Non-isothermal Water and Organic Solute Transport in the Soil Vadose Zone

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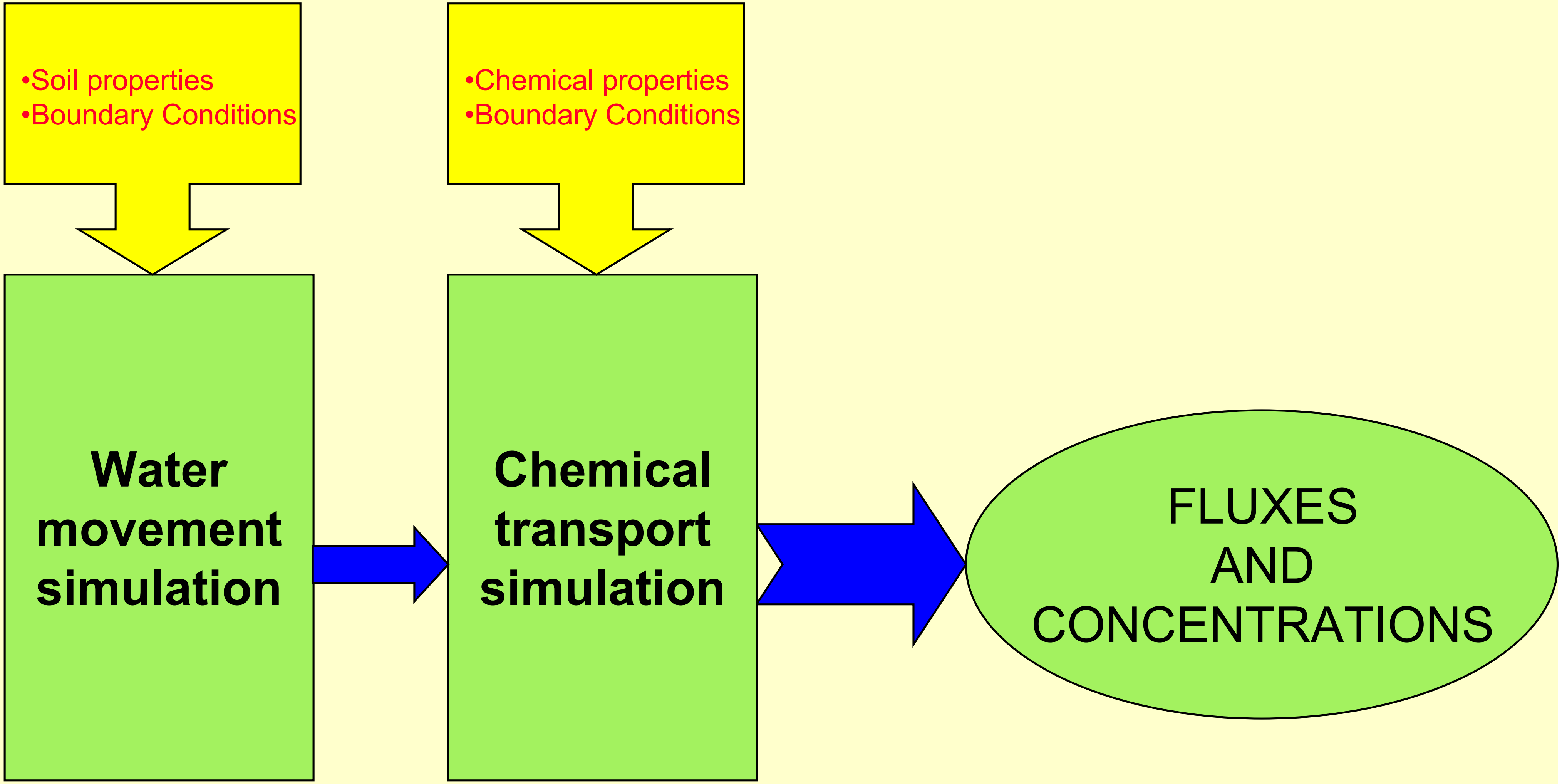
Solute transport simulation



- Soil properties
- Boundary Conditions

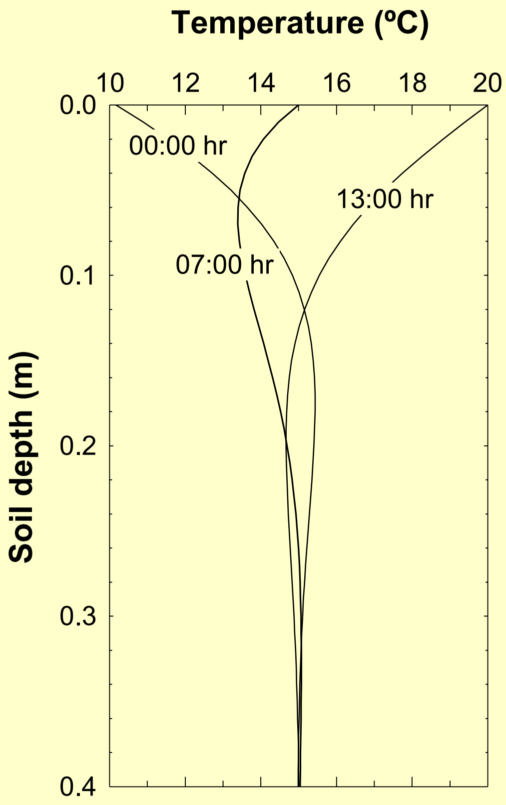
- Chemical properties
- Boundary Conditions

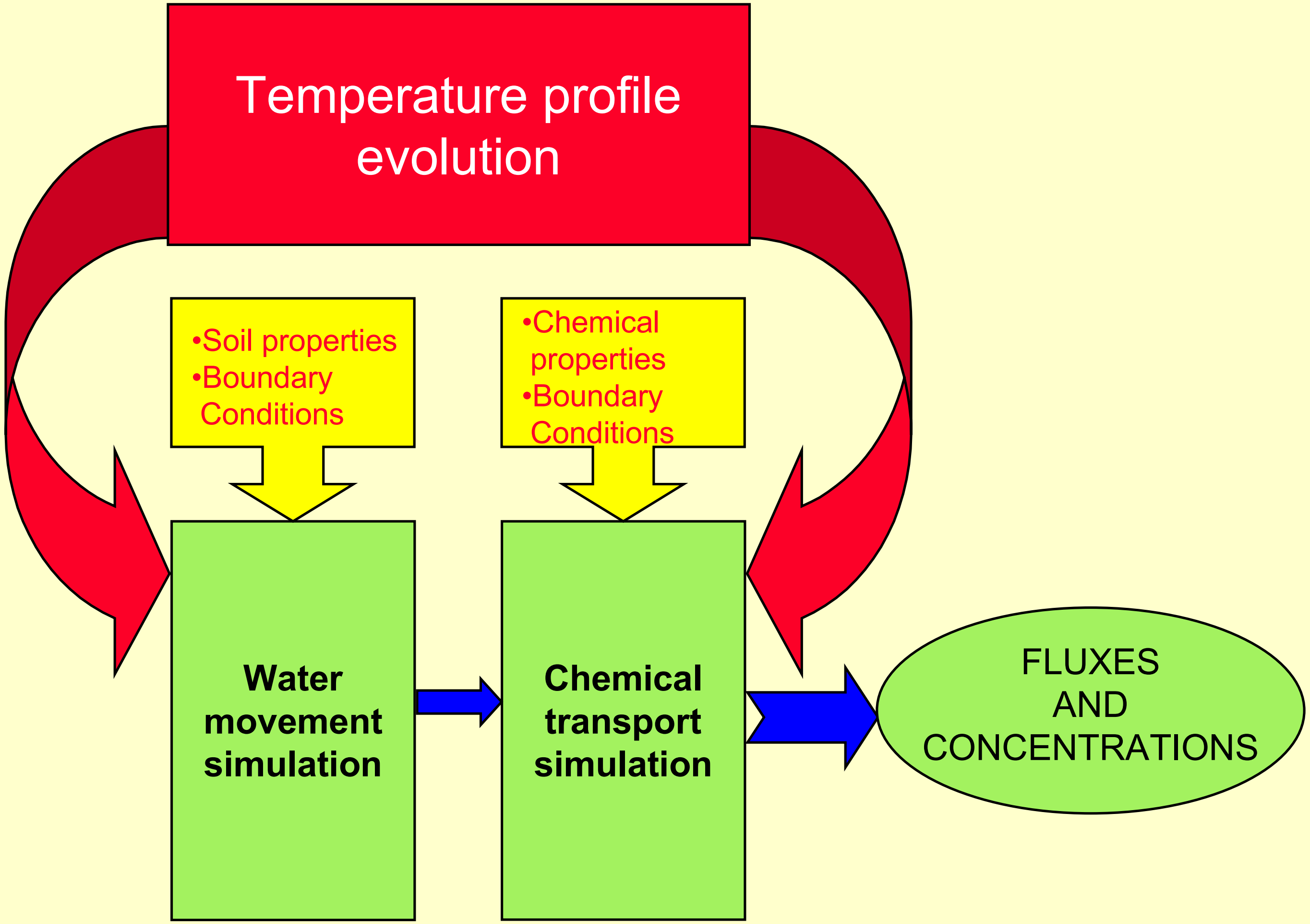
Water movement simulation

Chemical transport simulation

FLUXES
AND
CONCENTRATIONS

Temperature Varies with Soil Depth





Temperature profile evolution

- •Soil properties
- •Boundary Conditions

- •Chemical properties
- •Boundary Conditions

Water movement simulation

Chemical transport simulation

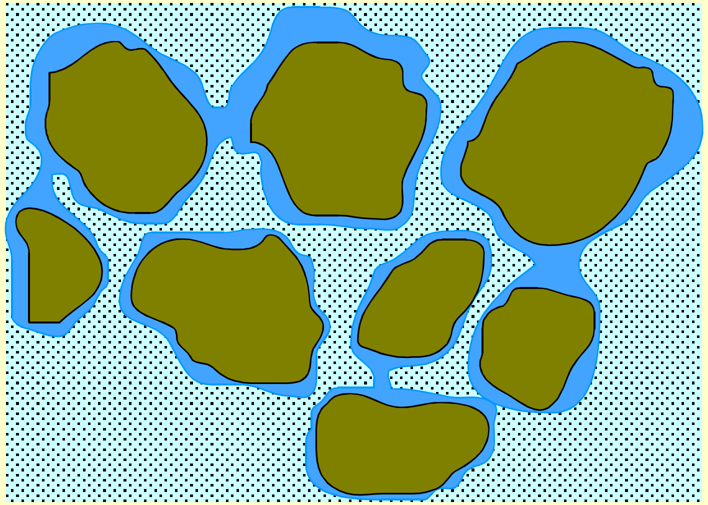
FLUXES AND CONCENTRATIONS

Objectives of the work

- **Water movement**
  - ⇨ Develop a model for the non-isothermal water transport in a homogeneous soil
  - ⇨ Implement a numerical code of the model; and
  - ⇨ Analyze the effects of various transport mechanisms.

- **Chemical transport**
  - ⇨ Develop a mathematical model for the non-isothermal solute transport under the influence of the water movement,
  - ⇨ Implement a numerical code of the model; and
  - ⇨ Compare results with isothermal conditions.

