{2\zeta}.$$
 (19b)

We express (18) and (19) as a convolution integral [Abramowitz and Stegun, 1972] and so deduce a formal expression for p

$$\frac{p}{p_s} = 1 + \int_0^t f(t-\tau) \, \frac{d\rho}{d\tau} \, (\tau) \, d\tau. \tag{20}$$

Shan [1995] derives and calibrates equations similar to (20) in a study of pneumatics of the unsaturated zone. We express the convolution integral in terms of the gradient of ρ to avoid differentiation of f(t), which would yield a divergent series solution for v' [Farlow, 1982]. The fluctuating specific discharge, which follows from (13b), (14), and (20), in turn yields the concentration fluctuations through a temporal integration of (12a)



Figure 2. Site location-Plattsburgh Air Force Base, New York.

$$v' = -D_P(n - \theta_F) \int_0^t \frac{\partial f}{\partial z} (t - \tau) \frac{d\rho}{d\tau} (\tau) d\tau \quad (21a)$$

$$\frac{C'}{C_{SC}} = -\frac{D_P}{R_D \zeta} \int_0^t \int_0^{t'} \frac{\partial f}{\partial z} (t'' - \tau) \frac{d\rho}{d\tau} (\tau) d\tau dt'' \quad (21b)$$

with negligible initial fluctuation. Equations (20) and (21) suggest that atmospheric pressure fluctuations drive pressure, specific discharge, and soil gas concentrations in the unsaturated zone. The convolution integrals may be evaluated by combining observed ρ values with (19).

3. Steady Model Calibration With Plattsburgh Data

The site of the bioventing study is the former Fire Training Area denoted as FT-002 at Plattsburgh Air Force Base, Plattsburgh, New York (Figure 2). Fire training area FT-002 was used to train fire-fighting personnel from the mid-1950s until the facility was closed in May 1989. The pits were unlined until 1980 when two of the pits, designated 1 and 2, were modified with cement stabilized soil liners. Pits 3 and 4 had been removed from service at this point. Previous investigations indicated that the four fire pits were filled with off-spec JP-4 jet fuel mixed with waste oil, solvents, and other miscellaneous chemicals before being set on fire as training exercises. Figure 2 displays the approximate lateral extent of the light nonaqueous phase liquid (LNAPL) spill of jet fuel and solvents resulting from the training [Parsons Engineering Science, 1995]. The LNAPL extends through the water table and capillary fringe, \sim 12–13 m below the ground surface in the University of Massachusetts (UMASS) study area (Figure 3). The entire UMASS study area overlies separate phase contamination.

3.1. Air Porosity Profile

We obtained soil samples from boreholes SPK1, SPK2, and 12AY for grain size analysis in general accordance with *American Society for Testing Materials (ASTM)* [1996a] protocol. The average grain size for 108 samples is 0.439 mm, while the average uniformity coefficient (d_{60}/d_{10}) is 3.0, indicating uniform, medium sand. *Parsons Engineering Science* [1995] ran in situ permeability tests in the sand, which yield an average saturated permeability k_{SAT} value of $4.8 \times 10^{-12} \text{ m}^2$.

Soil moisture contents were determined gravimetrically in 203 samples from boreholes 12AG, 12AA, 12AD, 12AK, 12AS, and 12AM in general accordance with ASTM [1996b]. Figure 4 displays the mass based moisture content profile M from six boreholes sampled during the field investigation at Plattsburgh Air Force Base. The sample dates are indicated on Figure 4 as well. We infer the air porosity from M when the porosity and the solid grain specific gravity s_G are known

$$\theta = n(1 + s_G M) - s_G M \tag{22a}$$

$$n = \left(1 + \frac{1}{s_G M}\right)^{-1} \qquad (M \text{ saturated}). \tag{22b}$$

Table 1 lists the calibrated parameter values for Plattsburgh. The porosity is estimated to be 0.349, based on 96 samples taken below the water table from the six boreholes shown in Figure 4, while the solid specific gravity is taken as 2.65. The resulting air porosities (estimated in accordance with (22a)) appear as symbols in Figure 5. We use these data to calibrate the capillary fringe depth, field capacity, and air porosity fraction exponent appearing in (8). We zero the air porosity error mean and minimize the air porosity error standard deviation σ_{θ} by a nested Fibonacci search [*Beveridge and Schechter*, 1970] for α , ζ , and θ_F . The error statistics for this and all calibrations are defined by [*Benjamin and Cornell*, 1970]

$$\delta$$
 = measured - predicted (23a)

$$\delta_M = \frac{1}{N} \sum_N \delta$$
 (N samples) (23b)

$$\sigma = \sqrt{\frac{1}{N} \sum_{N} \delta^2 - \delta_M^2}$$
(23c)



Figure 3. Site location-University of Massachusetts study area.

with individual error δ , mean error δ_M , and error standard deviation σ . The calibration appears as a solid curve in Figure 5, based on a uniformity exponent of 0.115, a field capacity of 0.066, and a capillary fringe depth of 12.14 m. The fit is reasonable, as evidenced by an error standard deviation of 0.099. We note that the pore size distribution is uniform at Plattsburgh, since $\alpha \ll 1$.

3.2. Soil Gas Sampling Methods

Soil gas samples were obtained on 0.3 m increments from a rapid deployment vapor probe (Figure 6) driven by a drill rig equipped with a 140 pound Standard Penetration Test hammer. Soil gas samples were vacuum pumped to the surface through a 3 mm diameter flexible teflon or polypropylene line, routed through the annulus of the drill rods. Vapor probe profiles were measured from 0.6 to 11.6 m below the ground surface at location VP1 on October 11, 1995, and over a 0.3-6.1 m interval at VP3 on October 13, 1995. We also installed permanent, dedicated soil gas sampling points set in 0.30 m sandpacks with 0.60 m bentonite seals at 32 depths in 17 boreholes distributed over the separate phase spill (Table 2). Two additional sampling points were constructed in a control borehole located 100 m away from the contaminated soil (Figure 2). These tubing clusters were sampled on October 26, 1995, November 16, 1995, and January 16, 1996. Figure 7 displays construction of a typical dedicated cluster sampling point. The stainless steel soil gas points were installed at depths ranging from 0.9 to 11 m below grade.

Two L soil gas samples were collected from the vapor probes and permanent clusters in evacuated, nitrogen-rinsed, tedlar bags. Oxygen and carbon dioxide soil gas concentrations were measured in the field using a model 302 sniffer and a PMI-300 analyzer, equipped with internal vacuum pumps. Serial dilution [*Robbins et al.*, 1990] was employed for soil gas samples with carbon dioxide contents in excess of 10% by volume or oxygen contents less than 5% by volume. *Hinlein* [1999] provides additional details describing soil gas sampling methods.

