

# Impact of non-conventional waters on the unsaturated zone

Joaquin Jimenez-Martinez

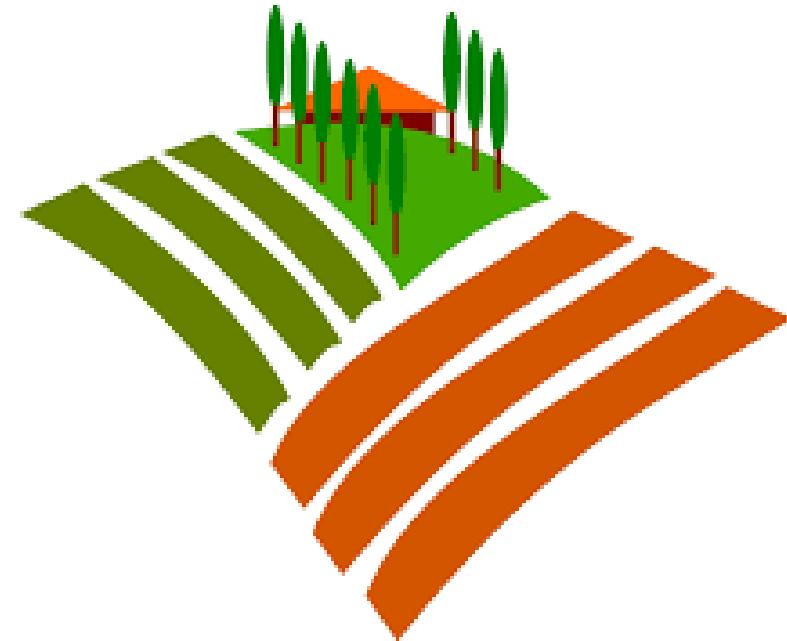
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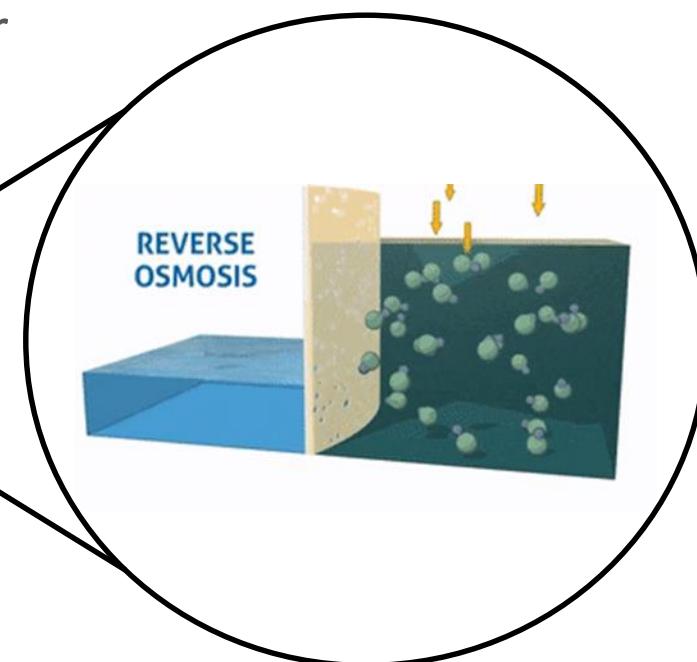
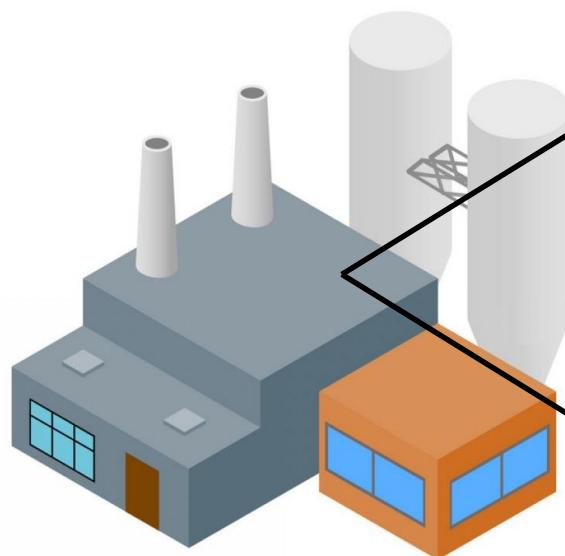
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# Non-conventional waters