BASIC EQUATIONS for WATER TRANSPORT



- **Liquid water conservation**

Interphase flux from L to G

$$\frac{\partial\left(\theta_{liq}\cdot\rho_{liq}\right)}{\partial t}=\nabla\left(\rho_{liq}\,\mathbf{q}_{\mathbf{liq}}\right)-f_{LG}$$

- **Gaseous phase conservation**

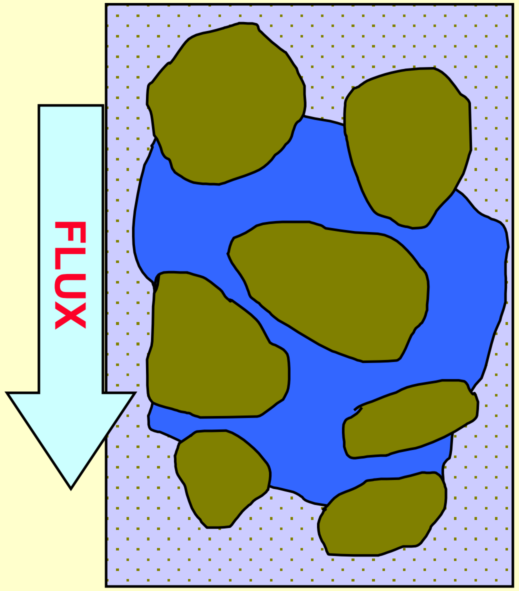
$$\frac{\partial\left(\theta_{gas}\cdot\rho_{gas}\right)}{\partial t}=\nabla\left(\rho_{gas}\,\mathbf{q}_{\mathbf{gas}}\right)+f_{LG}$$

- **Conservation Water vapor in the gaseous phase**

Dispersion and diffusion

$$\frac{\partial\left(\theta_{gas}\cdot\rho_{vap}\right)}{\partial t}=\nabla\left(\theta_{g}\,J_{h}+\rho_{vap}\,\mathbf{q}_{\mathbf{gas}}\right)+f_{LG}$$

Flux calculations

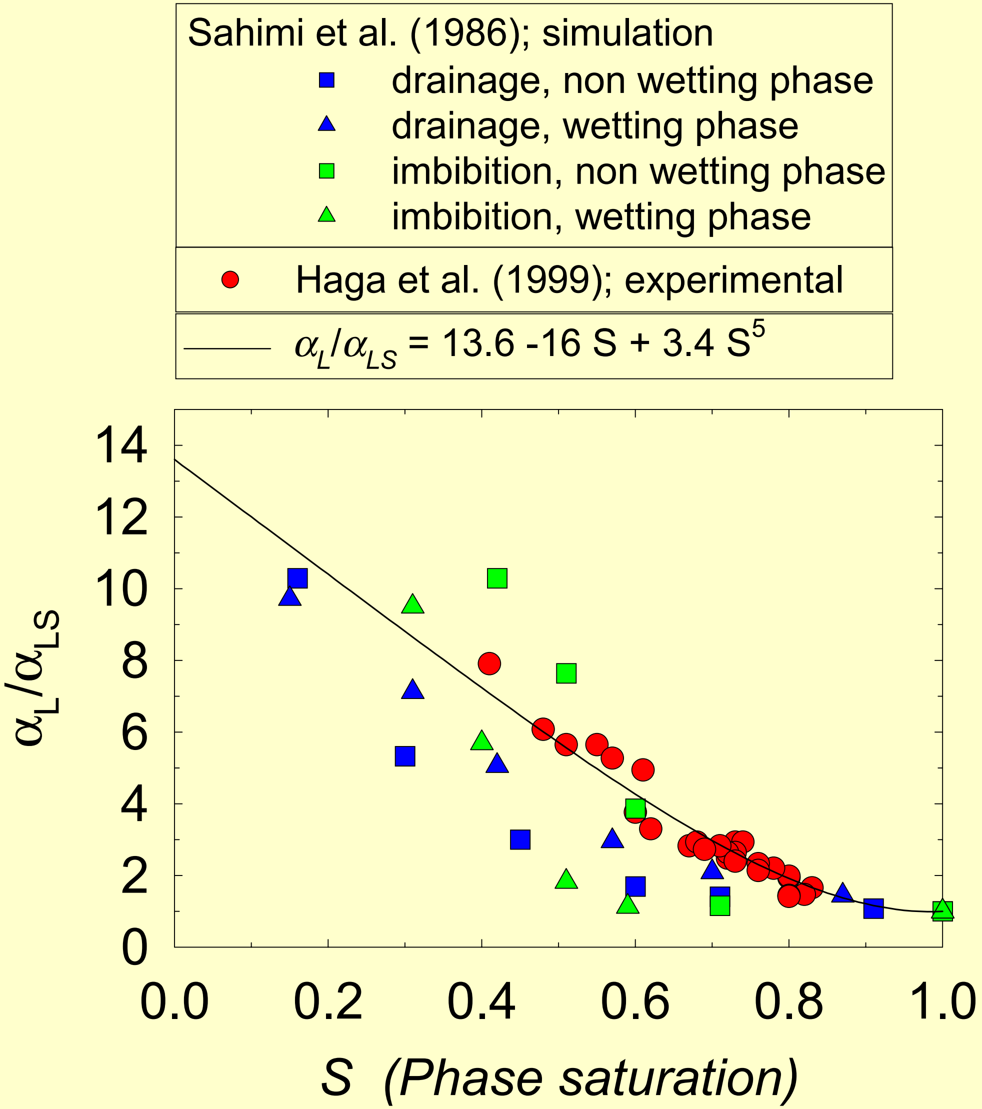


Darcy's law $$q_{liq} = -\left[\frac{k_i \cdot k_r}{\mu_l} \cdot \left(\nabla P_l - \rho_{liq}\, g\, \nabla z\right)\right]$$

Hydraulic dispersion $$\mathbf{J}_{\mathbf{h}} = -\left(\frac{D_G}{\tau_G} + \mathbf{D}_{\mathrm{v}G}\right) \cdot \nabla \rho_v$$

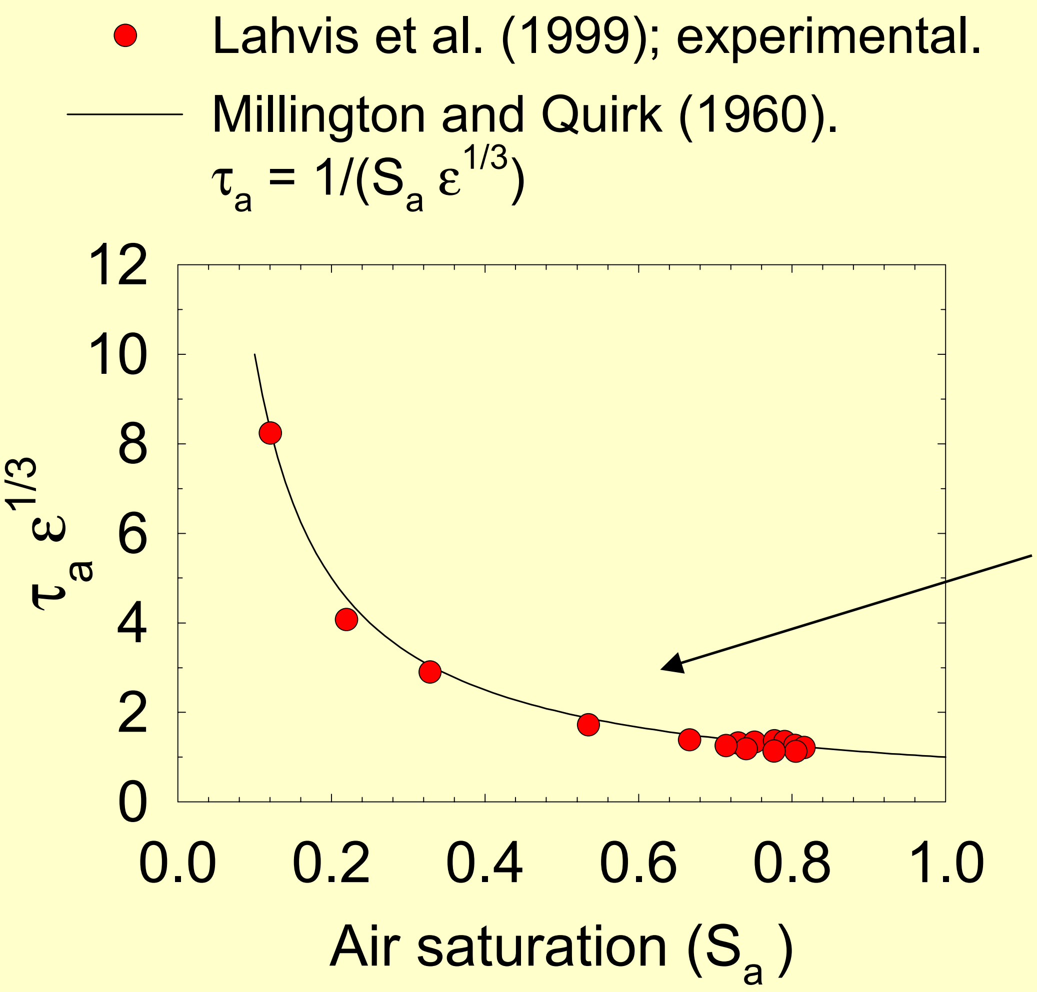
In vertical flux $$D_{vG} = \alpha_{lG} \cdot \frac{q_G}{\theta_G}$$

Longitudinal dispersivity



Longitudinal dispersivity in the unsaturated zone ranges, typically, between 5 and 20 cm [Jury et al., 1991]. The experimental value at saturation, α_{LS} = 7.8 cm, given by Biggar and Nielsen (1976), has been adopted in all simulations.

TORTUOSITY



Tortuosity can be estimated from the second model of Millington and Quirk, as proposed by the study of Jin and Jury (1996) based on a recompilation of available laboratory data.

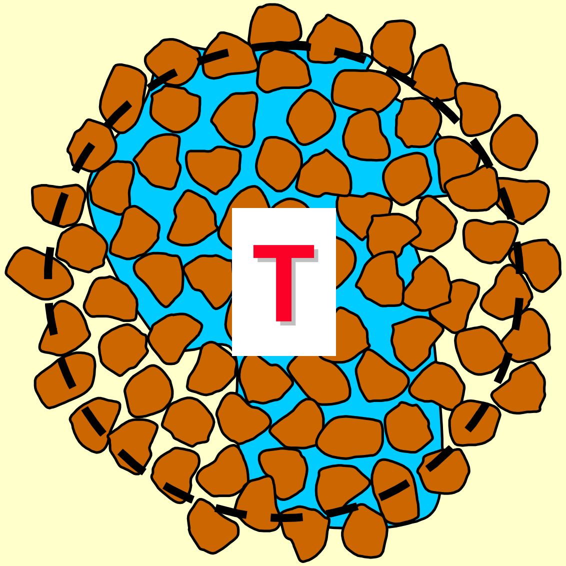
Here, the field data of Lahvis et al. (1999) is compared to the Millington and Quirk model.

