A thermodynamic interpretation of soil water retention and dynamics

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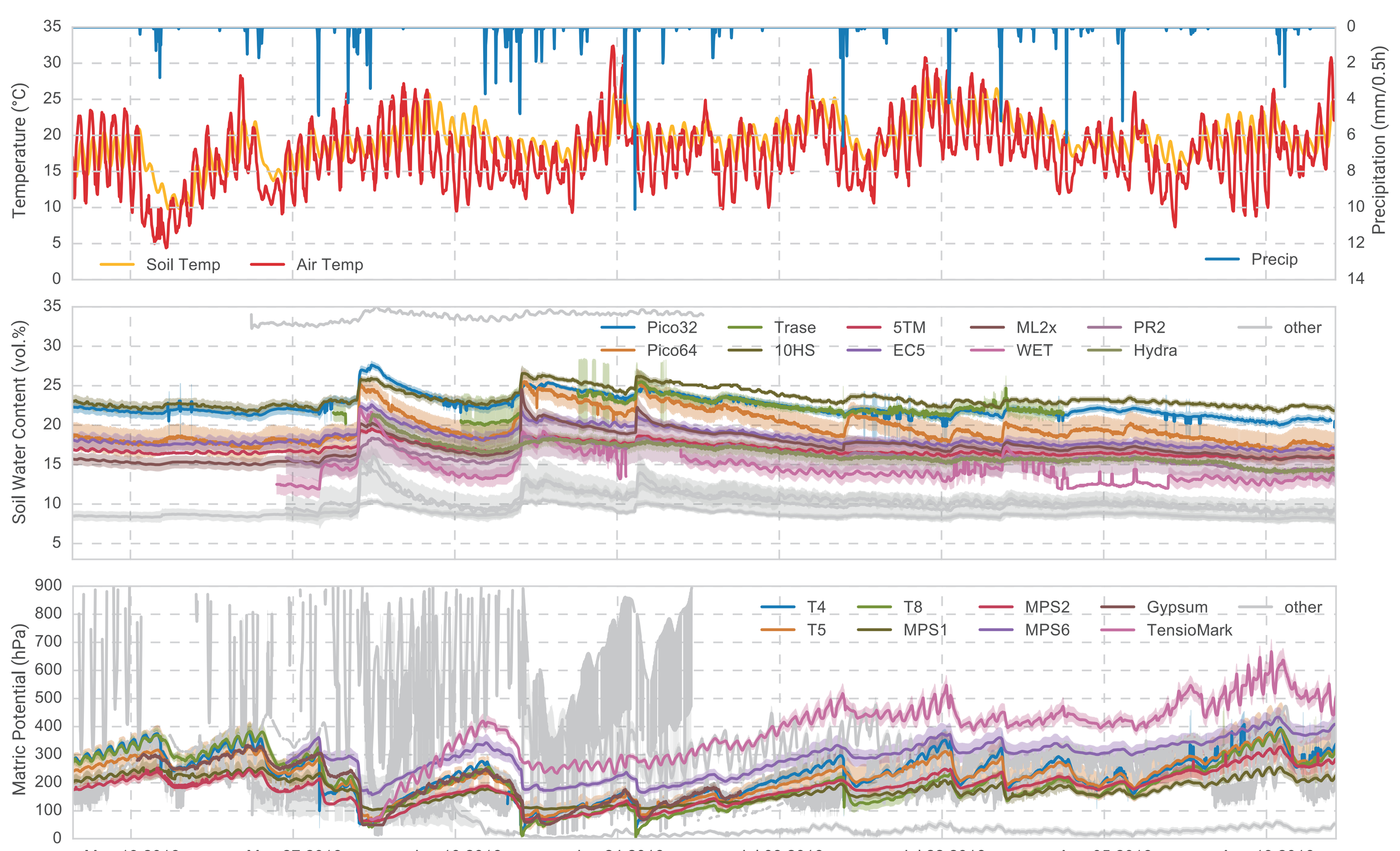
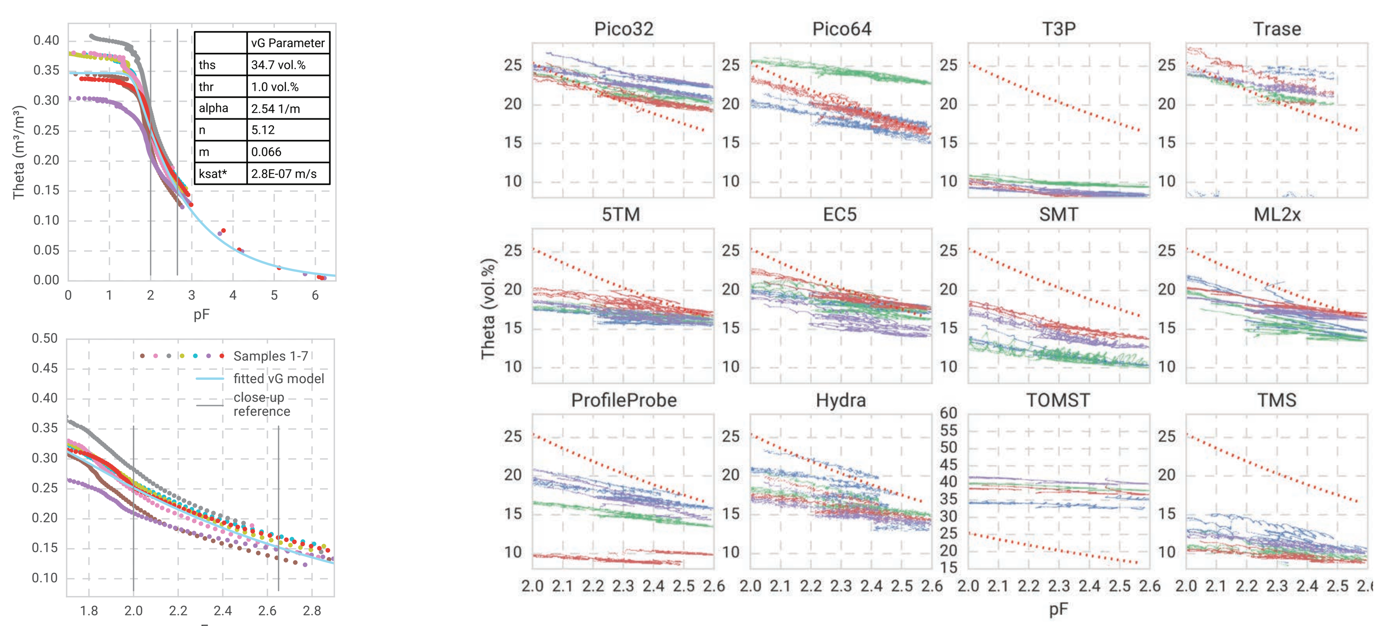
1 Motivation: Hydrological system state observation