3.3. Soil Gas Oxygen and Carbon Dioxide Calibration

We measured the partial pressure p_X of soil gas oxygen (X subscript) on five different dates at Plattsburgh, with the re-

sults shown as symbols in Figure 8. The ideal gas law [*Eastman*, 1975] and observed soil temperature (discussed below) convert the data to oxygen concentration C_X ,

$$C_X = \frac{m_X p_X}{R_U T} \tag{24a}$$

$$R_U = 8.31 \frac{m^3 (\text{Pa})}{\text{mol} (^\circ\text{K})}$$
(24b)

with molar mass m_X equal to 0.032 kg/mole for oxygen and universal gas constant R_U . Weast [1967] cites an oxygen free air diffusivity value of 273°K, which we use as a reference condition for oxygen and all other constituents

$$D_{\text{REF}} = 1.78 \times 10^{-5} \frac{\text{m}^2}{\text{s}}$$
 (oxygen at 273°K). (25)

The oxygen diffusivity $D_{SX\zeta}$ of 8.13×10^{-6} m²/s follows from (9c).

We calibrate the soil gas oxygen profile with a nested Fibonacci search for the optimal oxygen flux and steady capillary fringe concentration, with the error statistics defined by (23). Reactions are ignored in the unsaturated zone, so that Λ_s is set equal to zero. Transient concentrations induced by barometric pumping are included in the calibration (although they are small, as discussed below). Table 3 summarizes the soil gas calibration, based on the calibrated steady oxygen flux J_{SX}

$$J_{SX} = -33.5 \frac{\mu g}{m^2 - s}$$
 (calibrated). (26)

The pressure exerts little effect on the concentrations, so that the calibrated oxygen concentration profile is sketched as a single curve in Figure 8; the negative sign suggests that oxygen diffuses down from the atmosphere into the soil. The error standard deviation σ_X is 0.020 kg/m³ for the five soil gas sampling dates at Plattsburgh. The calibrated fringe oxygen concentration of 0.000 kg/m³ and (21a) imply a surface oxygen concentration of 0.287 kg/m³. The ideal gas law yields an oxygen pressure of 21,000 Pa at the site average temperature, corresponding to 21.0% by volume. This is comparable to the atmospheric oxygen partial pressure of 20.9% [Eagleson, 1970].



Figure 3. (a) Vectors in plane of cross section x/d = 3. (b) Surface vectors. (c) Bed vectors. (d) Contours of pressure (interval of 10 Pa) at the bed for a symmetrical and asymmetrical confluence.

single cell on the side of the curved tributary in the asymmetrical confluence (Figure 3a). This can be explained by consideration of flow curvature and pressure gradients. In the symmetrical confluence, convergence of the flow from the two tributaries results in high pressure in the center of the channel (Figure 3d, symmetrical (S) confluence) with low pressure at the banks where flow separation occurs (Figure 3b, S confluence). The lower momentum flow at the bed responds more quickly to this pressure gradient (Figure 3c, S confluence) than the faster flow at the surface (Figure 3b, S confluence). This results in the divergent flow at the bed and convergent flow at the surface associated with twin cells (Figure 3a, S confluence). However, in the asymmetrical confluence there is only pronounced curvature on one side of the channel (Figure 3b, asymmetrical (A) confluence and 3c, A confluence). There is some deflection of flow from the straight tributary at the surface which results in high pressure at the center of the channel at x/d = 0.1 (Figure 3d, confluence A), but by x/d = 1.0 the highest pressure has migrated to the true-left bank (defined as the left bank when looking in the downstream direction). Thus the pressure gradient is in the same direction across the whole channel width, no bed divergent flow occurs (Figure 3c, confluence A), and only a single cell is formed (Figure 3a, A confluence). If the simulation is repeated with the tributary velocity reduced to 0.15 m s^{-1} , such that the momentum ratio equals 0.5, the flow patterns are qualitatively similar to those shown in Figure 3 (A). However, the tributary flow penetrates less far into the confluence resulting in a reduction in the length of the lateral flow separation zone and in the strength of the secondary circulation cell [*Bradbrook et al.*, 2000a].

It seems that only the patterns of flow vectors and pressure contours for the symmetrical confluence resemble those of two back-to-back meanders. However, comparison of key parameters for the confluence simulations with those for the single bend (Figure 1b) suggests some important differences (Table 3). The surface elevation at the outer bank of the meander is greater than that in the center of the symmetrical confluence because of flow confinement at the outer bank. The model also predicts a much greater surface depression at the inside of the meander bend. The resulting water surface slope provides a greater centrifugal force to turn the flow within the confines of the meander banks, preventing any lateral flow separation at the inside of the curve. Although two high velocity cores can still be identified in the confluence at x/d = 3 (Figure 3a, S confluence), the secondary circulation is efficient in redistributing the downstream momentum, and by x/d = 6 the maximum velocity of $1.32u_{av}$ (Table 3) occurs at the center of the channel. The highest velocity at the outer wall of the meander bend is lower, and kinetic energy values here are also lower than those that occur in the mixing layer of the confluence just downstream of the downstream junction corner.

The small degree of deflection of flow in the straight channel in the asymmetrical confluence (Figure 3b, A confluence and 3c, A confluence) is partly a function of the lack of width reduction in the postconfluence channel. As the width ratio (WR) decreases, the distance between the upstream and downstream junction corners increases ("A" to "B" in Figure 1). This has the effect of increasing the deflection of flow in the straight channel, creating flow curvature in the opposite direction to that from the curved tributary (Figure 4a). With a width ratio of 0.5, bed divergent flow (Figure 4b, 0.5 WR), associated with twin cells (Figure 4c), is predicted in this region. The center of rotation of these cells is very close to the bed, and convergent flow dominates over most of the flow depth. If the frame of reference of Rhoads and Kenworthy [1998] is used, in which secondary velocity direction is defined separately at each vertical so no net secondary discharge occurs across a vertical, these cells are more pronounced, with a center of rotation that is higher in the flow [Lane et al., 2000]. The flow pattern does not persist beyond the downstream junction corner and is replaced by a single circulation cell, similar to that shown in Figure 3a with A confluence, further downstream [Bradbrook et al., 2000a]. These observations accord with the conclusions reached by Rhoads and Kenworthy [1998] for a low momentum ratio flow in the confluence of the Kaskaskia-Copper Slough: back-to-back helical circulation cells can form at the entry to a confluence, even with pronounced planform asymmetry.