ENERGY TRANSPORT: BASIC EQUATIONS

Hypothesis: local thermal equilibrium

Included mechanisms:

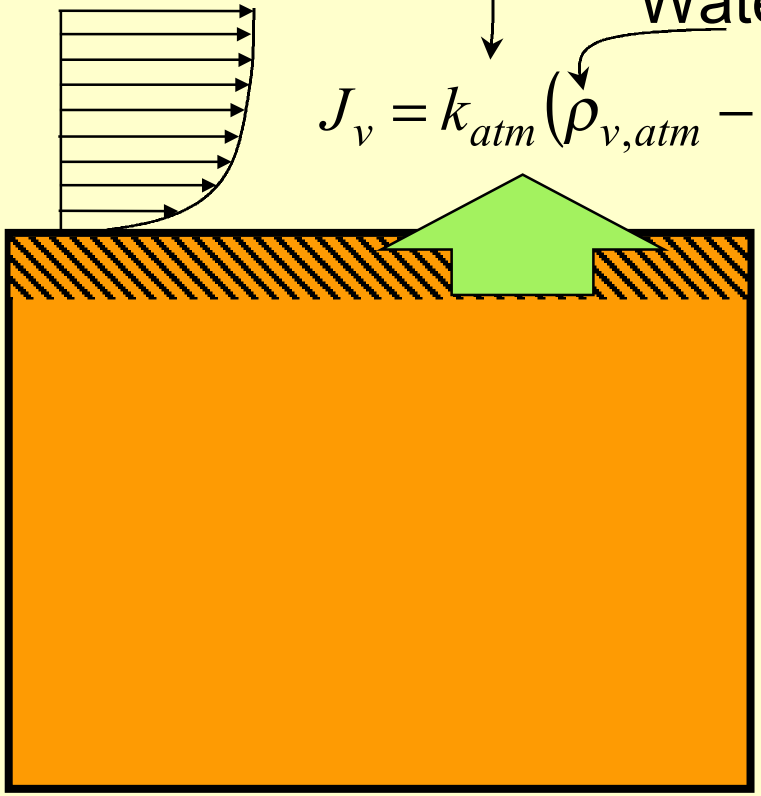
- Convection (liquid and gaseous phases)
- Water vapor dispersion
- Conduction
- Thermal dispersion



$$\frac{\partial\left(\theta_l\,\rho_l u_l+\theta_g\,\rho_g u_g+(1-\varepsilon)\rho_s u_s\right)}{\partial t}=$$

$$\nabla\left(\rho_l\,q_l h_l+\rho_g\,q_g h_g+\theta_g\,J_{hg}\left(u_v-u_a\right)-\left(\lambda_{eff}+\theta_{l\cdot}D^H_{ml}\right)\cdot\nabla T\right)$$

TOP BOUNDARY CONDITION FOR WATER TRANSPORT



Atmospheric-side mass transfer coefficient

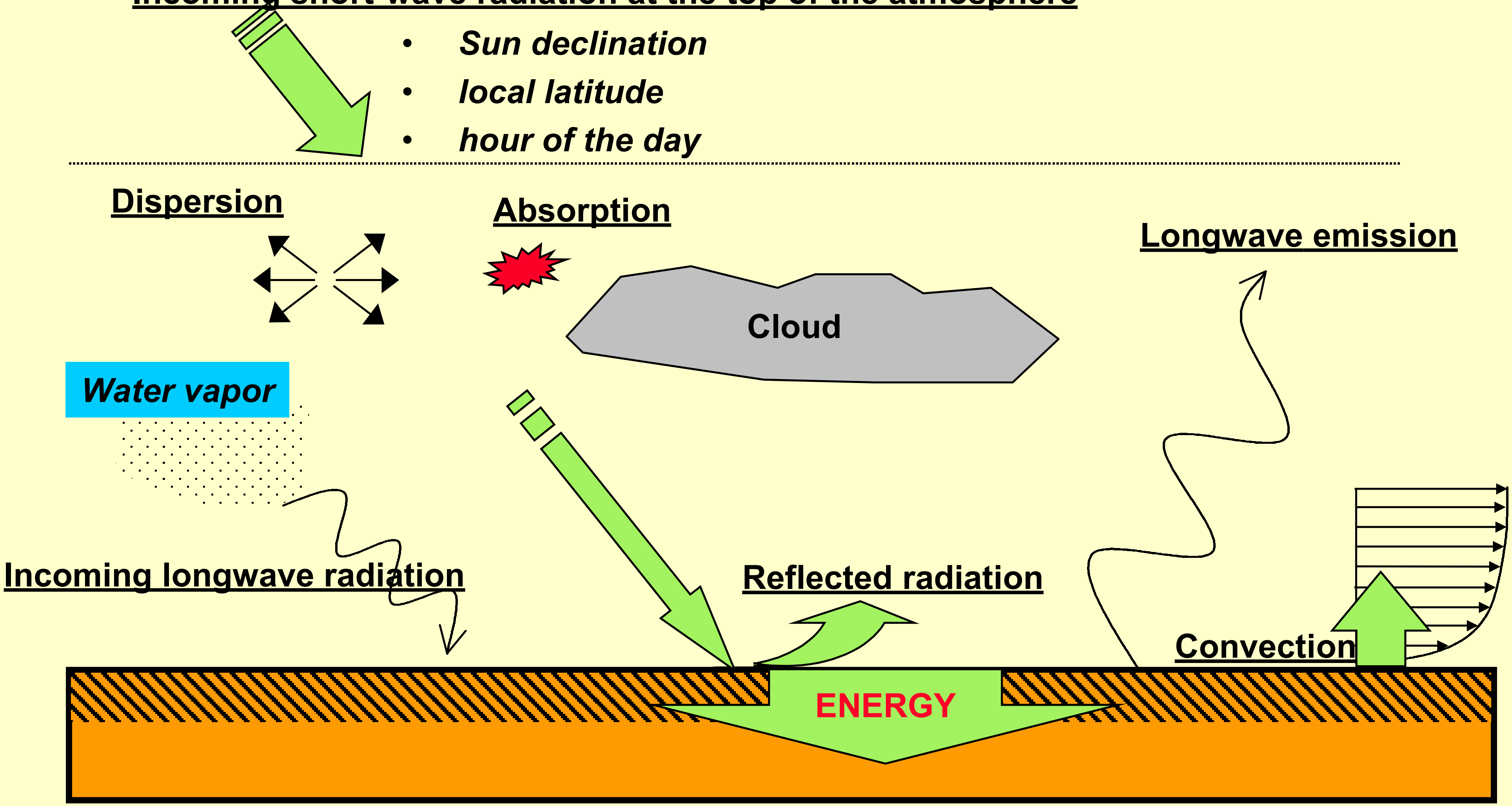
Water vapor concentration in the atmosphere

$$J_v = k_{atm}\left(\rho_{v,atm} - \rho_{v,0}\right)$$

$$\frac{\rho_v}{\rho_v^*} = \exp\left(\frac{P_l\, M}{\rho_l\, R\, T}\right)$$

Lord Kelvin’s equation,
relating water concentration in soil-gas phase and capillary pressure

TOP BOUNDARY CONDITIONS FOR ENERGY TRANSFER



Incoming short-wave radiation at the top of the atmosphere

- ***Sun declination***
- ***local latitude***
- ***hour of the day***

Dispersion

Absorption

Longwave emission

Cloud

Water vapor

Incoming longwave radiation

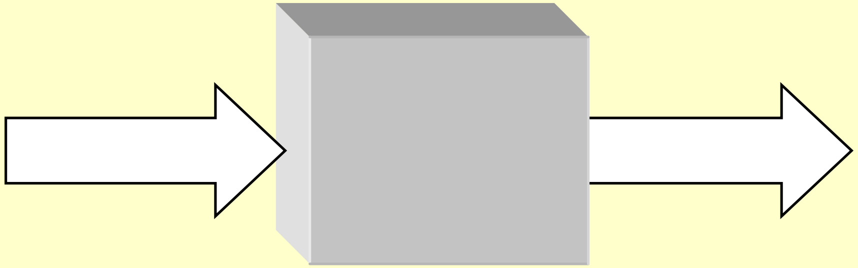
Reflected radiation

Convection

ENERGY

DISCRITIZATION

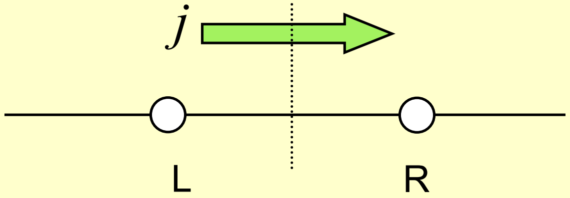
- Conservation equations formulated with the Finite Volume Method



Accumulation rate = Input fluxes - Output fluxes

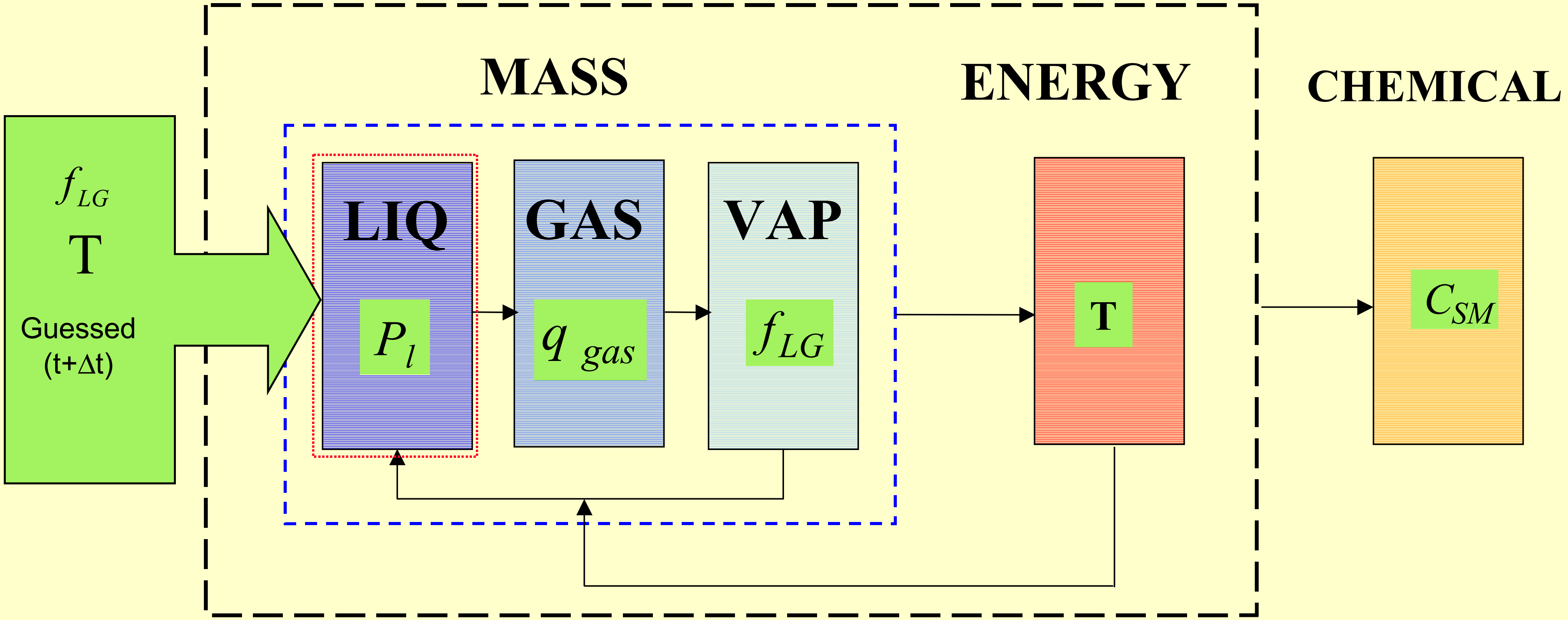
- Fluxes are calculated using Finite Differences

$$j = -\alpha \frac{\partial \zeta}{\partial z} = -\bar{\alpha} \frac{\zeta_R - \zeta_L}{z_R - z_L}$$



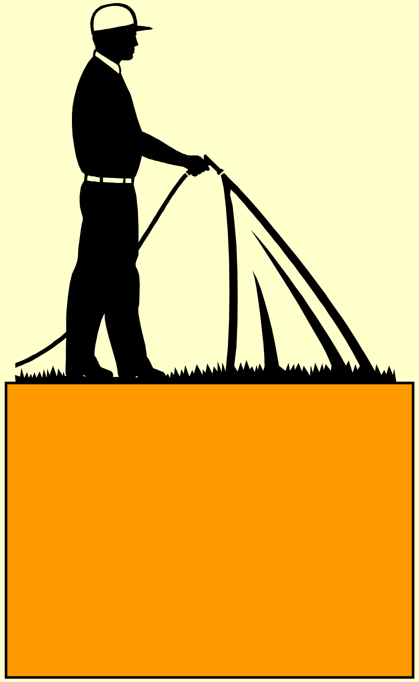
Numerical solution

Time step from *t* to *t* + *Δ t*



Literature Field Data

- **Procedure:**
  - ⇨ Soil irrigation.
  - ⇨ Water content measured gravimetrically.
  - ⇨ Evaporation measured using lysimeters.