There is wide agreement on soils being structured heterogeneous systems being shaped by past work of biotic and abiotic processes. Although the science about soil water physics in such systems roots back to thermodynamic theory of Gibbs and others in the 19th and early 20th century, the vast majority of hydrological and pedophysical studies today relate to measurements of the volumetric soil water content and a specific retention curve. This mass balance related focus obscures system-related findings with intrinsic heterogeneity and non-uniqueness of soil water content and configuration of capillary system.

Data from sensor comparison study: Plausible but non-coherent.

58 sensors (15 systems) measuring soil moisture and 50 sensors (14 systems) recording matric potential have been compared in a specifically homogenised field trial.





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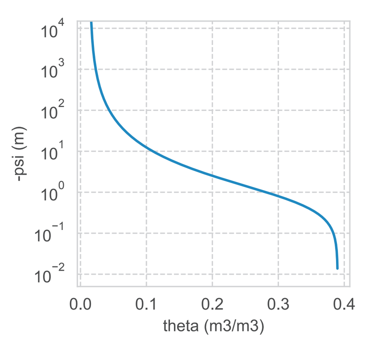
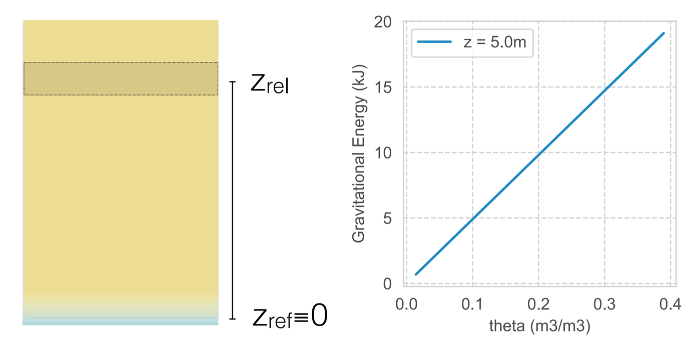
2 Relative total hydraulic energy