3.2. Confluence of the Kaskaskia River and Copper Slough

Figure 5 shows contours of downstream velocity and vectors in the plane of seven cross sections (defined by *Rhoads and Kenworthy* [1998] and shown in Figure 2) for the Kaskaskia River-Copper Slough confluence. At the farthest upstream

Table 3. Comparison Between the 90° Symmetrical Confluence and 45° Meander Bend Where d is the Channel Depth and u_{av} Is the Bulk Mean Velocity

	Symmetrical	45° Bend
Surface elevation, mm	4.02	4.64
Surface depression, mm	5.95	14.3
Lateral separation zone length d^{-1}	1.60	0.0
Maximum downstream velocity at the center of channel or meander wall or u_{ev}	1.32	1.10
Maximum turbulent kinetic energy at the center of channel or meander wall or u_{av}^2	0.036	0.018



Figure 4. Effect of reduction in overall cross-sectional area in the postconfluence channel: (a) surface vectors in central region of the confluence, (b) bed vectors in central region of the confluence, and (c) vectors in plane of cross section "A" with view downstream and perpendicular to cross section.

section, A3, the flow in the center of the channel is very slow (less than 0.4 m s^{-1}). The convergence of the flow from each tributary is clear, and there is some downwelling in the center of the channel. There is no sign of bank-directed flow at the bed, but the magnitude of cross-stream flow is lower here. The flow acceleration between cross sections A3 and A1 is much greater than that farther downstream. At section A2 the zone of downwelling is broader, particularly in the lower half of the flow, and there is the beginning of reverse flow at the bed on the true left. At section A1 the downwelling zone is broader still, and there is bed divergent flow, but no closed circulation cells can be identified. *Rhoads and Kenworthy* [1998] describe a similar pattern in measurements of cross-stream velocity at cross sections A1 to A3 on June 7, 1993.

At section A the model predicts that flow on the true left is dominated by tributary flow toward the true right. After rotation of a similar pattern of cross-stream velocity measurements to produce the cross-stream component of the secondary velocity, Rhoads [1996] is able to identify a secondary circulation cell on this side since the cross-stream component at the bed is smaller than at the surface. On the true right of center the model predicts flow near the bed out of the scour hole and toward the true-right bank. This forms part of a small circulation cell near the true-right bank, with flow toward the channel center at the surface. This pattern is also evident in the crossstream measurements of Rhoads [1996]. At section B the predicted flow vectors show an element of rotational flow on the true-left side, with flow near the bed upward and toward the true left and that at the surface toward the center of the channel where strong downwelling is evident. This downwelling leads to some migration of downstream velocity into



Figure 5. Predictions of vectors in the plane of seven cross sections with contours of downstream velocity (in $m s^{-1}$ with an interval of 0.5 $m s^{-1}$) superimposed for confluence of Kaskaskia River and Copper Slough, July 8 [*Rhoads*, 1996]. View is upstream with vertical magnification times 3.

the scour hole (section B in Figure 5) and initiates divergent flow at the bed. At section C the rotational flow on the true left continues, but the center of rotation has moved closer to the surface. Flow on the true-right side of the channel is predominantly toward the true left with a strong upward component out of the scour hole (section C in Figure 5). By section E the model predictions now show a single core of high velocity on the true-right side of the channel, but there has been flow deceleration over all of the cross section. The predicted vectors indicate strong flow near the bed on the true left toward the center of the channel, with strong upwelling, reflecting the reverse gradient out of the scour hole. Near the true-right bank, flow is generally downward.

Although the aim was not to reproduce exactly the data measured at this confluence, the flow patterns are qualitatively similar to those measured by *Rhoads* [1996], with flow acceleration and the gradual merging of the two cores of high velocity from each tributary into a single core on the true right.

The secondary flow patterns become more asymmetrical throughout the confluence with an initial weak counterrotating pattern replaced farther downstream by a single clockwise (viewed in the direction of flow) rotation on the true left. Thus, while there are differences in quantitative terms in the predictions, these qualitative patterns are similar to those identified by *Rhoads* [1996] and thus allow this approach to provide theoretical support for the inferences made by *Rhoads* [1996, Figure 24.15] from patterns of empirical data.

Figure 6 shows the surface streamlines and water surface elevation predicted by the model. The pressure at the bed mirrors the pattern of water surface elevation. Throughout the confluence the streamlines (Figure 6a) from the tributary curve strongly in an anticlockwise manner (viewed from above), as the flow becomes aligned with the postconfluence channel. The streamlines from the main channel have a much smaller degree of curvature. Deflection by the incoming tributary flow at cross section A3 causes them to curve initially in a clockwise direc-



(b)



Figure 6. (a) Surface streamlines and (b) contours of free-surface displacement from the initial planar surface for Kaskaskia-Copper Slough confluence on July 8, 1992.

tion, but downstream of section A1 this continued deflection causes an inflection in the direction of curvature, so that they curve in the same direction as the tributary streamlines. Thus water surface superelevation (Figure 6b) is found at the center of the channel at cross sections A1, A2, and A3 where, as *Rhoads and Kenworthy* [1998] note, there will be a zone of flow that is analogous to a back-to-back meander. Farther downstream, the superelevation migrates to the true right (outer bank), with the greatest relative surface depression at the true left (inner bank). At section A, predicted elevation of the water surface is about 2 cm higher at the outer bank compared to the inner bank which is similar to that surveyed in the field [*Rhoads*, 1996]. Therefore, with distance down through the confluence, there is a critical transformation of the planform streamline curvature, and the meander analogy breaks down [e.g., *Rhoads*, 1996].

Presentation of the evidence thus far has emphasized the role of planform streamline curvature, which is steered primarily by the channel banks. The inflection of the main channel streamlines is mirrored by an inflection in the true-right bank at A1 (Figure 6a). However, downstream of section A1 there are strong deviations from the flow structures expected from a consideration of planform streamline curvature alone. This indicates the steering effect of bed topography. For example,



Figure 9. Observed (symbols) and calibrated (curve) soil gas carbon dioxide.

diffusivities, total porosities, and unsaturated zone thickness of the Plattsburgh site. Oxygen is at atmospheric levels at the ground surface and zero at the capillary fringe, while carbon dioxide vanishes at the ground surface and attains a common value at the capillary fringe. Case I is the calibrated profile (Figures 8 and 9), featuring an α of 0.114 and a Λ_s equal to zero. Case II eliminates the variation of porosity by setting α and Λ_s equal to zero, resulting in a linear profile. We see that the reduction of air porosity near the capillary fringe imparts a concave shape to both the oxygen and carbon dioxide profiles; a shape that is also evident in the data (Figures 8 and 9). Case III zeros α and J_{SO} , so that the degradation is assumed to be carried by a finite Λ_s value. Reactions in the unsaturated zone impart a convex shape to the oxygen and carbon dioxide profiles, as measured by Ostendorf and Kampbell [1991]. The Plattsburgh oxygen and carbon dioxide profiles are not convex nor do we observe appreciable hydrocarbon vapors in the unsaturated zone.