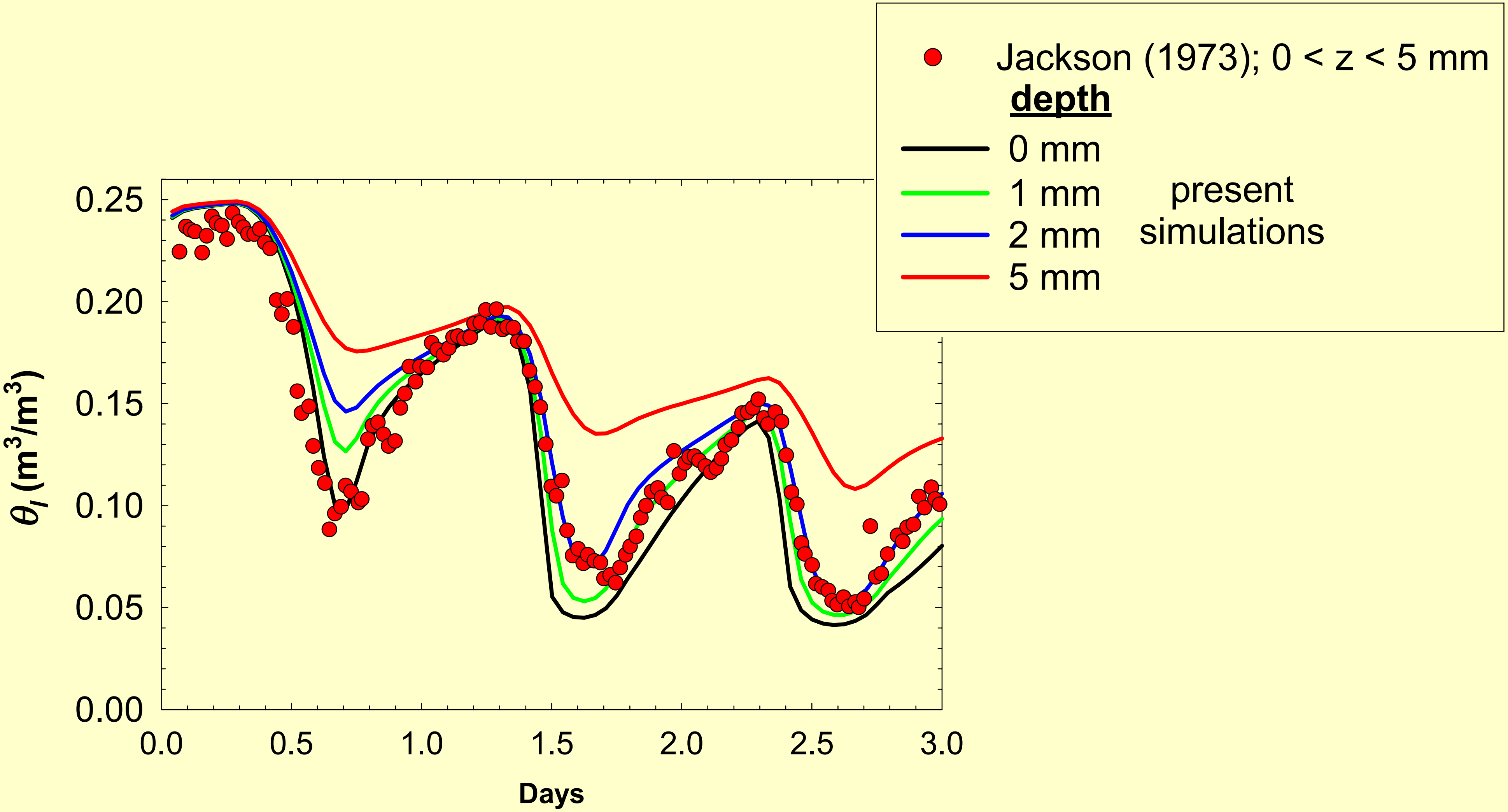
Jackson, R.D. (1973)
Diurnal changes of soil water content during drying

- Adelanto loam soil
- Initial irrigation 10 cm.

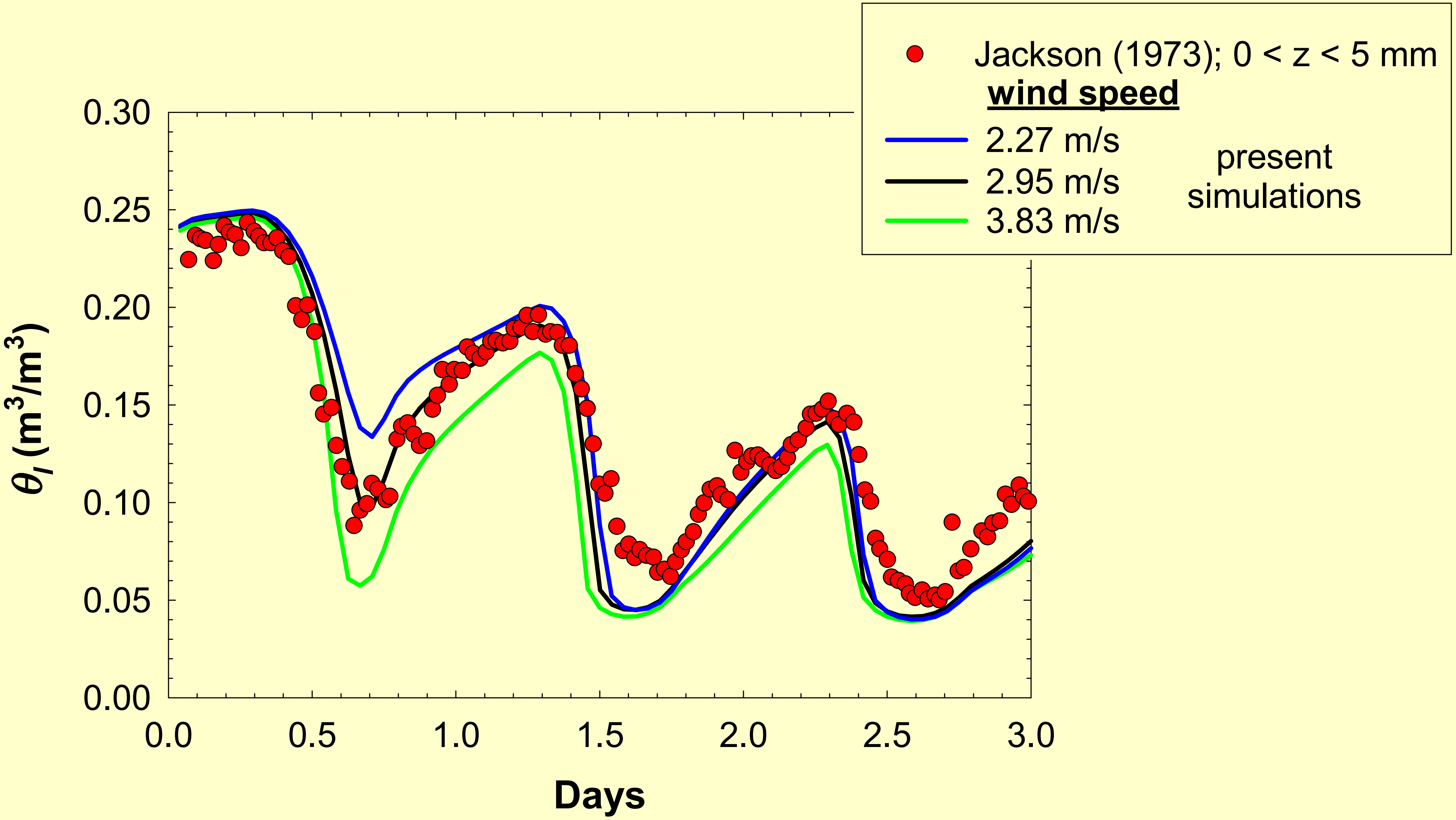
Rose, C.W. (1968)
Water transport in soil with a daily temperature wave

- Loamy sand soil
- Initial irrigation 30 cm.

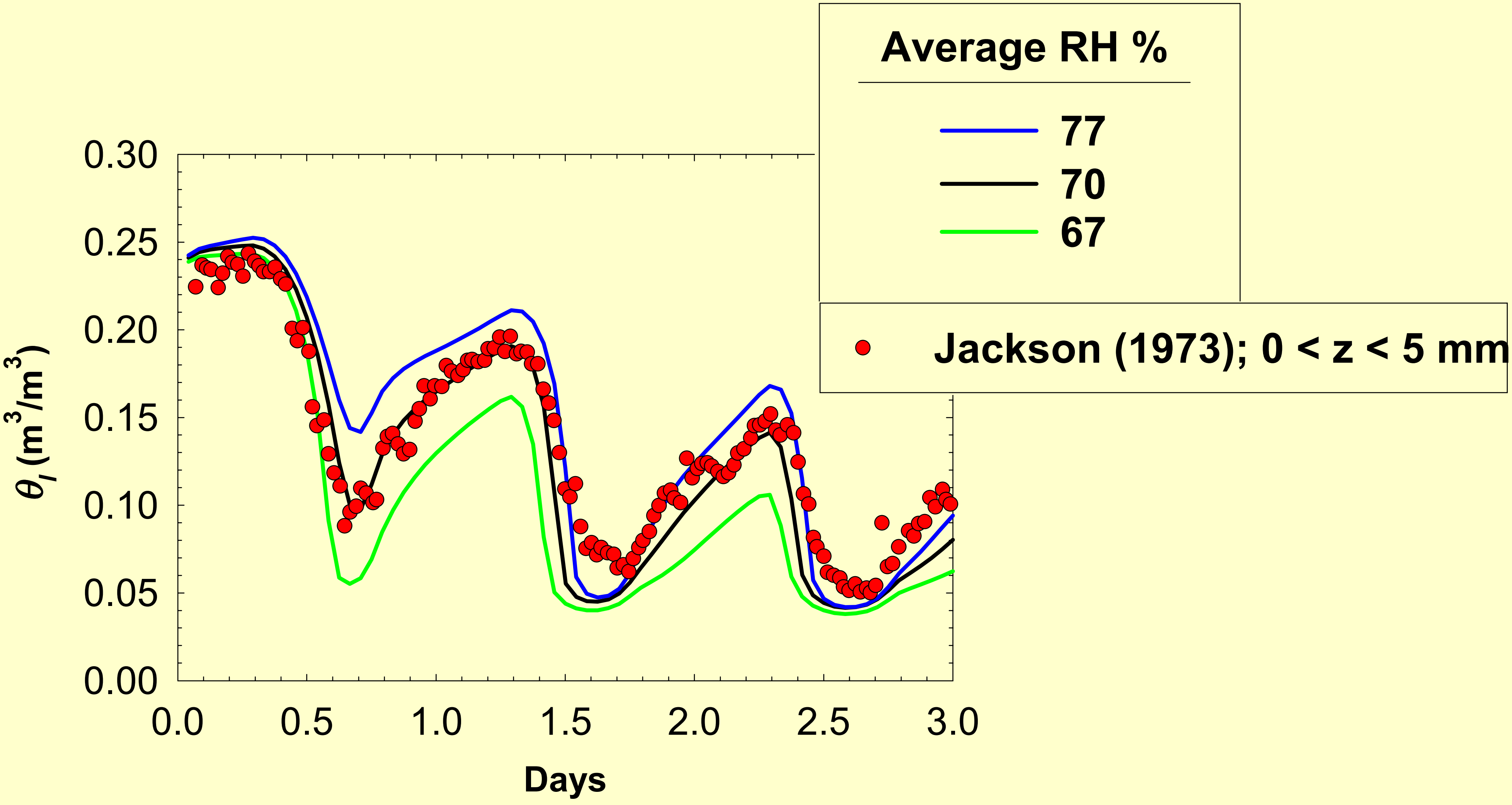
Water Content at Surface: Field Data and Simulations