Soil water retention curve (sandy loam)

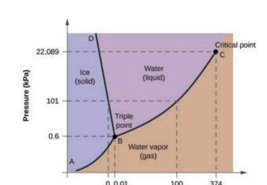


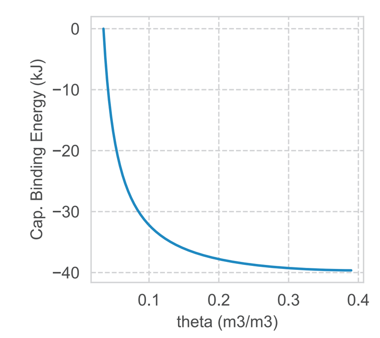
Gravitational energy $dU_{\text{grav}} = dm_\theta g z_{\text{rel}}$



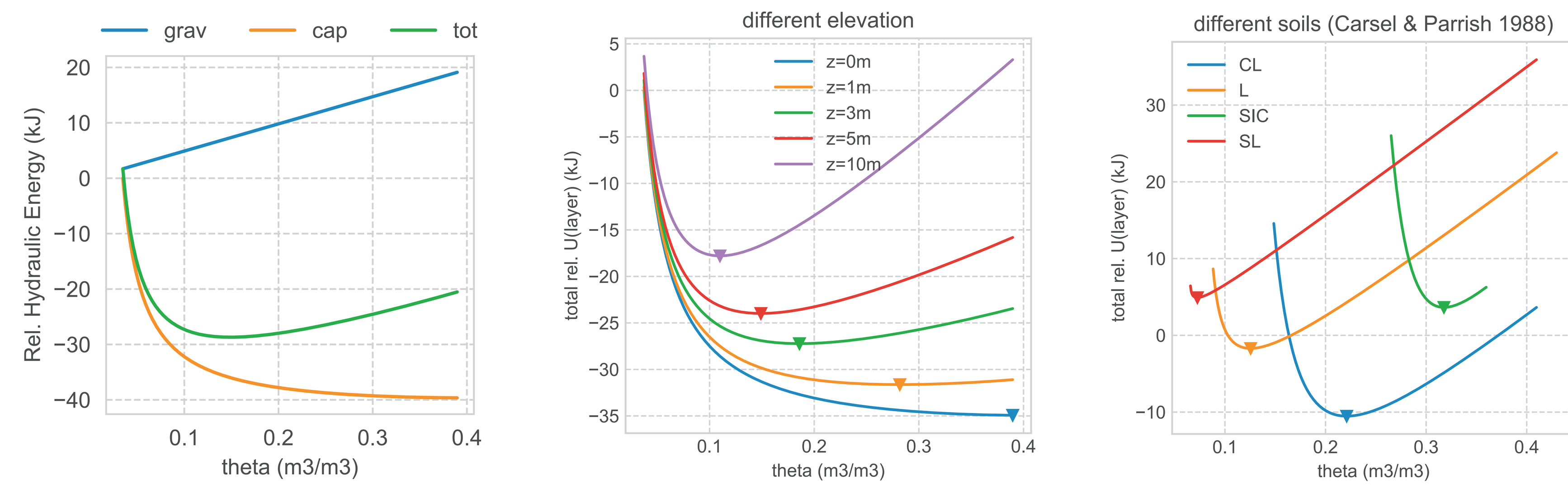
Capillary binding energy $dU_{\text{bind}} = d\psi_\theta g dm_\theta$

ψ_{ref} = 2 MPa





$$U_{tot,\theta} = g \int_{\theta_{\min}}^{\theta} dm_\theta z_{\text{rel}} + g \int_{\theta_{\min}}^{\theta} \psi_\theta dm_\theta$$