4.3. Barometric Pressure Corrections at Plattsburgh

Figure 13a displays (as symbols) the reported daily average barometric pressure fluctuation observed at Burlington International Airport for September 1, 1995, through January 31, 1996. The National Weather Service maintains a first-order weather station (Average Daily Station Pressure is available at http://www.ncdc.noaa.gov) at the airport, which is about 20 miles southeast of the site. The average of the 138 atmospheric pressures is cited as $p_s(1.01 \times 10^5 \text{ Pa})$ in Table 1. This value is subtracted from the data, yielding a set of observed atmospheric pressure fluctuations that we use to predict barometric corrections at the site through (20) and (21).

We use a finite difference approximation of the temporal derivative of the barometric pressure over the Kth sampling interval $K\Delta\tau$ in order to estimate the convolution integrals

$$\frac{d\rho}{d\tau} \cong \frac{\rho_{K} - \rho_{K-1}}{\Delta \tau} \qquad [(K-1)\Delta \tau < \tau < K\Delta \tau]. \quad (34)$$

Appendix 3 derives the resulting soil gas pressure p_I at the *I*th sampling time as the sum of contributions Δp_K created by the *K*th atmospheric pressure fluctuation ρ_K

$$\frac{p_I}{p_S} \approx 1 + \sum_{K=1}^{I} \Delta p_K \tag{35a}$$

$$\Delta p_{K} = (\rho_{K} - \rho_{K-1}) \Biggl\{ 1 + \frac{16\zeta^{2}}{\pi^{3}D_{P}\Delta\tau} \sum_{J=1}^{\infty} \Biggl[\frac{(-1)^{J}}{(2J-1)^{3}} \cos(A_{J}z) \\ \cdot [\exp(A_{J}^{2}D_{P}(K-I)\Delta\tau) - \exp(A_{J}^{2}D_{P}(K-I)\Delta\tau) - \exp(A_{J}^{2}D_{P}(K-I)\Delta\tau) \Biggr] \Biggr\}.$$
(35b)

Figure 13a displays the calibration (35) as a line, based on the pneumatic diffusivity value estimated in Appendix 2 and cited in Table 1. The calibration closely matches the data, and a typical barometric fluctuation has a one week timescale, so that t_P is 5×10^5 s.

The specific discharge v'_I at the *I*th sampling time is also derived in Appendix 3 as the sum of contributions $\Delta v'_K$ from the *K*th interval

$$v_I' = \sum_{K=1}^{I} \Delta v_K'$$
(36a)



Figure 10. Observed (symbols) and calibrated (curves) vapor concentrations of total hydrocarbons and trichloroethylene.



Figure 11. Observed (symbols) and calibrated (curves) separate phase concentrations of total hydrocarbon (T, mg kg⁻¹ dry soil) and trichloroethylene (T_{TCE} , mg kg⁻¹ dry soil).

$$\Delta v'_{K} = -(\rho_{K} - \rho_{K-1}) \frac{8\zeta(n - \theta_{F})}{\pi^{2}\Delta\tau} \sum_{J=1}^{\infty} \left\{ \frac{(-1)^{J+1}}{(2J-1)^{2}} \sin(A_{J}z) \right.$$

$$\left. \cdot \left[\exp(A_{J}^{2}D_{F}(K-I)\Delta\tau) - \exp(A_{J}^{2}D_{F}(K-I-1)\Delta\tau) \right] \right\}$$
(36b)

$$\frac{v'\zeta}{D_{S\zeta}} = O\left[\frac{\zeta^2 \rho(n-\theta_F)}{D_{S\zeta} \Delta \tau}\right].$$
 (36c)

We substitute the Table 1 values into (36c) and recover a value of unity, justifying the first-order importance of barometric specific discharge (12c). The estimate uses a daily sampling interval and a characteristic pressure fluctuation of 1000 Pa, so that ρ is of order 10^{-2} (Figure 13a). The specific discharge fluctuations are of order 10^{-7} m/s at Plattsburgh, as indicated by Figure 13b, which displays predicted surface specific discharge values at the site. The transient flux $v'C_s$ advected by these fluctuations is of order 10^{-8} kg/(m² s⁻¹), which is the same magnitude as the steady fluxes. We note, of course, that the average of these transient fluxes is zero.

The fluctuating concentration C'_I at time $I\Delta\tau$ is the sum of contributions $\Delta C'_K$ induced by the Kth atmospheric fluctuation, as suggested by Appendix 3:

$$\frac{C'}{C_{sc}} = \sum_{K=1}^{I-1} \Delta C'_K \tag{37a}$$

$$\Delta C_{K}^{\prime} = (\rho_{K} - \rho_{K-1}) \frac{32\zeta^{2}}{\pi^{4}R_{D}D_{P}\Delta\tau} \sum_{J=1}^{\infty} \left\{ \frac{(-1)^{J}}{(2J-1)^{4}} \sin(A_{J}z) \right.$$

$$\left. \cdot \left[1 - \exp\left(-A_{J}^{2}D_{P}\Delta\tau\right) + \exp\left(A_{J}^{2}D_{P}(K-I-1)\Delta\tau\right) - \exp\left(A_{J}^{2}D_{P}(K-I)\Delta\tau\right) \right] \right\}.$$
(37b)

Figure 13c displays the fluctuating concentrations implied by (37) and the Plattsburgh driving pressure gradient. The steady concentration dominates C', so that concentrations measured at any instant of time may be used to calibrate a steady state concentration profile. This contrasts markedly with flux based data, which measure contamination by accumulating mass over time at a given location. Since $v'C_s$ is comparable to the steady diffusive flux in magnitude, these traps measure an unsteady quantity. One may infer steady state fluxes either by repeated sampling of flux or by using a trapping interval larger than t_P in magnitude.



Figure 12. Sensitivity study of steady soil gas profiles. Case I: $\alpha = 0.114$, $\Lambda_S = 0 \ \mu g \ m^{-2} \ s^{-1}$; Case II: $\alpha = 0$, $\Lambda_S = 0 \ \mu g \ m^{-2} \ s^{-1}$; Case III: $\alpha = 0$, $J_{SO} = 0 \ \mu g \ m^{-2} \ s^{-1}$.



Figure 13. (a) Observed (symbols) and calibrated (curve) surface pressure; (b) predicted surface specific discharge; and (c) predicted surface concentration fluctuation.