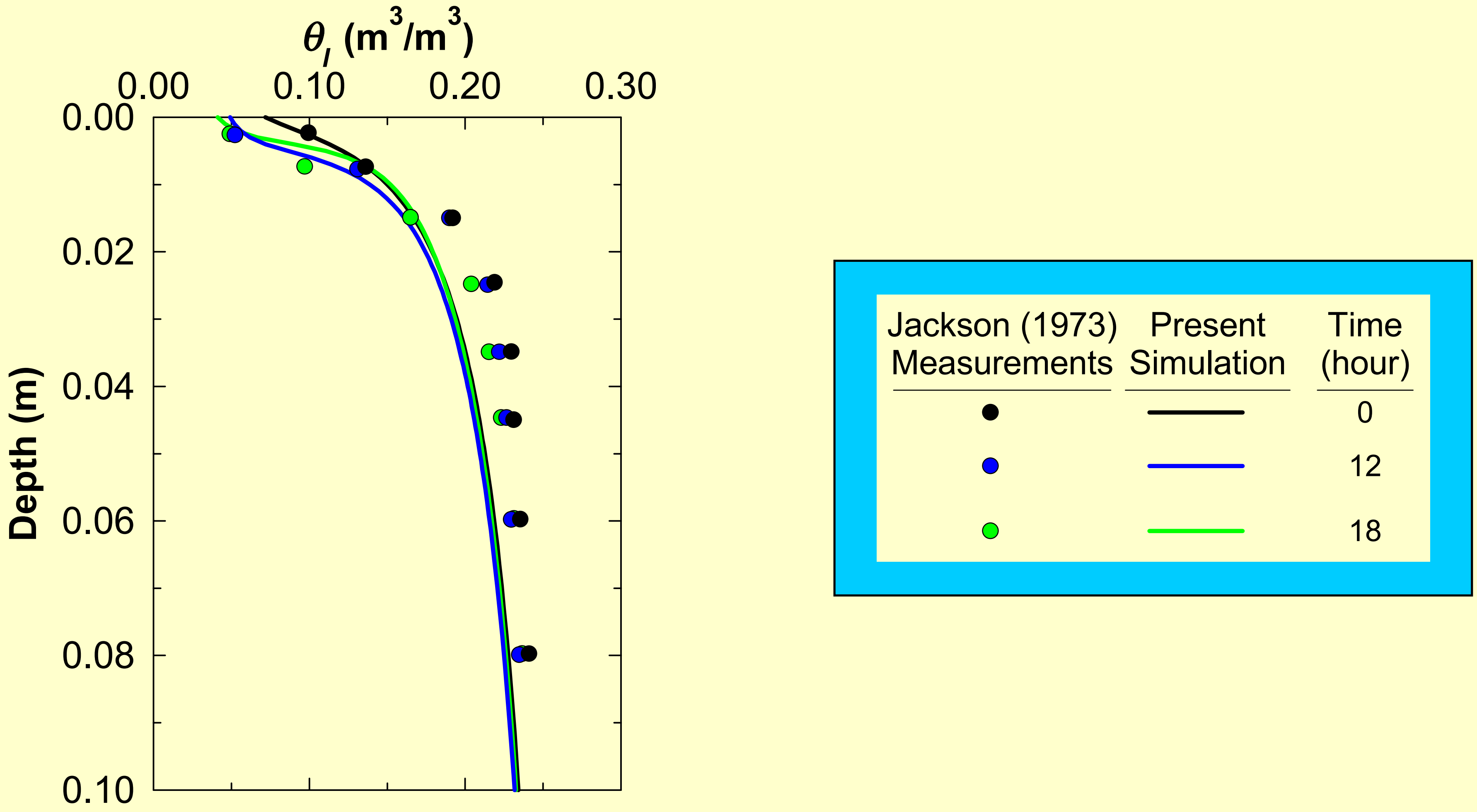
Water Content at Surface: Sensitivity to Wind Speed



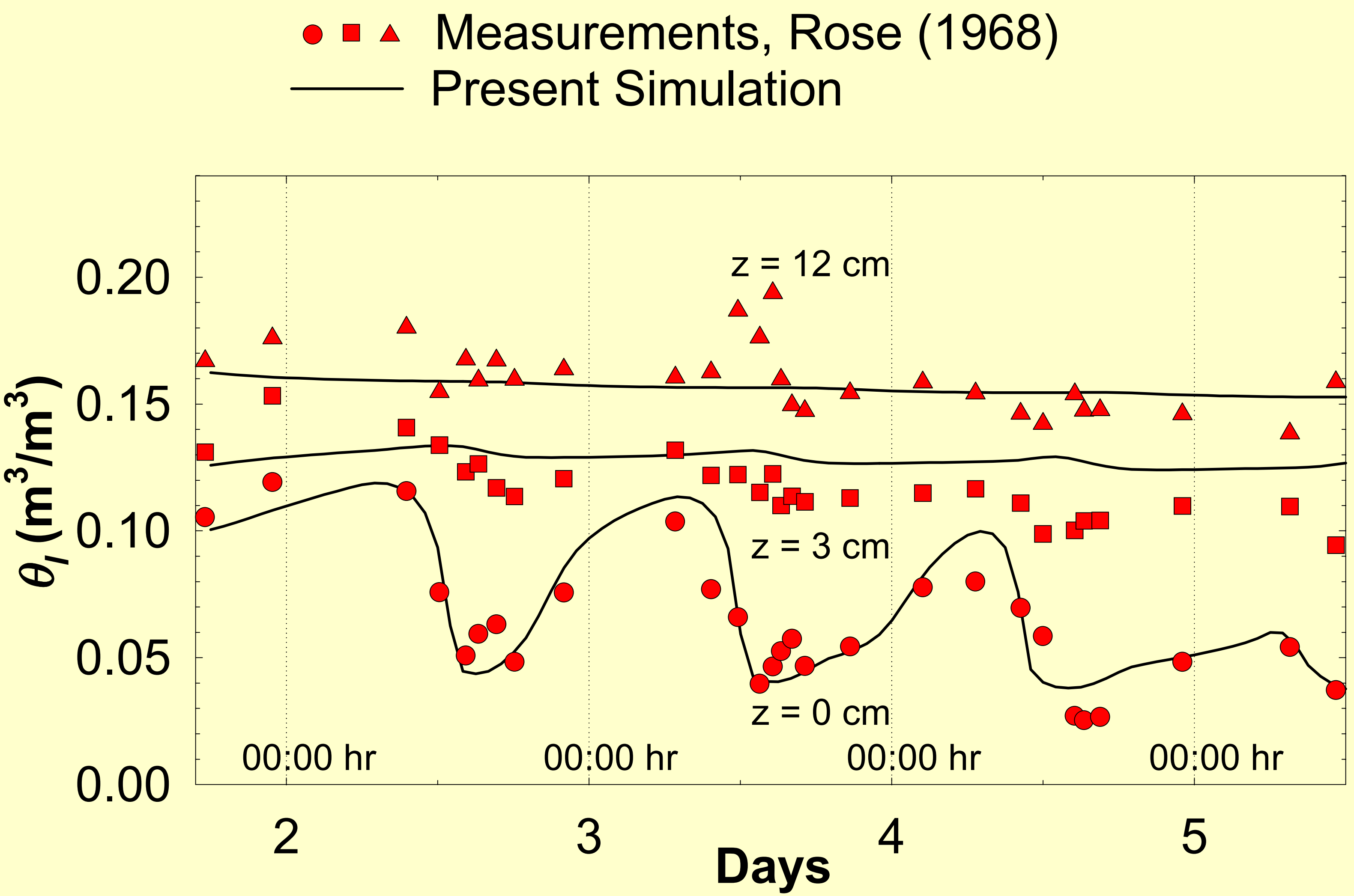
Water Content at Surface: Sensitivity to Air Relative Humidity