*treated wastewater + sewage sludge*

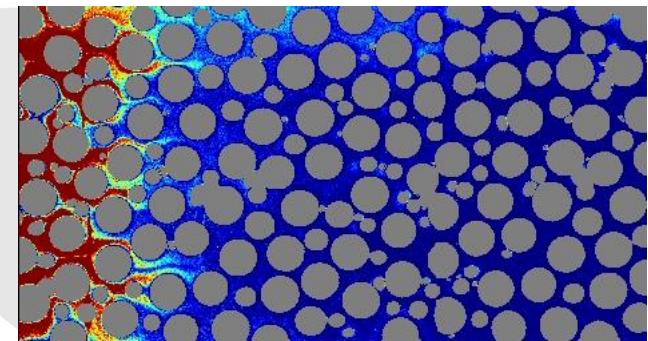
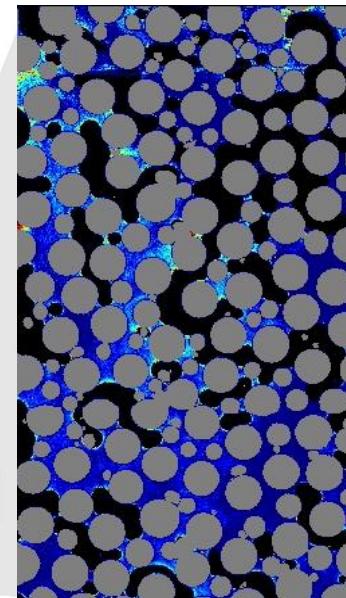
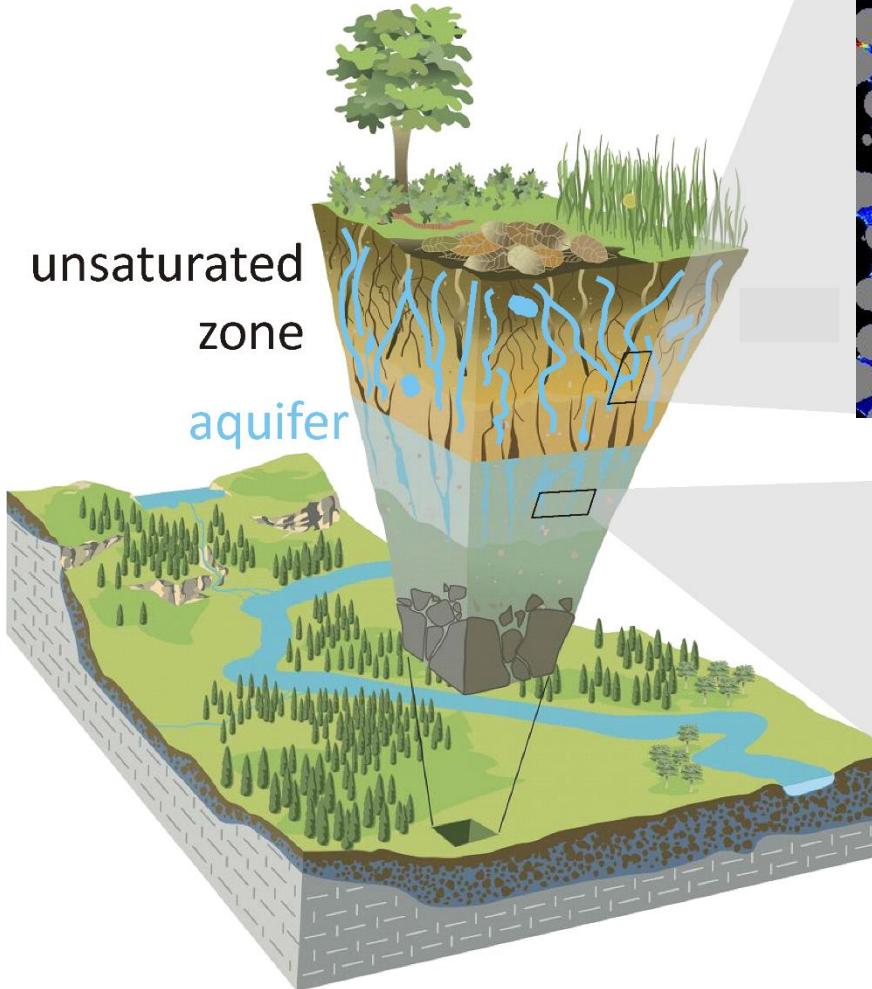


*desalinated water*



# The unsaturated zone

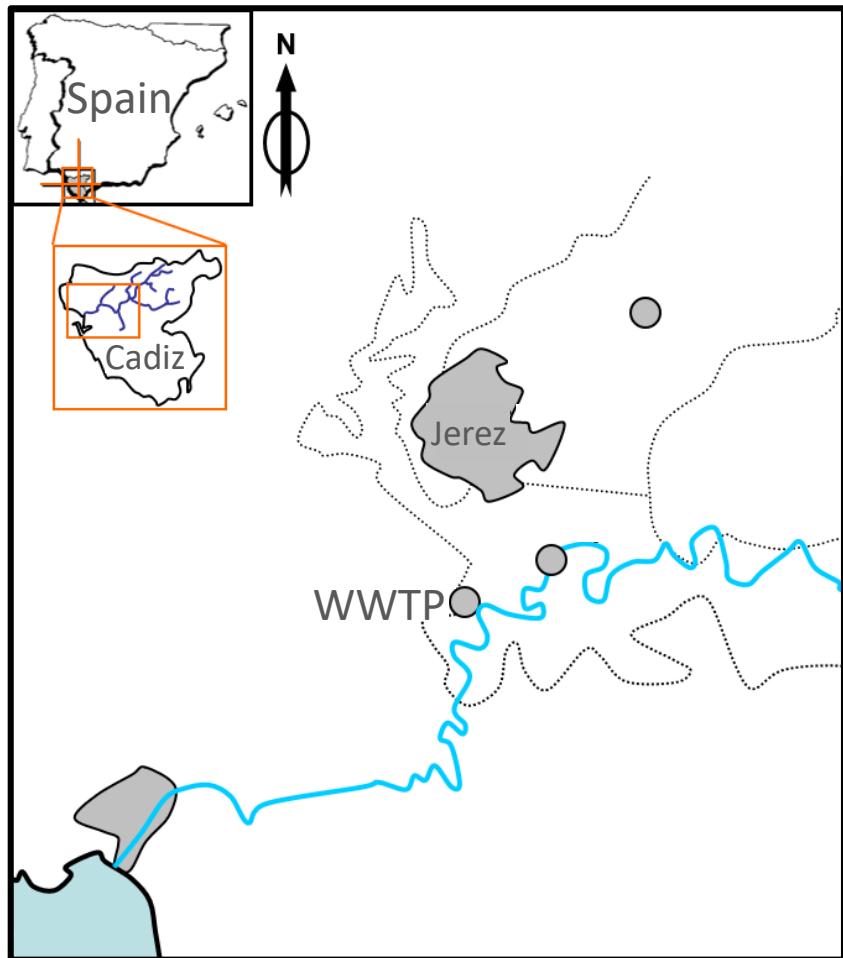
*as reactor and buffer  
for contaminants*



modified from Chorover et al. *ELEM.* (2007)