4.4. Temperature Fluctuations at Plattsburgh

We ignore temperature induced concentration fluctuations at Plattsburgh, since steady diffusivity dominates temperature induced diffusive fluctuations in (3). Temperature may cause periodicity in a shallow aquifer, however, by altering the saturated vapor pressure of the hydrocarbon source [Van Vliet et al., 1993] or by altering the kinetics of biodegradation [Ostendorf et al., 1997]. Seasonal temperature fluctuations are governed by the classical heat diffusion equation [Hillel, 1982]

$$\frac{\partial T}{\partial t} - D_T \frac{\partial^2 T}{\partial z^2} = 0$$
 (38a)

$$T = T_s + T_{\zeta} \sin \left[(\omega_T t + \phi_T) \right] \qquad (z = \zeta) \qquad (38b)$$

$$T = T_s \qquad (z = 0) \tag{38c}$$

with thermal diffusivity D_T , surface amplitude T_{ζ} , frequency ω_T , and phase shift ϕ_T . The answer can be expressed as the imaginary part of a complex solution

$$T = T_{s} + T_{\zeta} \exp\left[-(\zeta - z)\sqrt{\frac{\omega_{T}}{2D_{T}}}\right]$$

$$\cdot \sin\left[\omega_{T}t + \phi_{T} - (\zeta - z)\sqrt{\frac{\omega_{T}}{2D_{T}}}\right]$$
(39a)
$$\zeta^{2}\omega_{T} \approx -1$$
(201)

$$\frac{\zeta^2 \omega_T}{D_T} \gg 1 \tag{39b}$$

Equation (39a) is valid for a deep unsaturated zone (39b), so that surface temperature variations decay without materially influencing the capillary fringe. Equation (39b) precludes periodic boundary conditions from the unsaturated zone transport equation.

We confirmed (39b) at Plattsburgh by measuring soil temperatures using a nested thermocouple cluster constructed from copper-constantan wire fitted with a miniature connector at the top. A typical installation uses thermocouples installed at 0.5 m intervals in the upper 3 m and at intervals of 1 m thereafter. Figure 14 displays some of the soil temperature data from the thermocouple arrays in Plattsburgh boreholes SPK and 12AT from October 1995 to December 1996. A sinusoidal temporal variation is evident in the four depths shown, with a phase shift and a damped amplitude with depth. We calibrate (39) with data from these depths and nine additional depths, with the values cited in Table 1. The temperature frequency of 1.99×10^{-7} rad/s is annual, and T_s (281.8°K) is the average of 377 observations at 15 depths for 21 dates from October 13, 1995, to December 19, 1996. The phase shift corresponds to a temporal origin of September 1, 1995, for Plattsburgh. We calibrate the model with a nested Fibonacci search for phase shift, thermal diffusivity, and seasonal disturbance amplitude, with the error statistics defined by (23). The calibration appears as curves in Figure 14, based on a ϕ_T value of 1.91 rads, a D_T value of 1.51×10^{-6} m²/s, and a T_{ζ} of 13.3°K. The fit is excellent, as evidenced by an error standard deviation σ_T of 3.0°K.

The calibrated thermal diffusivity of $1.51 \times 10^{-6} \text{ m}^2/\text{s}$ implies that $\zeta^2 \omega_T / D_T = 19$, satisfying (39b). The insulating effect of the soil is evident in Figure 14: Soil temperature fluctuations are damped and delayed with increasing depth in the soil, and the Plattsburgh water table is deep enough to preclude appreciable thermal effects on conditions in the capillary fringe. This would not be the case in a shallower site, however. Equations (39) and (46) would serve as a starting point for temperature corrected concentration model. The corresponding concentration correction would have to satisfy a diffusion equation instead of (12a).

5. Conclusions

We calibrate a stoichiometrically coupled soil gas transport model with spatially resolved observations of carbon dioxide, oxygen, total hydrocarbon, and trichloroethylene vapor concentrations in the unsaturated zone above a weathered jet fuel/solvent spill at Plattsburgh Air Force Base in upstate New York. The oxygen and carbon dioxide calibration suggests that aerobic microorganisms in the subsurface degrade jet fuel vapor at a steady rate of 9.5 μ g total hydrocarbons (m⁻² s⁻¹). The absence of appreciable total hydrocarbon vapors from the unsaturated zone suggests that nearly all of the evaporating jet fuel is consumed in the capillary fringe. The solvent does not degrade in the fringe, however, and the model and data estimate a steady stripping rate of 0.012 μ g TCE (m⁻² s⁻¹), which persists through the unsaturated zone. This solvent vapor flux is consistent with a set of separate phase core samples and calibrates an estimate of total hydrocarbon evaporation from the capillary fringe. The total hydrocarbon stripping rate is stoichiometrically equal to the oxygen and carbon dioxide fluxes entering and leaving the fringe, supporting the hypothesis of jet fuel biodegradation in the fringe.

Barometric pumping slightly alters the steady, first-order, diffusive concentration profile at Plattsburgh, although the corresponding transient advective flux is comparable to the steady diffusive flux. We derive a simple, perturbation theory for the small, transient concentration corrections and include it in the calibration, based on observed atmospheric pressures. The second-order theory is valid at Plattsburgh because the soil is uniform and permeable, with a relatively deep capillary fringe. It should be noted that the corrections are too small to materially affect the soil gas concentration profiles and the pneumatics are not calibrated with subsurface pressure or specific discharge data at the site. Thus the barometric theory is not tested with field data.

Appendix 1: Transient Soil Gas Transport Equation

We pursue a simple analytical account of the transient concentration profile for a uniform soil by assuming that the air porosity and diffusivity are constant to leading order, so that the right-hand side of (6) is approximated by a diffusion equation

$$(\theta_{s} + K_{w}\theta_{ws}) \frac{\partial C'}{\partial t} - \frac{\partial}{\partial z} \left(\theta_{s}D_{s} \frac{\partial C'}{\partial z} \right)$$

$$\approx (n - \theta_{F} + K_{w}\theta_{F}) \frac{\partial C'}{\partial t} - (n - \theta_{F})D_{s\zeta} \frac{\partial^{2}C'}{\partial z^{2}} \qquad (40)$$

$$(\alpha \ll 1).$$

The unsteady equation simplifies further if the unsaturated zone is far less biologically active than the capillary fringe (so that $J_{SO} \gg \Lambda_S$). The steady flux is constant in the absence of sources or sinks in the unsaturated zone, so that (7) reduces to

$$-\theta_{S}D_{S}\frac{dC_{S}}{dz}=J_{SO}\qquad(\Lambda_{S}\ll J_{SO}).$$
(41)