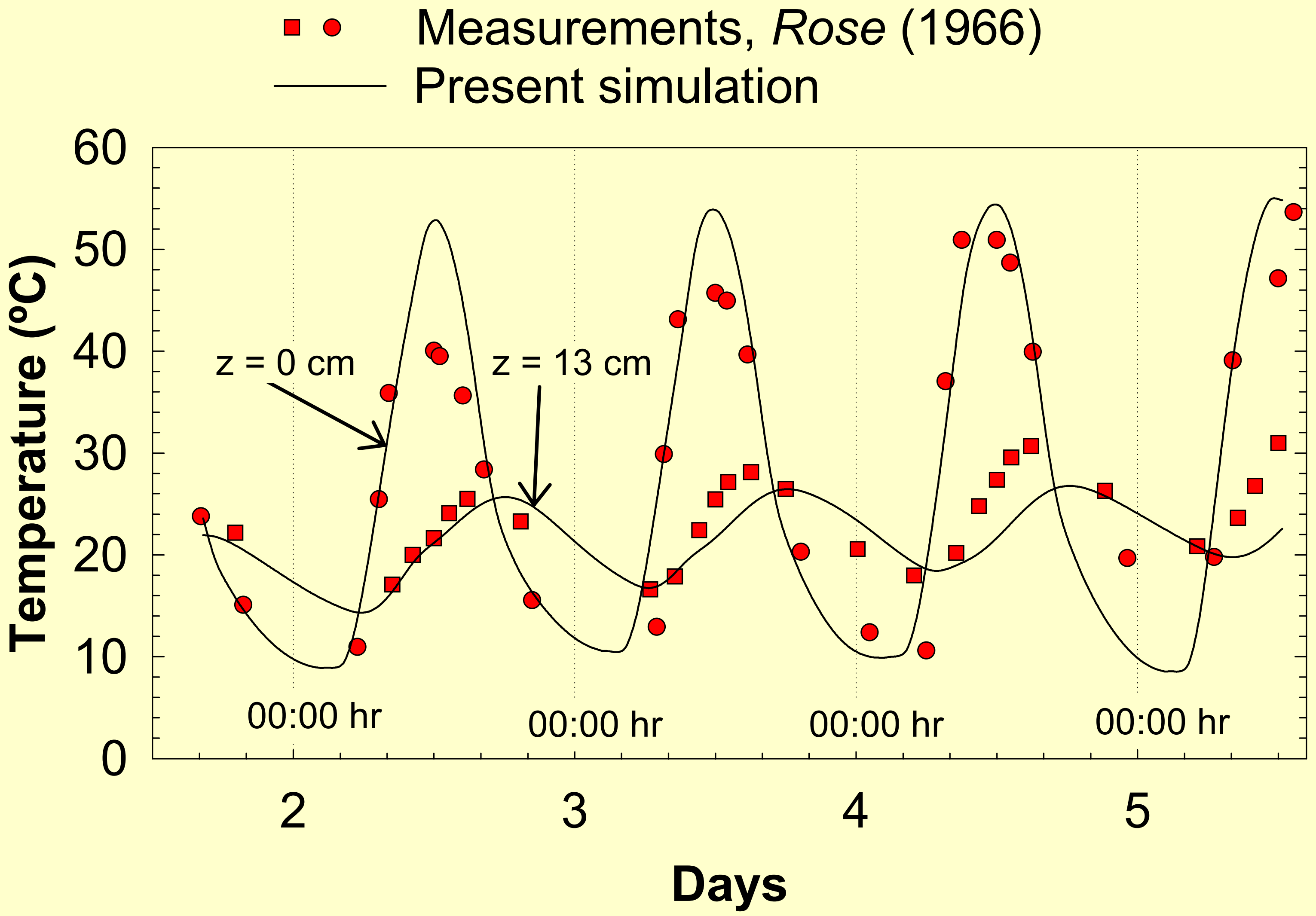
Water Content Profiles



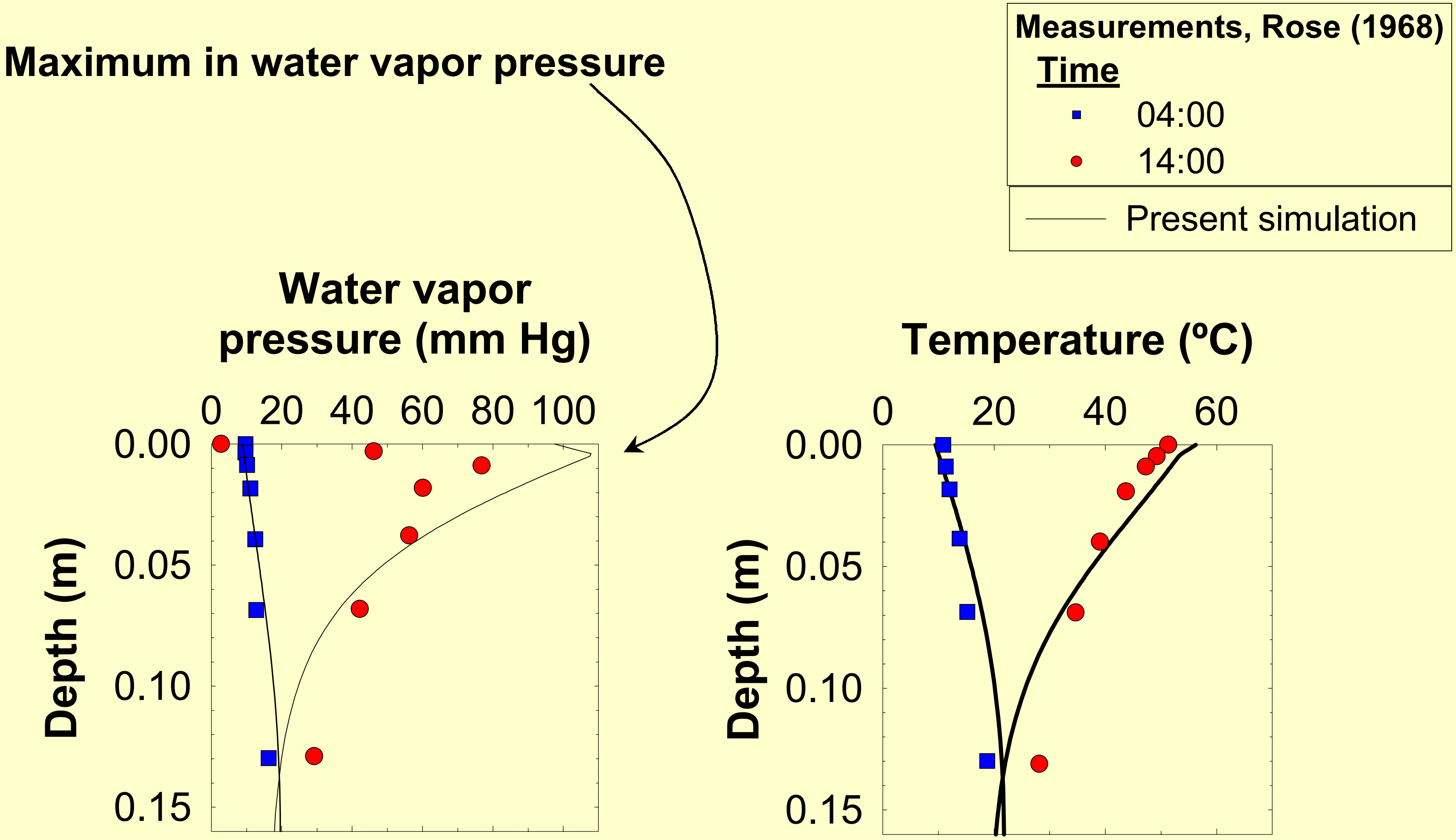
Water Content at Surface: Field Data and Simulations



Temperature at Surface: Field Data and Simulations

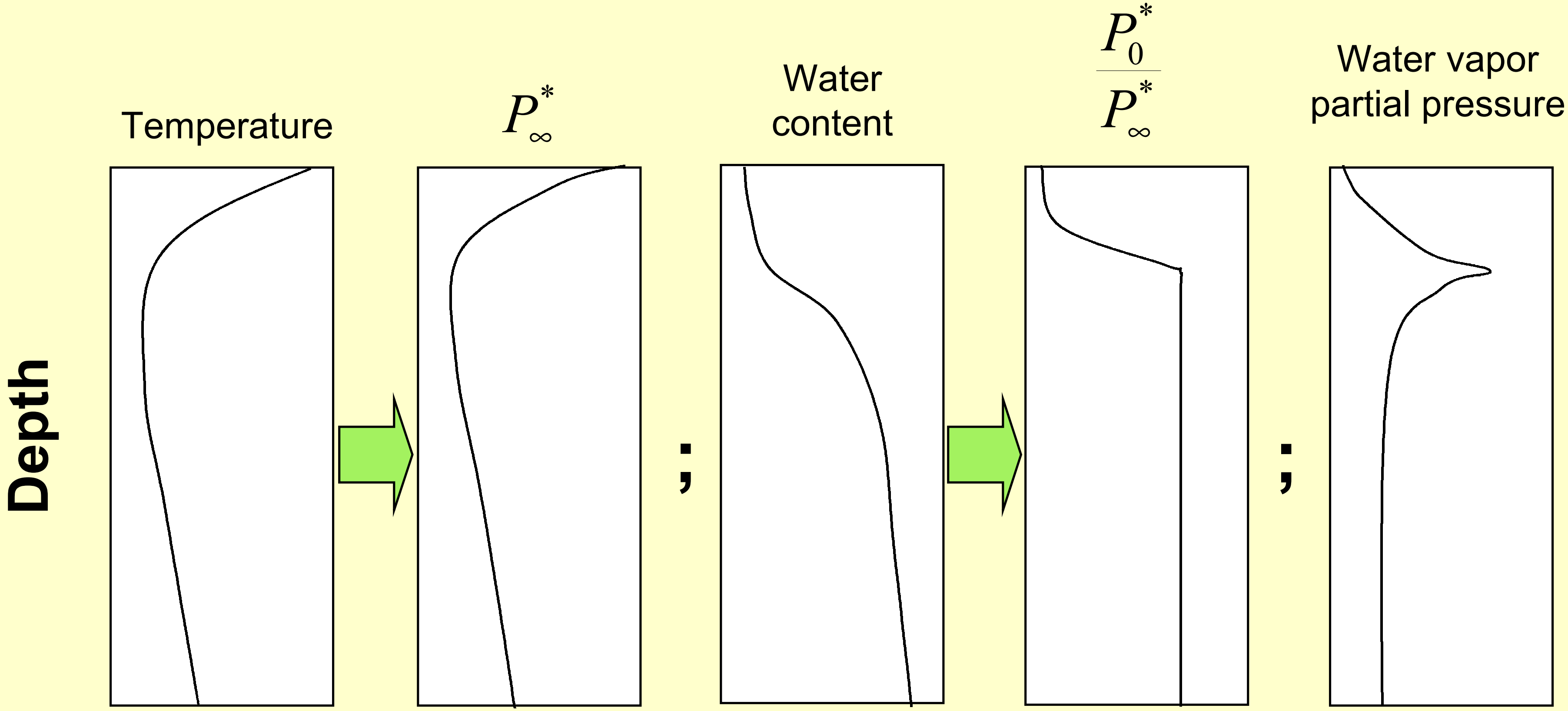


Water vapor and Temperature profiles: Field Data and Simulations



Maximum in water vapor pressure

Occurrence of a Maximum Water Vapor Pressure



$$Water\ vapor\ partial\ pressure = \left(P_\infty^*\right)\left(\frac{P_0^*}{P_\infty^*}\right)$$

Solute Transport

- **Included mechanisms**
  - ⇨ Hydrodynamic dispersion in fluid phases
  - ⇨ Convection in fluid phases

$$\frac{\partial C_{sm}}{\partial t} = \frac{\partial}{\partial z}\left(D_{ap} \frac{\partial \left(C_{sm} \big/ \zeta \right)}{\partial z} - V_{eff}\, C_{sm} \right)$$

where

$$C_{sm} = \theta_L C_L + \theta_G C_G + (1-\varepsilon) C_S = \zeta\, C_L = \frac{mass\ of\ chemical}{unit\ volum\ of\ soil\ matrix}$$

and

$$\zeta = \theta_L + \theta_G H_{GL} + (1-\varepsilon) H_{SL}$$

Partition Coefficients

- **Interphase transport**
  - ⇨ Hypothesis of Local Chemical Equilibrium
  - ⇨ Partition coefficients

$$H_{IJ} = \frac{C_I}{C_J}$$

Solid (organic matter)/liquid partition coefficient

$$H_{SL} = \frac{C_S}{C_L} = K_{OC}\, f_{OC}\, \rho_S$$

$$H_{SL} = H_{SL\_ref} \exp\left[-\frac{\Delta H_{SL}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

Gas/liquid partition coefficient

$$H_{GL} = H_{GL\_ref} \frac{T_{ref}}{T} \exp\left[-\frac{\Delta H_{GL}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \; ;$$

$\Delta H_{IJ} =$ Enthalpy change when the chemical is transported from phase J to I