Jimenez-Martinez et al. *GRL* (2015)

# Impact from treated wastewater



Corada-Fernandez et al. *CHEM* (2015)

pharmaceuticals (64 compounds)

using indicators such as  $pK_a$  /  $\log K_{ow}$  /  $D_{ow}$



non-polar compounds

tendency to be adsorbed in soil  
photodegradation



low concentrations

surfactants

linear alkylbenzene sulfonates (LAS)

alcohol ethoxysulfates (AES)

nonylphenol polyethoxylates (NPEOs)

**alcohol polyethoxylates (AOEs)**

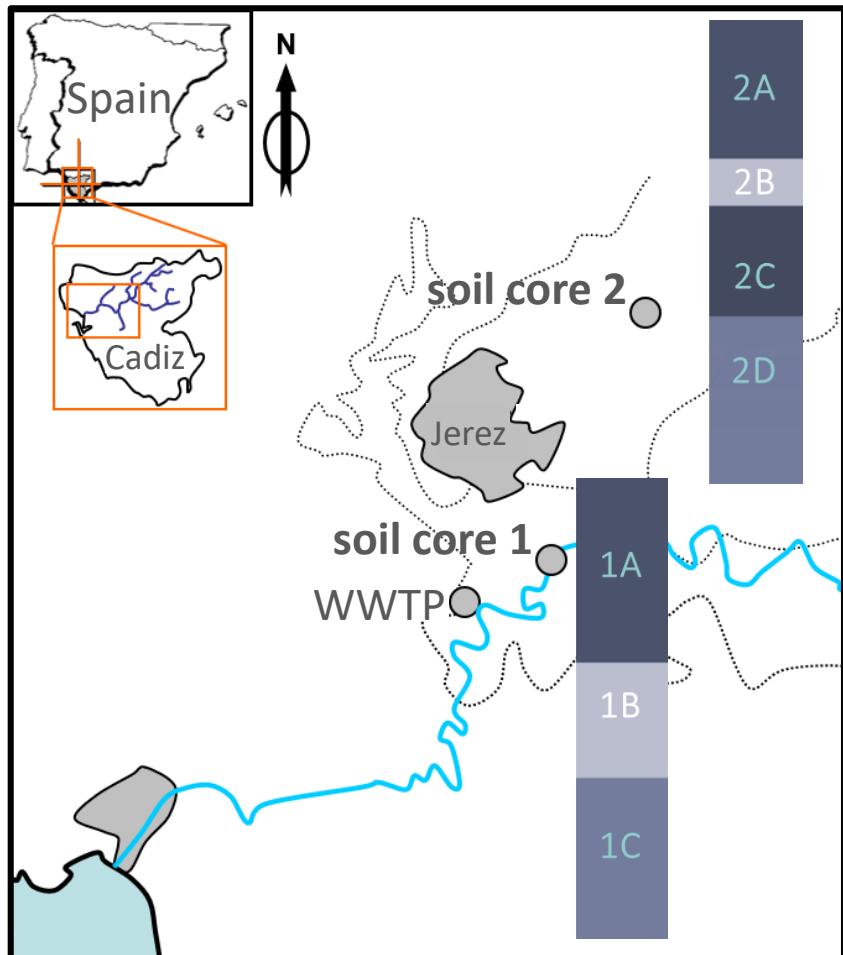


degradation

metabolites



# Impact from treated wastewater



Corada-Fernandez et al. *CHEM* (2015)

pharmaceuticals (64 compounds)

using indicators such as  $pK_a$  /  $\log K_{ow}$  /  $D_{ow}$



non-polar compounds

tendency to be adsorbed in soil  
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low concentrations



surfactants

linear alkylbenzene sulfonates (LAS)

alcohol ethoxysulfates (AES)

nonylphenol polyethoxylates (NPEOs)

**alcohol polyethoxylates (AOEs)**



degradation

metabolites



# Non-ionic surfactants – isotherms and transport

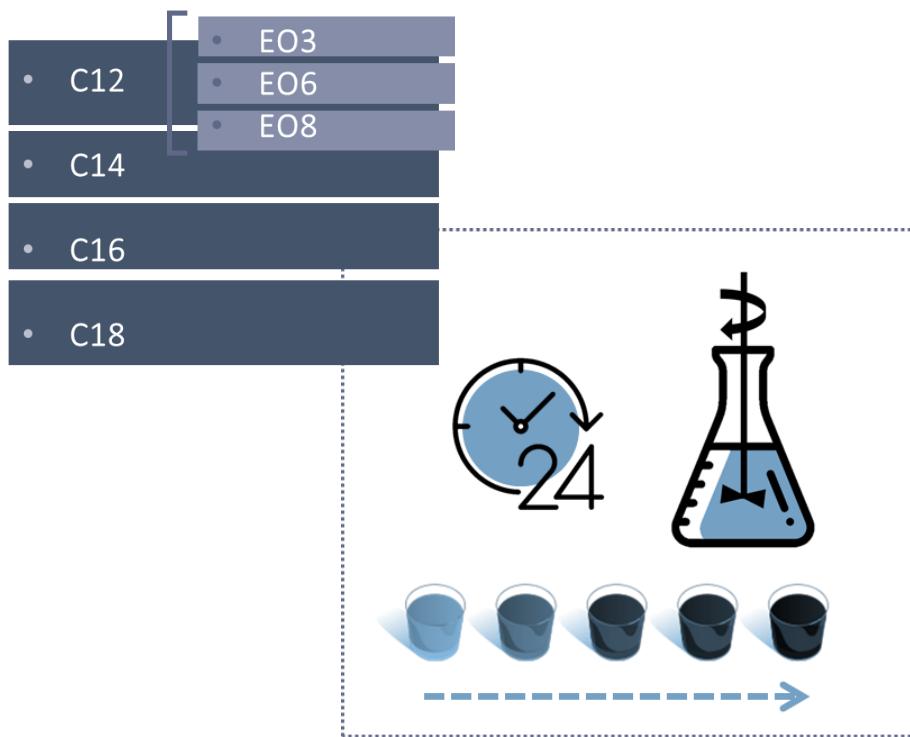
alcohol polyethoxylates (AEOs)