3 Derivation

Capillary forces as chemical potential (*Iwata et al., 1995*)

$$d\mu_w = \underbrace{\left(\frac{\partial \psi}{\partial z}\right) dz}_{(d,e,h)} + \underbrace{g dh}_{(e,g)} + \underbrace{-\overline{S}_w dT}_{(i)} + \underbrace{\overline{v}_w dP}_{(f)} + \underbrace{\frac{\overline{v}_w}{4\pi}\left(\frac{1}{\overline{\epsilon}} - 1\right) dD}_{(c)} + \underbrace{\sum_{j=1}^{k-1} \left(\frac{\partial \mu_w}{\partial C_j}\right) dC_j}_{(b)} + \underbrace{\frac{\partial}{\partial r}\left(\frac{2\sigma}{r}\overline{v}_w\right) dr}_{(a)}$$

a) surface tension effects at the soil-water-air interfaces
b) effect of solutes
c) the general electric field of charged clay and organic surfaces
d) the van der Waals force field
e) internal pressure and fluid configuration
f) external pressure effecting a reconfiguration of e)
g) the gravitational field
h) water content
i) temperature

The binding energy integrates the occurring surface tension of water in the changing film surface area in the soil pores:

$$dU_{\text{cap}} = dA_\theta d\sigma_\theta$$

$d\sigma_\theta$ $(\mathrm{N\,m^{-1}})$ surface tension
dA_θ $(\mathrm{m^2})$ surface area

With ψ as change of Gibbs free energy per change of mass:

$$\psi = \frac{\partial G}{\partial m}$$

and the soil chemical potential in very small soil water systems:

$$\mu = \frac{2\sigma_\theta}{r} V_\theta \qquad d\psi = \frac{2\sigma_\theta}{r} \frac{dV_\theta}{dV_\theta \rho g}$$

After rearranging for σ_θ derives the change of U_{cap}:

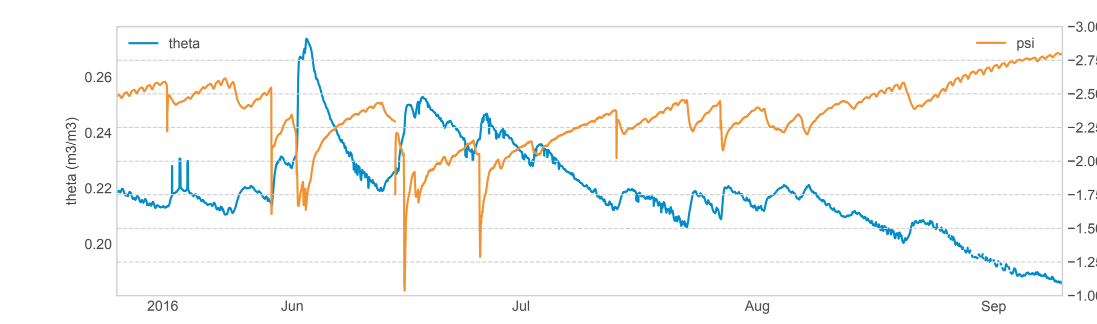
$$dU_{\text{cap}} = dV_\theta \frac{dA_\theta}{dV_\theta} \frac{r}{2} \psi_\theta \rho g$$

with sphere: $\frac{\partial A_\theta}{\partial V_\theta} = \frac{2}{r}$

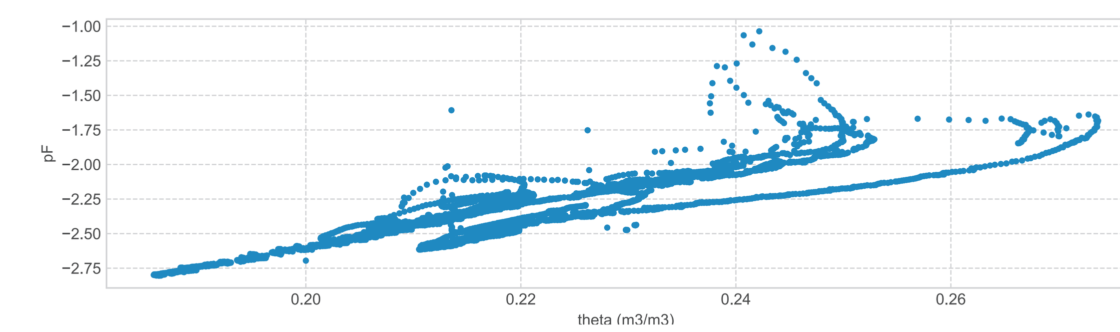
$$dU_{\text{cap}} = d\psi_\theta \rho g dV_\theta$$