Solute Transport Equations

Apparent diffusion coefficient

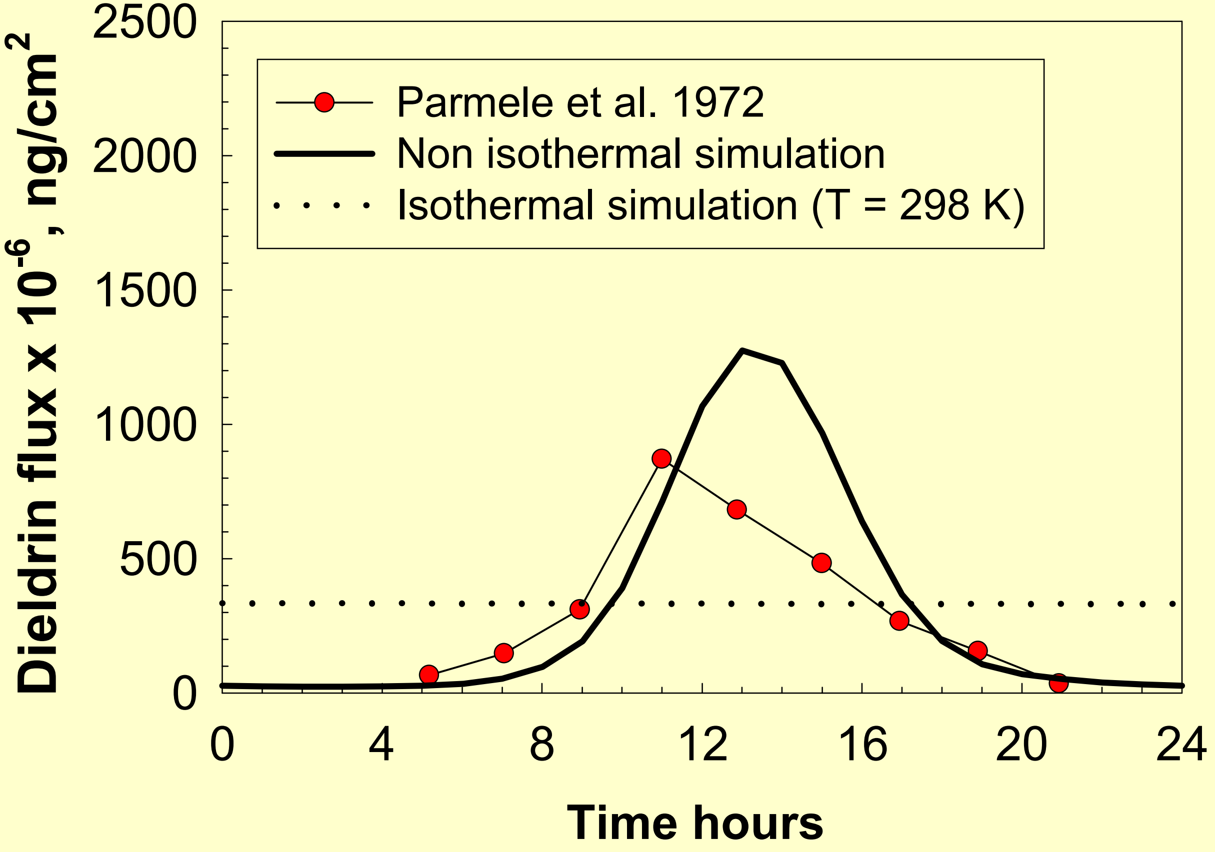
$$D_{ap} = \theta_G \left(\frac{D_G}{\tau_G} + D_{V\,G} \right) H_{GL} + \theta_L \left(\frac{D_L}{\tau_L} + D_{V\,L} \right)$$

Effective velocity

$$V_{eff} = \frac{1}{\zeta} \left[q_L + q_G H_{GL} \underbrace{- \theta_G \left(\frac{D_G}{\tau_G} + D_{v\,G} \right) \frac{\partial H_{GL}}{\partial z}} \right]$$

This term contains the variation of the partition coefficient with depth (e.g., due to changes in temperature).

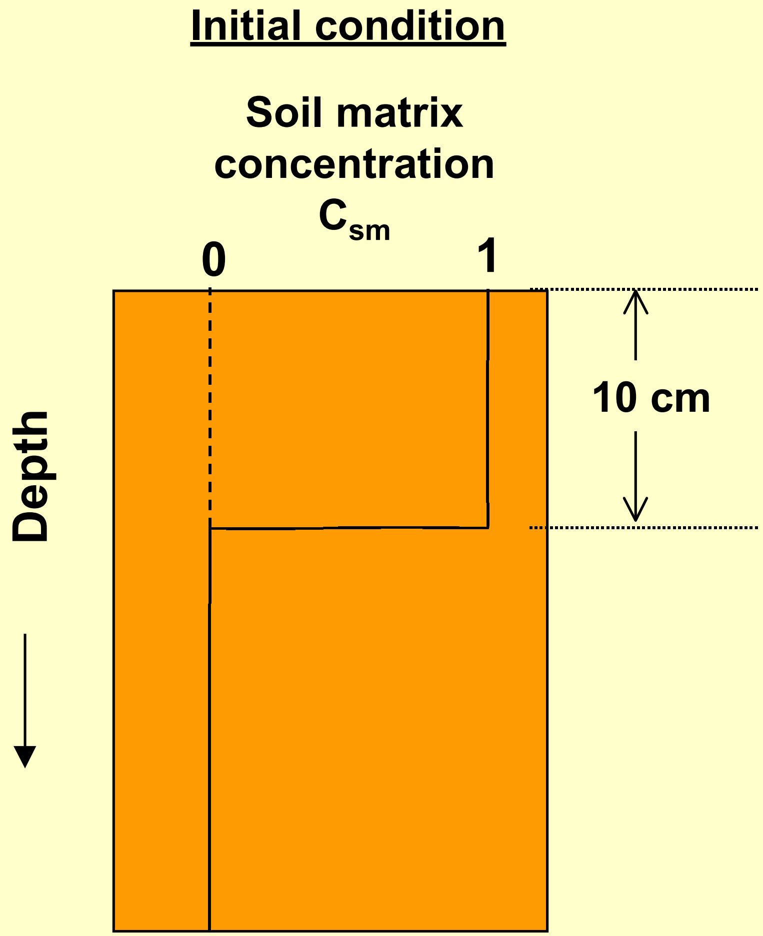
Comparison of Experimental and Simulated Volatilization Fluxes



Gas diffusion is the main transport mechanism.

The variation of vapor pressure with temperature is the main cause of volatilization cycles.

Simulation Scenarios

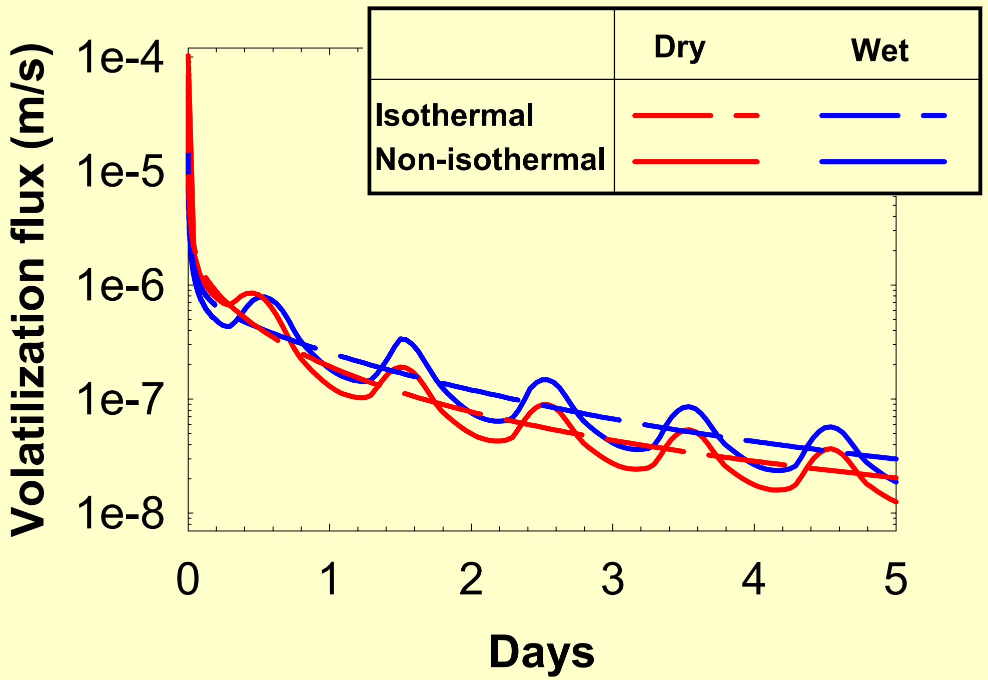


2 scenarios
- **Wet soil**
  (Start of Jackson's experiment)
- **Dry soil**
  (End of Jackson's experiment)

2 chemicals
- **Benzene (high volatility)**
- **Lindane (low volatility)**

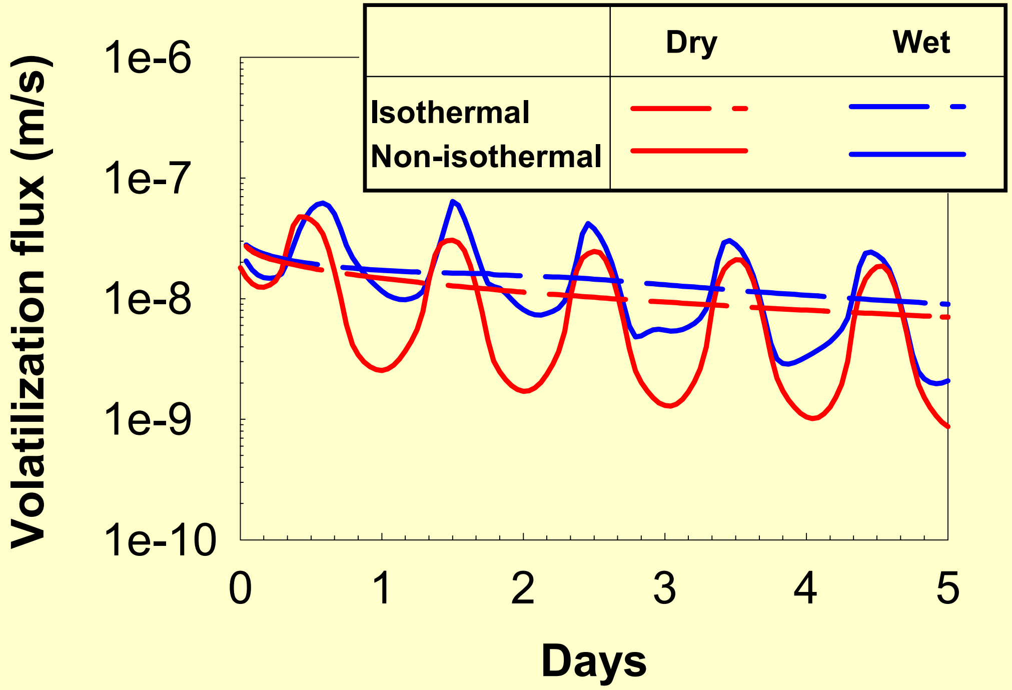
2 conditions
- **Isothermal system**
- **Non-isothermal system**

Benzene Volatilization



- High initial volatilization flux due to high Henry's constant.
- Cyclic volatilization flux due to cyclic temperature variations.
- Higher volatilization for dry conditions due to higher volume (and area) occupied by the gaseous phase.

Lindane volatilization



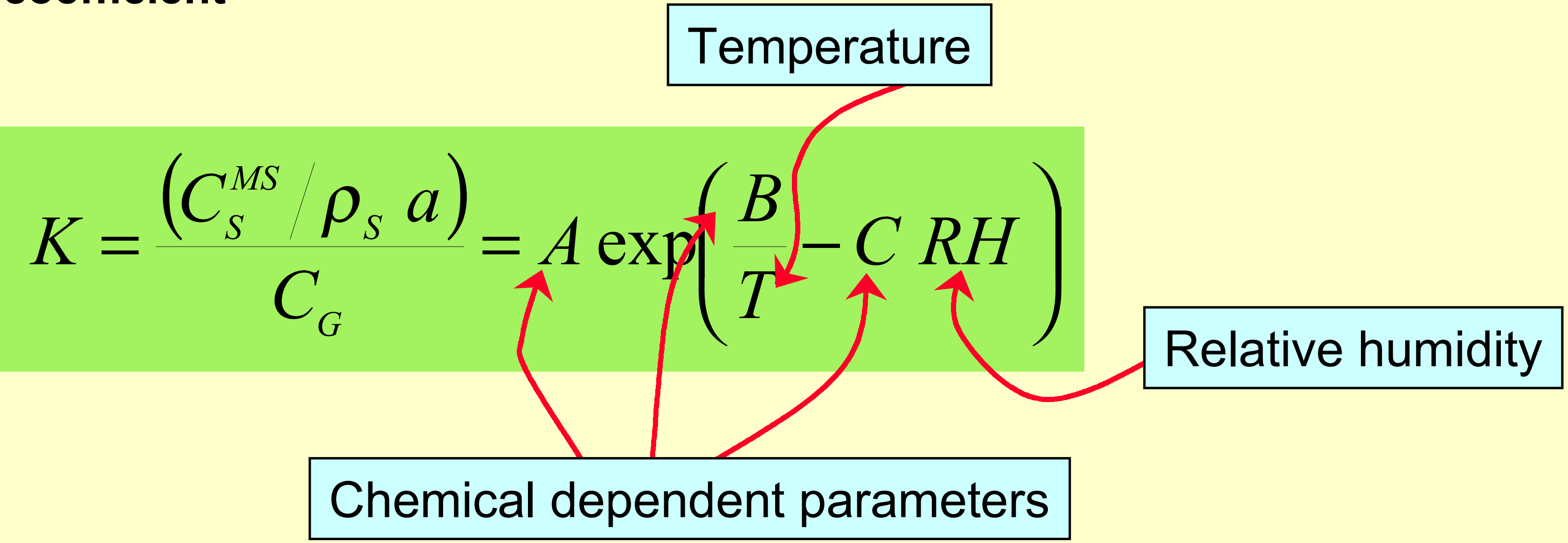
- Lower volatilization relative to benzene due to lower Henry’s constant and higher solid/liquid partition coefficient.
- Higher relative amplitude of oscillations compared to benzene.
- Higher volatilization flux for wet conditions since Lindane concentration in the gas phase is low and it partitions more favorably to the solid phase.