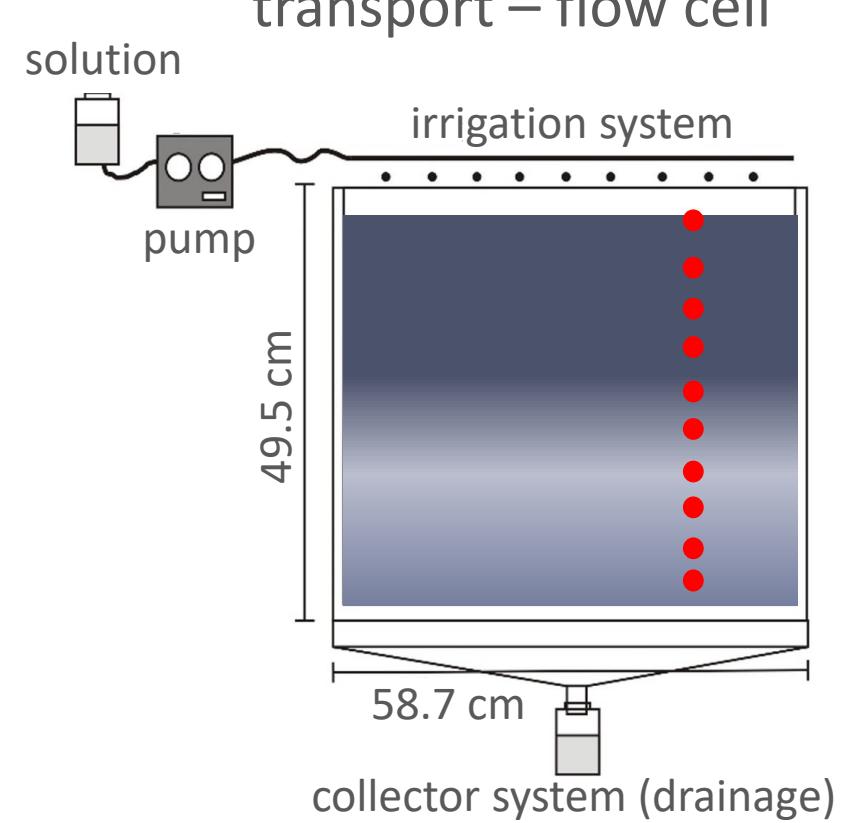
$$11 \leq \varepsilon \leq 17$$

$$1 \leq \varepsilon' \leq 20$$

adsorption isotherms – Batch



transport – flow cell



# Non-equilibrium chemical transport

unsaturated flow – impact on hydraulic properties (direct simulation)

$$h(\theta, C_w) = \frac{\sigma}{\sigma_o} h(\theta, C_{wo})$$

negligible at very low concentrations

$$K(\theta, C_w) = \frac{v}{v_o} K(\theta, C_{wo})$$

e.g., Paweena Kanokkarn et al. CSA (2017)

e.g., Smith and Gillham *WRR* (1994, 1999)

reactive processes (inverse method)

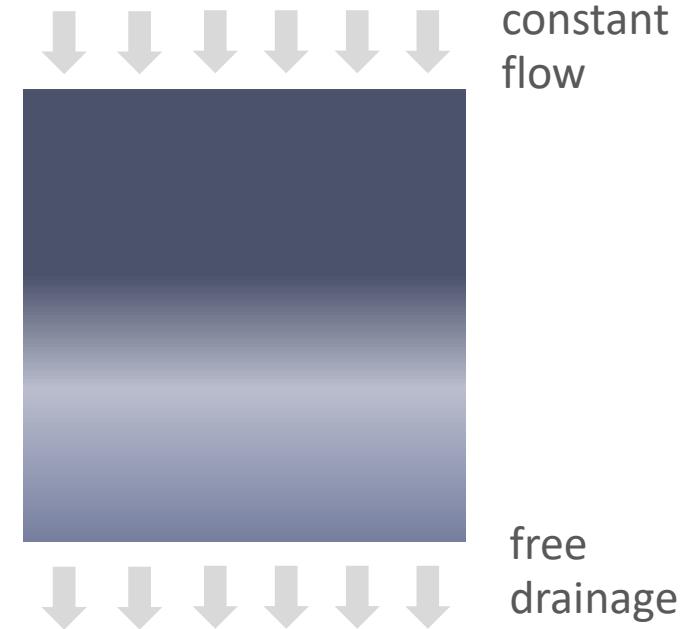
adsorption  $C_s = \frac{K_d C_w^\beta}{1 + \eta C_w^\beta}$

degradation  $C_w = C_{wo} e^{-\mu t}$

$$Pe = \frac{\tau_d}{\tau_a} = \frac{u}{D_m} \Delta x \quad Da = \frac{\tau_a}{\tau_r} \quad \tau_r = 1/(C_{wo} k)$$