4 Application to observed field and lab data

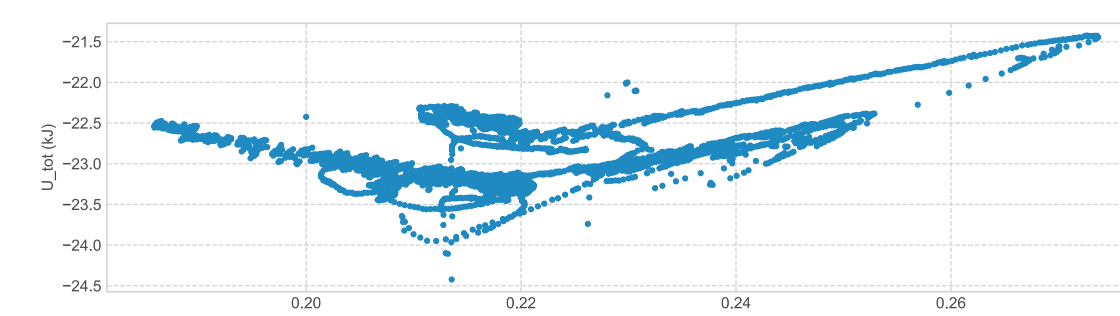
Recorded time series:



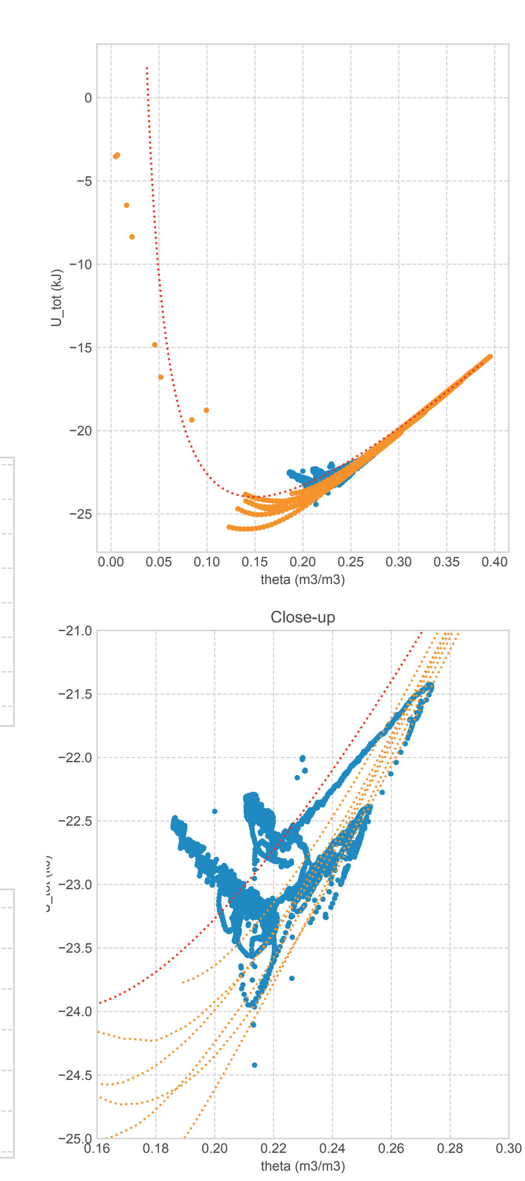
In situ soil water retention curves:



As relative hydraulic energy:



Lab and field WRC:



5 System state as deviation from local equilibrium

We can identify: General system regime, gradient and direction of its dissipation, system state dynamics