Sorption to Soil

Hypothesis: Concentration in the solid phase is the result of the combined contributions of the absorption to the **O**rganic **M**atter and adsorption to the **M**ineral **S**urface.

$$C_S = C_S^{OM} + C_S^{MS}$$

Adsorption coefficient



$$K = \frac{\left(C_S^{MS} / \rho_S\, a\right)}{C_G} = A \exp\left(\frac{B}{T} - C\, RH\right)$$

Temperature

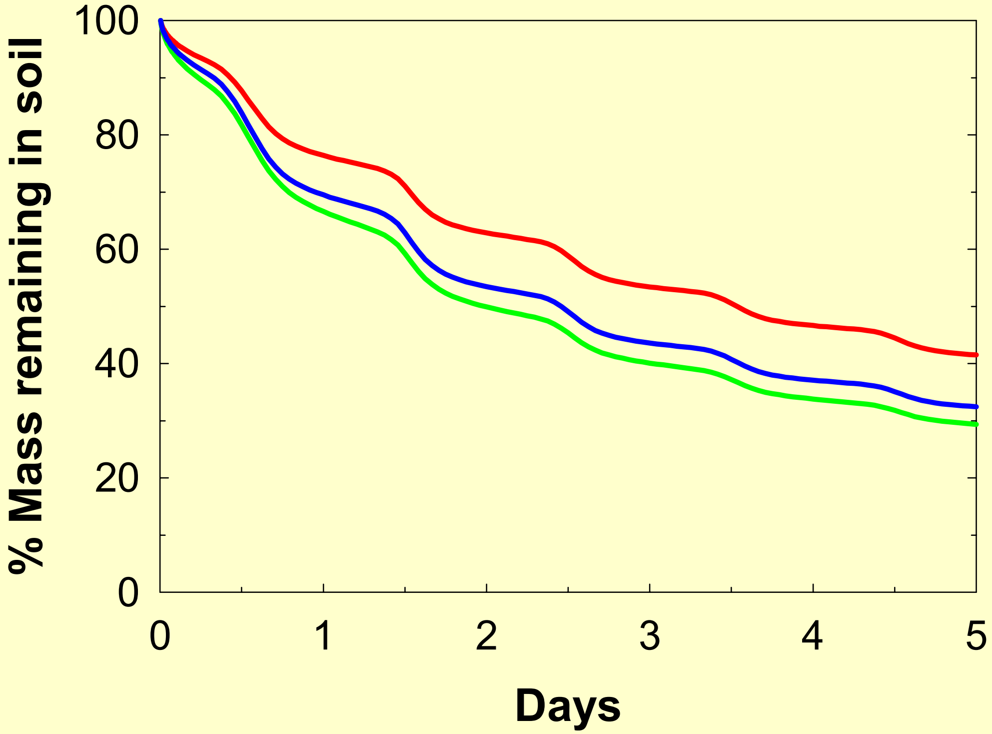
Relative humidity

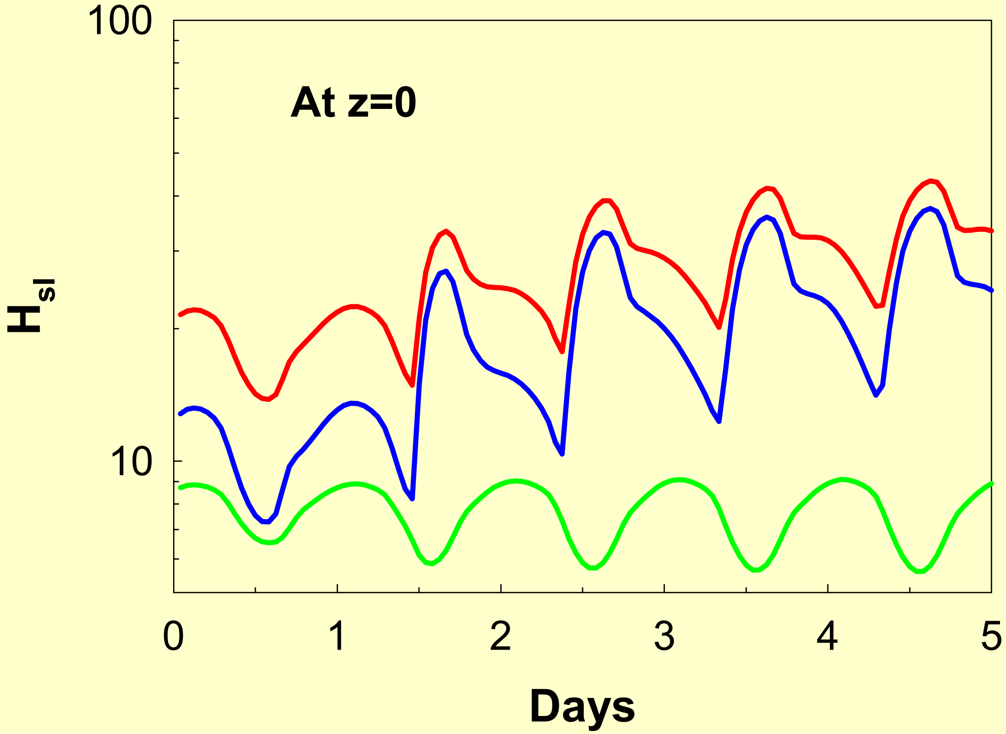
Chemical dependent parameters

Effect of Adsorption on 1,3–Dichlorbenzene Volatilization

🟥 both: adsorption and absortion
🟩 absortion only
🟦 adsorption only

$$H_{SL} = \frac{C_S^{OM} + C_S^{MS}}{C_L} = H_{SL}^{OM} + K\,\rho_S\,a\,H_{GL}$$





CONCLUSIONS

- A computer model was developed to simulate the transport of energy, water and chemical transport in the unsaturated soil zone.
- The observed diurnal cycles of temperature, water content and chemical volatilization fluxes are described by the model to a reasonable level of accuracy when compared with available field data.
- Chemical volatilization for compounds of low volatility fluxes are more sensitive to temperature fluctuations.
- Adsorption can significantly reduce chemical volatilization flux from dry soils.

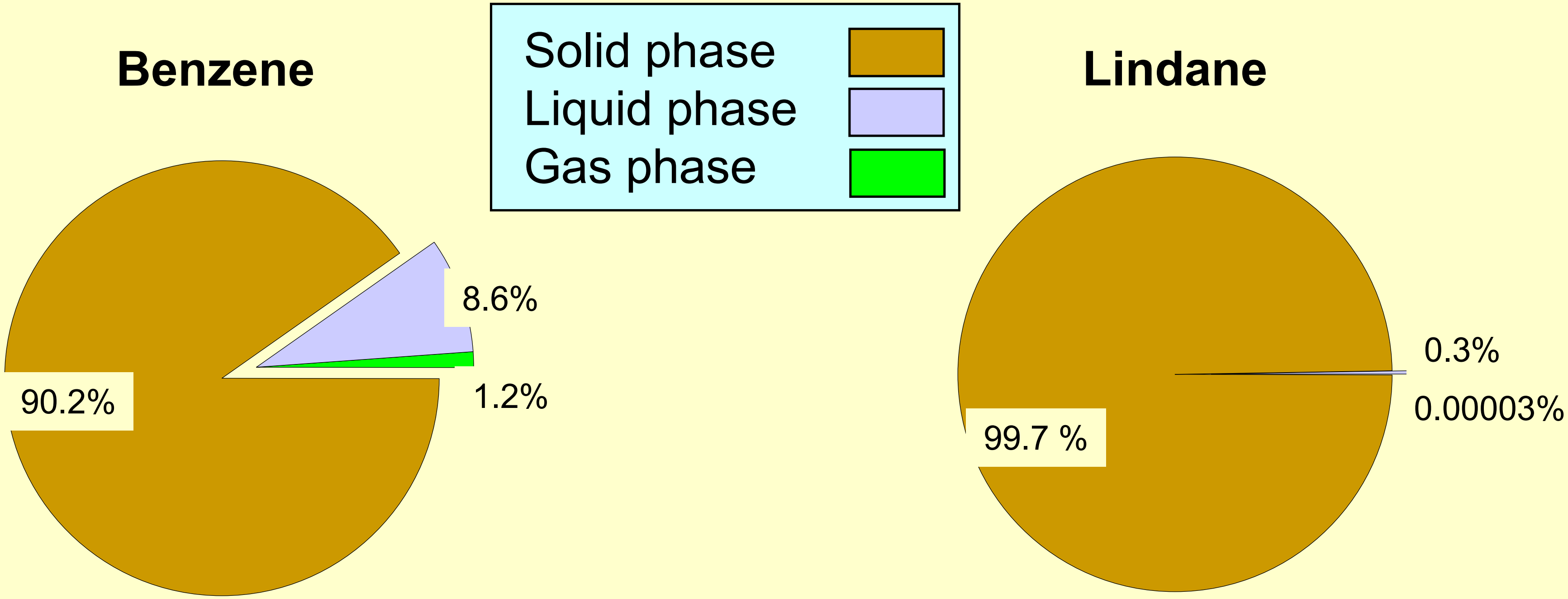
Chemical properties

Property	**Benzene**	**Lindane**	**1-3 dichlorobenzene**
Air Diffusion coefficient D_G (m^2/s)	8.8 E-6	5.8 E-6	6.9 E-6
Water Diffusión coefficient D_L (m^2/s)	9 E-10	5.5 E-10	7.9 E-10
Solubility, (kg/m^3)	1.78	7.3e-3	0.123
Gas/Liquid partition coefficient H_{GL}	0.18	1.485 E-4	0.15
Solid/Liquid partition coefficient H_{SL}	3.22	102.3	7.31
Organic carbon/water K_{oc}	59	1930	138

Chemical Distribution among Phases

Soil Phases composition: $\theta_L = 0.20$; $\theta_G = 0.15$

$$f_{oc} = 0.02$$



1,3-dichlorobenzene Adsorption

Adsorption coefficient, K (cm), is calculated according Goss (1994) as

$$\ln K = A^{*} - \frac{\Delta H_s}{R}\left(\frac{1}{T} - \frac{1}{323.15}\right) - C(100 - RH)$$

for 1,3-dichlorobenzene

$$\begin{aligned} A^{*} &= -9.09 \\ \Delta H_s &= -38.5\,\frac{kJ}{mol} \\ C &= -0.0313 \end{aligned}$$