We use (41) to simplify the right-hand side of (6) with the result

$$\frac{\partial}{\partial z} \left\{ \left[\alpha_L v' + \theta_S D_S \left(\frac{D'}{D_S} + \frac{\theta'}{\theta_S} \right) \right] \frac{dC_s}{dz} \right\}$$
$$= -J_{SO} \frac{\partial}{\partial z} \left(\frac{D'}{D_S} + \frac{\theta'}{n - \theta_F} \right) + \frac{\partial}{\partial z} \left(\alpha_L v' \frac{dC_s}{dz} \right)$$
(42)

We differentiate (11a) and approximate the result for uniform air porosity and relatively abiotic soil

$$\frac{dC_s}{dz} = -\frac{C_{sc}}{\zeta} \left(\frac{z}{\zeta}\right)^{-10\alpha/3} \qquad (\Lambda_s \ll J_{so}) \qquad (43a)$$

$$\frac{dC_s}{dz} \approx -\frac{C_{sc}}{\zeta} \qquad (\alpha \ll 1). \tag{43b}$$

Equation (43a) suggests that the slope of the concentration profile becomes linear with increasing elevation, particularly for uniform soils. Equation (43b) helps to establish a constraint for the neglect of dispersion from the right-hand side of (6)

$$-v' \frac{dC_s}{dz} + \frac{\partial}{\partial z} \left(\alpha_L v' \frac{dC_s}{dz} \right) \cong \frac{v' C_{SC}}{\zeta} \qquad (\alpha_L \ll \zeta) \qquad (44a)$$

$$\frac{\partial v'}{\partial z} \approx \frac{v'}{\zeta}.$$
 (44b)

Finally, we Taylor expand (3b) about the average temperature [Ostendorf et al., 1997] and air porosity in order to evaluate D'

$$\frac{D'}{D_s} \approx \frac{7}{4} \left(\frac{T - T_s}{T_s} \right) + \frac{7}{3} \left(\frac{\theta'}{n - \theta_F} \right)$$
(45a)

$$\frac{\partial}{\partial z} \left(\frac{D'}{D_s} \right) \approx \frac{7}{4T_s} \frac{\partial (T - T_s)}{\partial z} + \frac{7}{3(n - \theta_F)} \frac{\partial \theta'}{\partial z} \quad (45b)$$

We incorporate (40)-(45) into (6) and deduce a nonhomogeneous diffusion equation governing transient corrections in uniform, abiotic soil

$$R_{D} \frac{\partial C'}{\partial t} - D_{S\zeta} \frac{\partial^{2} C'}{\partial z^{2}}$$

= $\frac{C_{SC}}{\zeta} \left[\frac{v'}{n - \theta_{F}} - \frac{7D_{S\zeta}}{4T_{S}} \frac{\partial (T - T_{S})}{\partial z} - \frac{10D_{S\zeta}}{3(n - \theta_{F})} \frac{\partial \theta'}{\partial z} \right].$ (46)

The three transient diffusive terms are of second-order importance when unsteady advection is of first-order importance, leading to (12). Equation (46) describes second-order transience when unsteady advection, thermal fluctuations, and porosity fluctuations are all of second-order importance. The case may be considered analytically when the pressure [*Massman* and Farrier, 1992], temperature [*Hillel*, 1982], and infiltration [*Eagleson*, 1970] obey diffusion equations.

Appendix 2: Permeability Estimate

Figure 15 displays the monthly average precipitation fluctuation r'_I (cm month⁻¹) observed at Burlington from January 1994 through January 1996 (Monthly Average Station Precipitation is available at http://www.ncdc.noaa.gov). We assume that the field capacity θ_F supports the average monthly precipitation r_{IS} for the period (8.58 cm month⁻¹ downward). We note in passing that $r_{IS} \ll v'$, so that (4d) is satisfied at Plattsburgh. *Brooks and Corey* [1966] present a convenient power law for the moisture characteristic relating steady fluid saturation to matrix pressure ψ (a negative variable):

$$\frac{\theta_W}{n} = \left(\frac{\psi_B}{\psi}\right)^{\beta}.$$
(47)

Mualem [1976] derives an unsaturated permeability k model based upon the *Brooks and Corey* [1966] characteristic, which we combine with (47) to deduce

$$k = k_{\text{SAT}} \left(\frac{\theta_W}{n}\right)^{2.5 + 2/\beta}.$$
 (48)

We assume that the field capacity corresponds to the average monthly infiltration $(-3.26 \times 10^{-8} \text{ m/s})$ in the uniform region of the flow field above the elevation z_F , hence

$$r_{IS} = -\frac{kg}{\nu} \qquad (z > z_F, \ \theta_W = \theta_F) \qquad (49a)$$

$$\beta = \frac{2}{\frac{\ln\left(-\frac{\nu r_{IS}}{gk_{SAT}}\right)}{\ln\left(\frac{\theta_F}{n}\right)} - 2.5}} \quad (k_{SAT} = 4.8 \times 10^{-12} \text{ m}^2) \quad (49b)$$



Figure 14. Observed (symbols) and calibrated (curves) soil temperature.

with gravitational acceleration g. Thus β is equal to 1.14 for a water kinematic viscosity ν of 1.2×10^{-6} m²/s.

We estimate ψ_B from observed moisture content data (Figure 4) by equating the elevation and pressure heads near the capillary fringe on the assumption of negligible viscous losses

$$\psi = \psi_B - z \qquad (0 < z < z_F) \tag{50a}$$

$$\theta_W = n \left(\frac{\psi_B}{\psi_B - z} \right)^{\beta} \qquad (0 < z < z_F)$$
(50b)

$$\theta_W = \theta_F \qquad (z_F < z < \zeta).$$
 (50c)

The moisture content and air porosity are uniform above z_F , which is specified by matching (50b) and (50c) with the result

$$z_F = -\psi_B \left[\left(\frac{n}{\theta_F} \right)^{1/\beta} - 1 \right].$$
 (51)

We recall (8) and cast (50) in terms of θ^* and find the *Brooks* and *Corey* [1966] air porosity fraction characteristic

$$\theta^* = \left(\frac{n}{n - \theta_F}\right) \left[1 - \left(\frac{\psi_B}{\psi_B - z}\right)^{\beta}\right] \qquad (0 < z < z_F) \qquad (52a)$$

$$\theta^* = 1 \qquad (z_F < z). \tag{52b}$$

We minimize the air porosity mean error (23) with an air entry head of -0.324 m, sketched as a dotted line in Figure 5. The calibrated *Brooks and Corey* [1966] moisture characteristic parameters values are representative of sandy soil [*Eagleson*, 1970].