$$Pe < 1$$

$$Da \ll 1$$

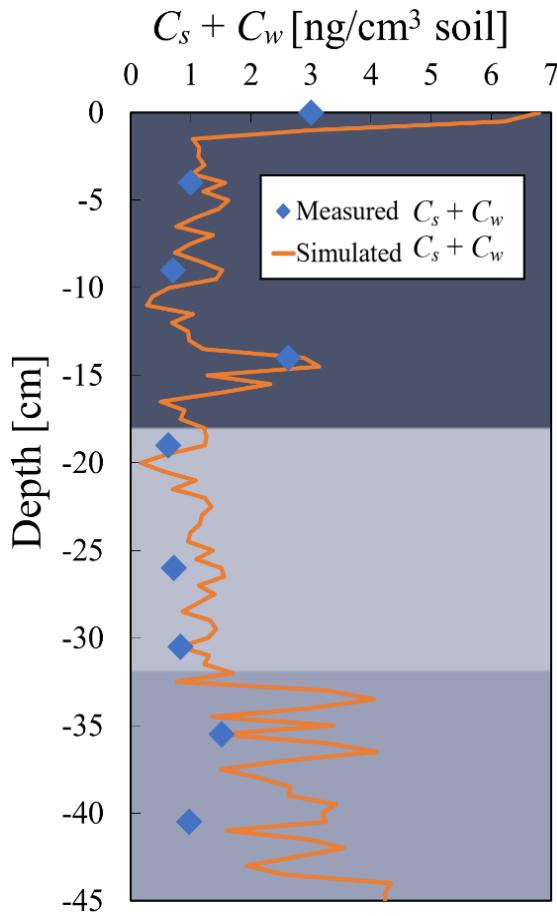


Hydrus 1D – Simunek et al. (2006)  
Rosetta – Schaap et al. *JofH* (2001)

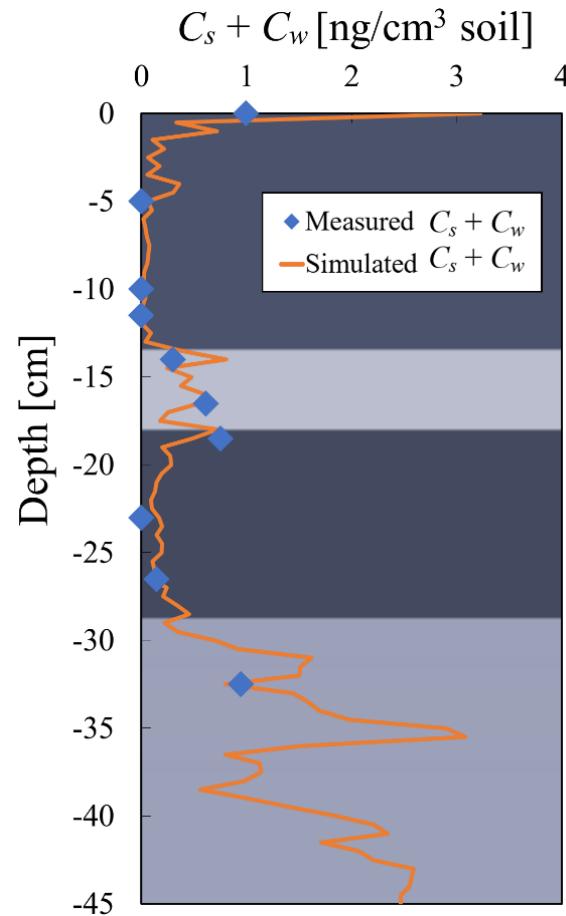
# Non-ionic surfactants – fate and transport

C14 AEO EO8

soil core 1 ( $t = 192\text{h}$ )



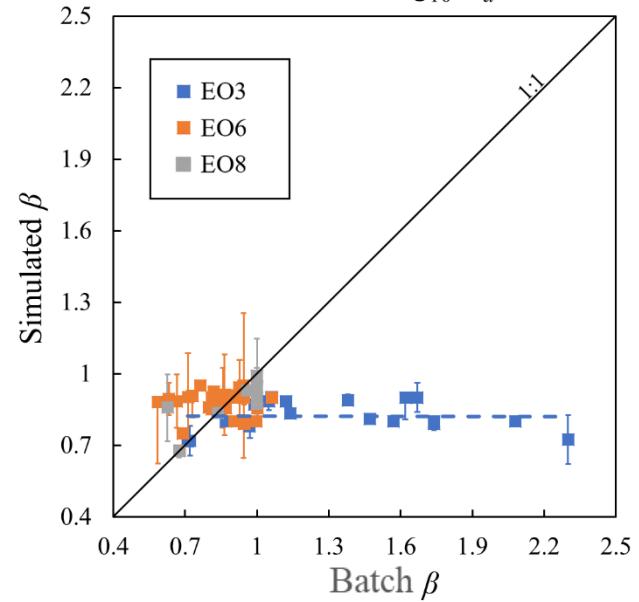
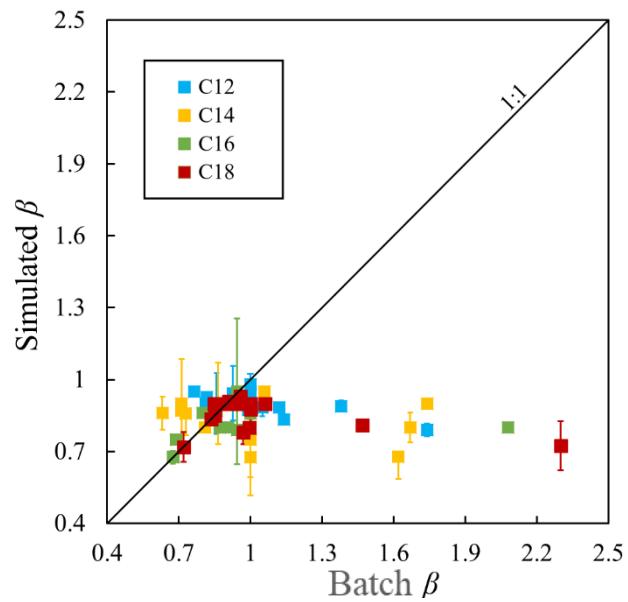
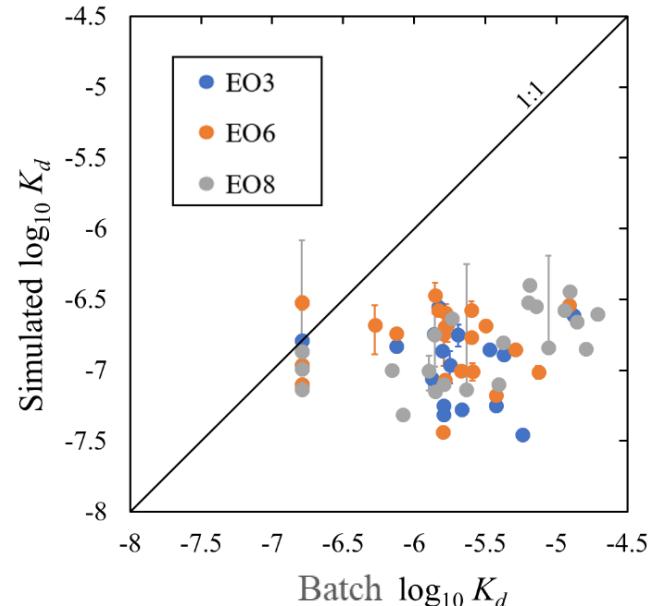
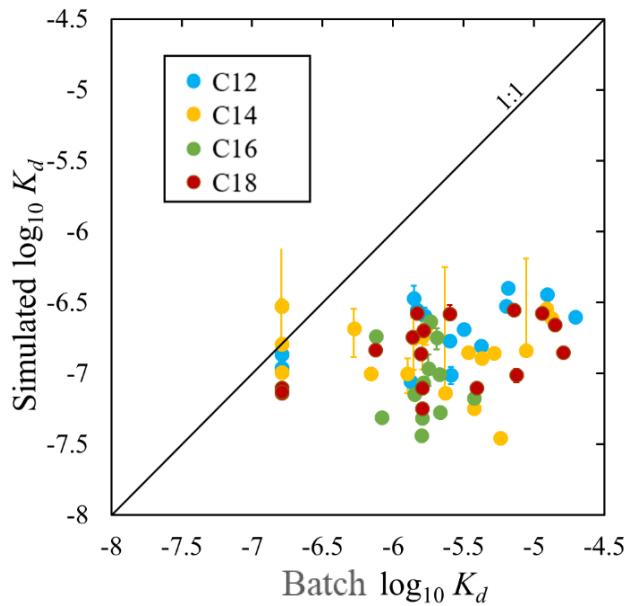
soil core 2 ( $t = 69\text{h}$ )