The Mualem [1976] and Brooks and Corey [1966] models also

combine to determine k_{AIR} , since the air flows through the large pore fraction of an unsaturated soil [Dury et al., 1999]

$$k_{\text{AIR}} = k_{\text{SAT}} \sqrt{1 - \frac{\theta_W}{n}} \left[1 - \left(\frac{\theta_W}{n}\right)^{1/\beta + 1} \right]^2.$$
(53)

We thus estimate a k_{AIR} value of 3.95×10^{-12} m², using the field capacity for θ_W . The air dynamic viscosity is 1.8×10^{-5} kg (m⁻¹ s⁻¹), so that a D_P value of 0.0783 m²/s may be computed with (13b), based on the observed average atmospheric pressure.

Appendix 3: Barometric Fluctuations

Equations (20) and (34) suggest that the soil gas pressure before the *I*th sampling time *t* is the superposition of contributions Δp_K induced by atmospheric fluctuations ρ_K during preceding times $K\Delta\tau$

$$\frac{p}{\rho_{s}} = 1 + \frac{1}{\Delta \tau} \left\{ \sum_{K=1}^{I-1} \left[(\rho_{K} - \rho_{K-1}) \int_{(K-1)\Delta \tau}^{K\Delta \tau} f(t-\tau) d\tau \right] + (\rho_{I} - \rho_{I-1}) \int_{(I-1)\Delta \tau}^{t} f(t-\tau) d\tau \right\}.$$
(54)

We invoke (19) and evaluate the convolution integrals with the result

$$\frac{1}{\Delta\tau}\int_{(K-1)\Delta\tau}^{K\Delta\tau} f(t-\tau) \ d\tau = 1$$

$$+ \frac{16\zeta^2}{\pi^3 D_P \Delta \tau} \sum_{J=1}^{\infty} \left\{ \frac{(-1)^J}{(2J-1)^3} \cos\left(A_J z\right) \exp\left(-A_J^2 D_P t\right) \right.$$
$$\cdot \left[\exp\left(A_J^2 D_P K \Delta \tau\right) - \exp\left(A_J^2 D_P (K-1) \Delta \tau\right) \right] \right\} (t > K \Delta \tau)$$
(55a)

$$\frac{1}{\Delta\tau} \int_{(I-1)\Delta\tau}^{t} f(t-\tau) d\tau = \frac{t}{\Delta\tau} - I + 1$$

+ $\frac{16\zeta^{2}}{\pi^{3}D_{P}\Delta\tau} \sum_{J=1}^{\infty} \left\{ \frac{(-1)^{J}}{(2J-1)^{3}} \cos(A_{J}z) \right\}$
 $\cdot [1 - \exp[A_{J}^{2}D_{P}[(I-1)\Delta\tau - t)]].$ (55b)

We recover pressure at the Ith sampling time (35) by setting t equal to $I\Delta\tau$ in (55).

Equations (13b), (14), and (54) suggest that the specific discharge before the Ith sampling time is comprised of contributions induced by the ρ_K fluctuations

$$v' = -\frac{(n-\theta_F)D_P}{\Delta\tau} \left\{ \sum_{K=1}^{I-1} \left[(\rho_K - \rho_{K-1}) \int_{(K-1)\Delta\tau}^{K\Delta\tau} \frac{\partial f}{\partial z} (t-\tau) d\tau \right] + (\rho_I - \rho_{I-1}) \int_{(I-1)\Delta\tau}^{t} \frac{\partial f}{\partial z} (t-\tau) d\tau \right\}.$$
(56)

Equation (19) is substituted into (56) with the result

$$\frac{D_P}{\Delta \tau} \int_{(K-1)\Delta \tau}^{K\Delta \tau} \frac{\partial f}{\partial z} (t - \tau) d\tau = \frac{8\zeta}{\pi^2 \Delta \tau} \sum_{J=1}^{\infty} \cdot \left\{ \frac{(-1)^{J+1}}{(2J-1)^2} \sin (A_J z) \exp (-A_J^2 D_P t) \right. \\ \left. \cdot \left[\exp \left(A_J^2 D_P K \Delta \tau \right) - \exp \left(A_J^2 D_P (K-1) \Delta \tau \right) \right] \right\} (t > K \Delta \tau)$$
(57a)

$$\frac{D_P}{\Delta\tau} \int_{(I-1)\Delta\tau}^t \frac{\partial f}{\partial z} \left(t - \tau\right) d\tau = \frac{8\zeta}{\pi^2 \Delta\tau} \sum_{J=1}^\infty \left\{ \frac{(-1)^{J+1}}{(2J-1)^2} \sin\left(A_J z\right) \right.$$
$$\left. \left. \left. \left[1 - \exp\left[A_J^2 D_P((I-1)\Delta\tau - t)\right]\right] \right\}.$$
(57b)

The specific discharge at time $I\Delta\tau$ (36) follows from (56) and (57).

We integrate (12a) from zero to time t with the formal result

$$\frac{C'}{C_{sc}} = \frac{1}{R_D \zeta(n - \theta_F)} \int_0^t v'(t'') dt''.$$
 (58)

Equations (56) and (57) specify the specific discharge as the sum of increments induced by atmospheric disturbances ρ_K , using series that converge for time t" greater than $K\Delta\tau$. We accordingly construe (58) as the sum of incremental contribu-



Figure 15. Observed monthly average precipitation fluctuation at Burlington International Airport available at http:// www.ncdc.noaa.gov.

tions, each integrated from $K\Delta\tau$ forward to preserve convergence

$$\frac{C'}{C_{SC}} = -\frac{D_P}{R_D \zeta \Delta \tau} \left\{ \sum_{K=1}^{I-1} \left[(\rho_K - \rho_{K-1}) \right] \right\} \\ \cdot \int_{K\Delta \tau}^t \int_{(K-1)\Delta \tau}^{K\Delta \tau} \frac{\partial f}{\partial z} (t'' - \tau) d\tau dt'' \right\}.$$
(59)

We substitute (57a) into (59) and derive

$$\frac{D_P}{\zeta\Delta\tau} \int_{K\Delta\tau}^{t} \int_{(K-1)\Delta\tau}^{K\Delta\tau} \frac{\partial f}{\partial z} (t'' - \tau) d\tau dt''$$

$$= \frac{32\zeta^2}{\pi^4 D_P \Delta\tau} \sum_{J=1}^{\infty} \left\{ \frac{(-1)^{J+1}}{(2J-1)^4} \sin (A_J z) \right.$$

$$\cdot [1 - \exp (-A_J^2 D_P \Delta \tau) + \exp [A_J^2 D_P ((K-1)\Delta \tau - t)]]$$

$$\cdot - \exp (A_J^2 D_P (K\Delta \tau - t))] \right\}$$
(60)

We evaluate (59) and (60) at the Ith sampling time to deduce (37).

Notation

- Fourier series coefficient, m^{-1} . A_{τ}
- soil gas concentration, kg/m³. С
- C_s steady soil gas concentration, kg/m³.
- C_{sc} characteristic steady soil gas concentration, kg/m³.

steady soil gas concentration at origin, kg/m³. C_{so}

 C_{TO} total hydrocarbon concentration at capillary fringe, kg/m³.