# Non-ionic surfactants – fate and transport

$$C_s = K_d \ C_w^\beta$$

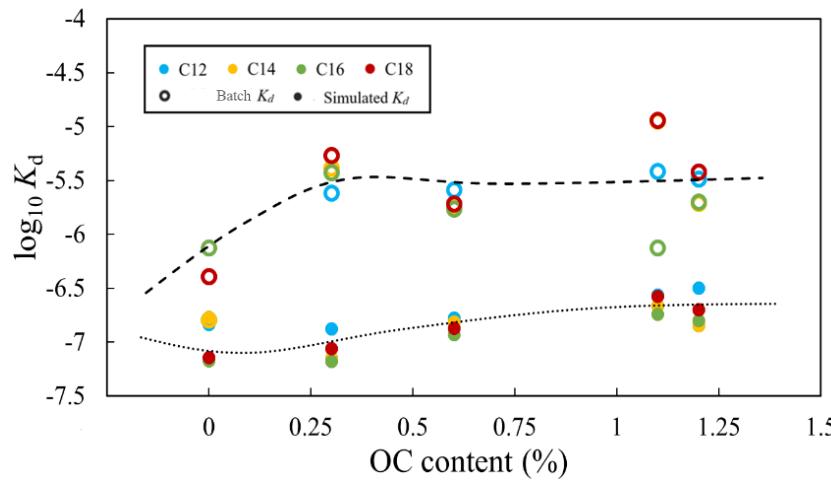
Freundlich



# Isotherm coefficients dependence on soil properties

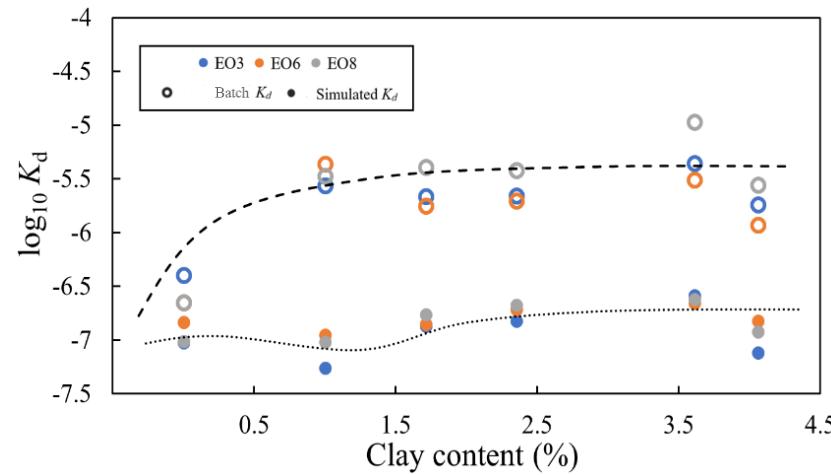
carbon chain length

OC content

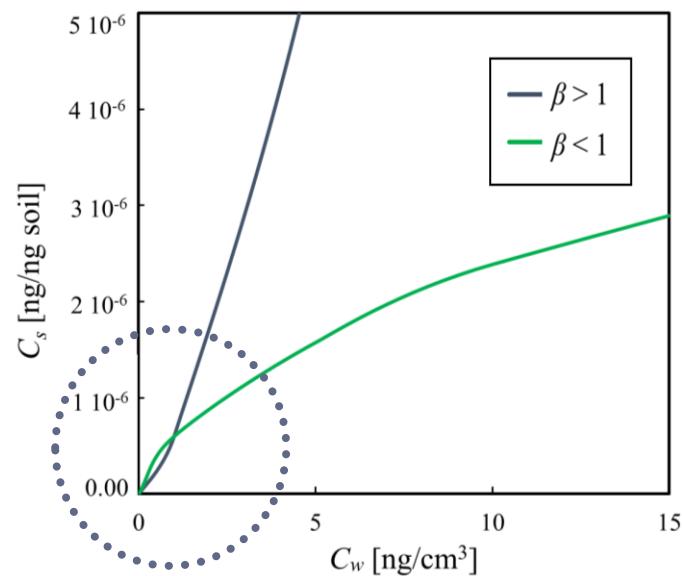
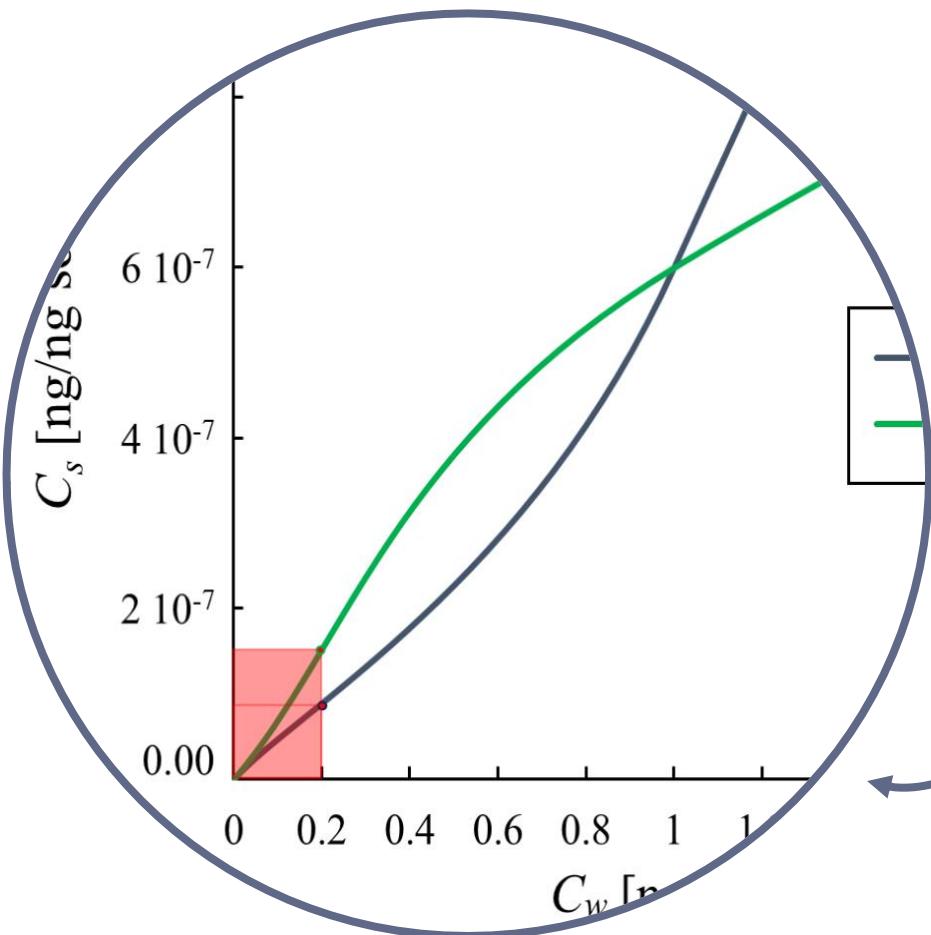


# ethoxylated groups

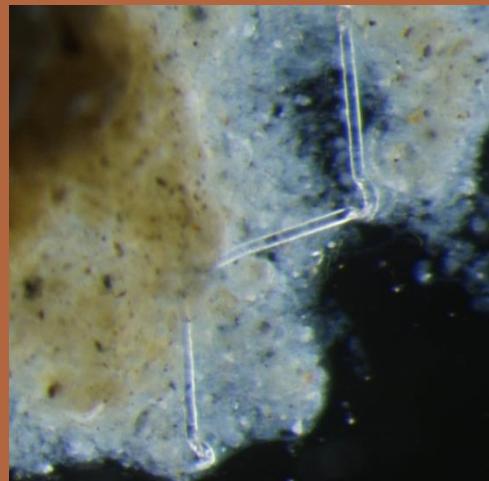
clay content



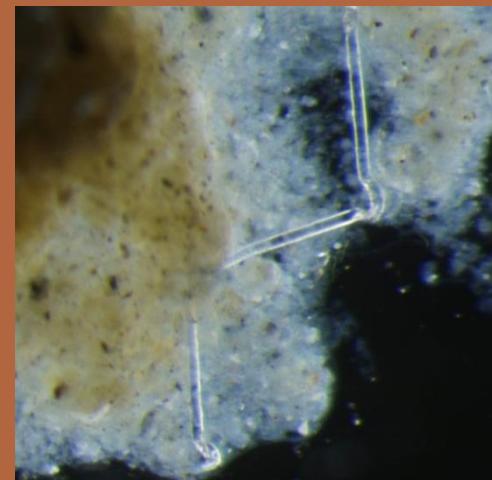
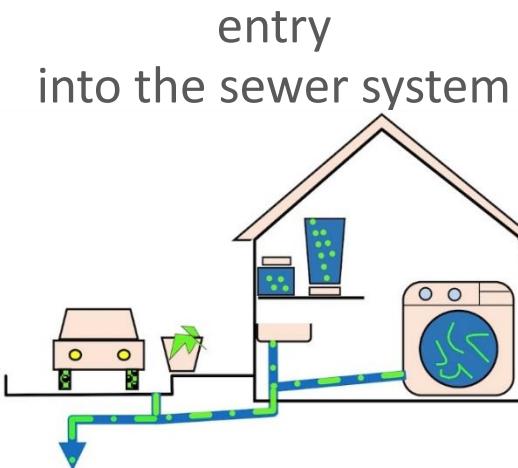
# Isotherm coefficients dependence on soil properties