 C_{TSAT} equilibrium total hydrocarbon concentration, kg/m³.

- TCE concentration at capillary fringe, kg/m³. C_{TCEO}
- C_{TCESAT} equilibrium TCE concentration, kg/m³.
 - $C_X \\ C'$ soil gas oxygen concentration, kg/m³.
 - transient soil gas concentration, kg/m³.
 - C'_I transient soil gas concentration at the Ith sampling time, kg/m³.

- С dissolved concentration, kg/m³.
- soil gas diffusivity, m^2/s . D
- D_P pneumatic diffusivity, m²/s.
- D_{REF} reference free air diffusivity, m²/s.
- D_s steady soil gas diffusivity, m²/s.
- D_{SI} steady diffusivity at the ground surface, m²/s.
- $D_{SX\zeta}$ steady oxygen diffusivity at the ground surface, m^2/s .
 - D_T thermal diffusivity, m²/s.
 - D_W liquid diffusivity, m²/s.
 - transient soil gas diffusivity, m²/s. D'
 - d_I grain size with cumulative density function I, m.
 - E_T evaporation of total hydrocarbons, kg (m⁻² s⁻¹).
 - g gravitational acceleration, m/s^2 .
 - J_s steady soil gas flux, kg (m⁻² s⁻¹).
 - J_{SC} steady carbon dioxide flux, kg (m⁻² s⁻¹).
 - steady soil gas flux at top of capillary fringe, J_{so} kg $(m^{-2} s^{-1})$.
- J_{ST} steady total hydrocarbon flux, kg (m⁻² s⁻¹).
- J_{STCE} steady trichloroethylene flux, kg (m⁻² s⁻¹).
 - J_{SX} steady oxygen flux, kg (m⁻² s⁻¹).
 - K_W Henry constant.
 - k unsaturated permeability, m^2 .
- k_{AIR} air permeability, m².
- k_{SAT} saturated permeability, m².
 - L thickness of contaminated soil, m.
 - mass based moisture content, kg moisture/kg dry М soil.
 - *m* molar mass, kg/mole.
- $m_{\rm REF}$ reference molar mass, kg/mole.
- m_T molar mass of total hydrocarbons, kg/mole.
- m_{TCE} molar mass of trichloroethylene, kg/mole.
 - m_X molar mass of oxygen gas, kg/mole.
 - number of sample points. Ν
 - total porosity, m³ voids/m³ total. n
 - barometric pressure, Pa. р
 - barometric pressure at the Ith sampling time, Pa. p_I
 - steady atmospheric pressure, Pa. p_s
 - oxygen partial pressure, Pa. p_X
 - p^* transformed pressure, Pa s⁻¹
 - retardation factor. R_D
 - universal gas constant, m³ Pa mole⁻¹ °K⁻¹. R_U
 - steady infiltration rate, m/s. r_{IS}
 - monthly infiltration rate, cm/month. r_{I}
 - transformed time, s^{-1} . S
 - specific gravity of soil grains. s_G
 - Т absolute temperature, °K.
- $T_{\rm REF}$ reference temperature, °K.
 - T_s steady temperature, °K.
 - T_T total separate phase hydrocarbon content, kg hydrocarbons/kg dry soil.
- T_{TCE} separate phase trichloroethylene content, kg TCE/kg dry soil.
 - T_{ζ} amplitude of surface temperature fluctuation, °K. time, s. t
 - t_P barometric timescale, s.
 - soil gas specific discharge, m/s.
 - v_W water specific discharge, m/s.
 - transient soil gas specific discharge, m/s. v'
 - soil gas specific discharge at Ith sampling time, v'_I m/s.
 - distance above capillary fringe, m. z
 - uniform flow field region boundary, m. Z_F

- α air porosity uniformity exponent.
- α_L longitudinal dispersivity, m.
 - Brooks and Corey [1966] uniformity exponent. β
- χ_{TCE} liquid mole fraction of TCE, moles TCE/moles hydrocarbons.
- $\Delta C'_{K}$ contribution to C'_{I} from Kth pressure fluctuation.
- Δp_K contribution to p_I from Kth pressure fluctuation.
- Δv_K contribution to v_I from Kth pressure fluctuation, m/s.
 - $\Delta \tau$ atmospheric pressure sampling interval, s. individual calibration error. δ
 - mean calibration error.
 - δ_M
 - thermal phase shift, rad. ϕ_T
 - Λ depth integrated reaction rate, kg ($m^{-2} s^{-1}$).
- Λ_s steady depth integrated reaction rate, kg $(m^{-2} s^{-1})$.
- transient depth integrated reaction rate, Λ' kg $(m^{-2} s^{-1})$.
- source strength, 1/s. λ
- air dynamic viscosity, kg $(m^{-1} s^{-1})$. μ
- water kinematic viscosity, m²/s. ν
- air porosity, m³ air/m³ total. θ
- field moisture capacity, m³ moisture/m³ total. θ_F
- steady air porosity, m³ air/m³ total. θ_{S}
- moisture content, m³ moisture/m³ total. θ_W
- steady moisture content, m³ moisture/m³ total. θ_{WS}
- transient air porosity, m³ air/m³ total. θ'
- θ'_{W} transient moisture content, m³ moisture/m³ total.
- θ* air porosity fraction.
- atmospheric pressure fluctuation. ρ
- atmospheric pressure fluctuation at Kth sampling ρ_K time.
- ρ^* transformed surface pressure fluctuation, s. error standard deviation for calibration. σ
- error standard deviation for carbon dioxide σ_{c} calibration, kg/m³.
- error standard deviation for temperature σ_T calibration, °K.
- error standard deviation for trichloroethylene σ_{TCE} calibration, kg/m³.
 - error standard deviation for oxygen calibration, σ_X kg/m³.
 - σ_{θ} error standard deviation for air porosity calibration.
 - temperature fluctuation frequency, rad/s. ωτ
 - matrix pressure head, m. ł
 - air entry pressure head, m. ψ_B
 - thickness of unsaturated zone, m.

Acknowledgments. This research was funded by the Air Force Center for Environmental Excellence (AFCEE) under Contract F41624-95-C-8012 with the University of Massachusetts at Amherst. The authors acknowledge and appreciate the logistical and sampling support provided by AFCEE and the Base Realignment and Closure Civil Engineering Office at Plattsburgh Air Force Base. The views, opinions, and findings contained in this paper are those of the authors and do not necessarily reflect AFCEE official views or policies.

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(Received February 25, 2000; revised April 24, 2000; accepted April 25, 2000.)