# Impact from sewage sludge – particulate plastic

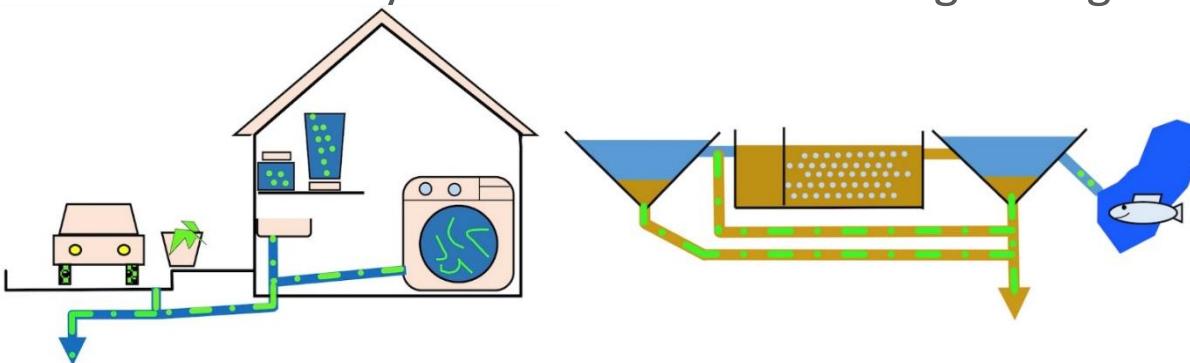


# Impact from sewage sludge – particulate plastic

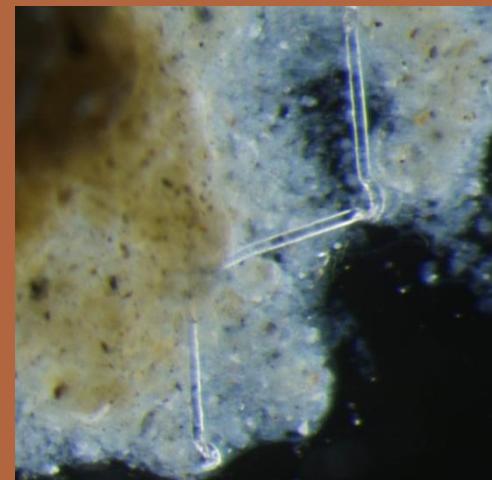


# Impact from sewage sludge – particulate plastic

entry  
into the sewer system

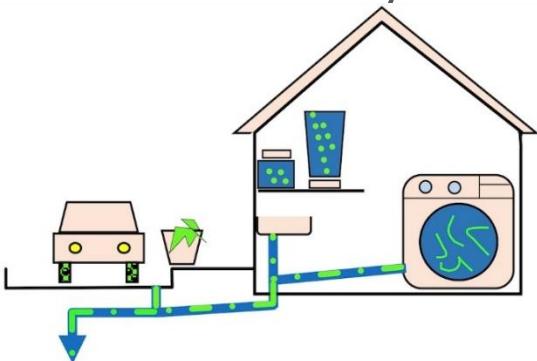


accumulation  
in the sewage sludge

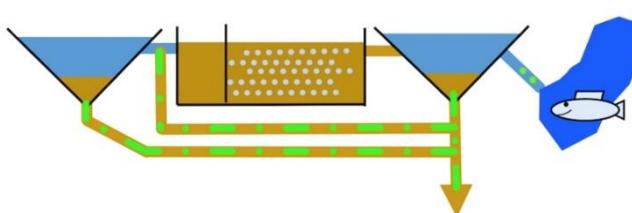


# Impact from sewage sludge – particulate plastic

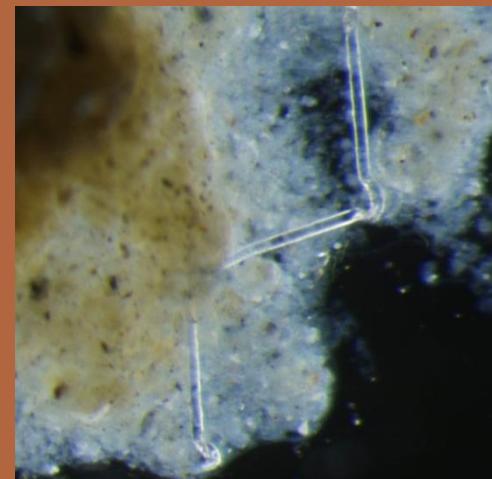
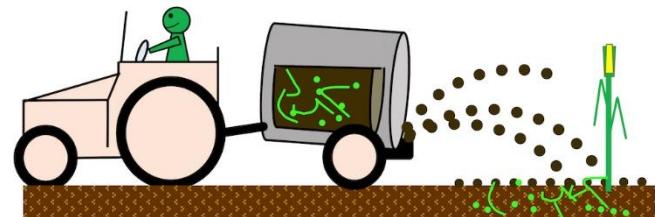
entry  
into the sewer system



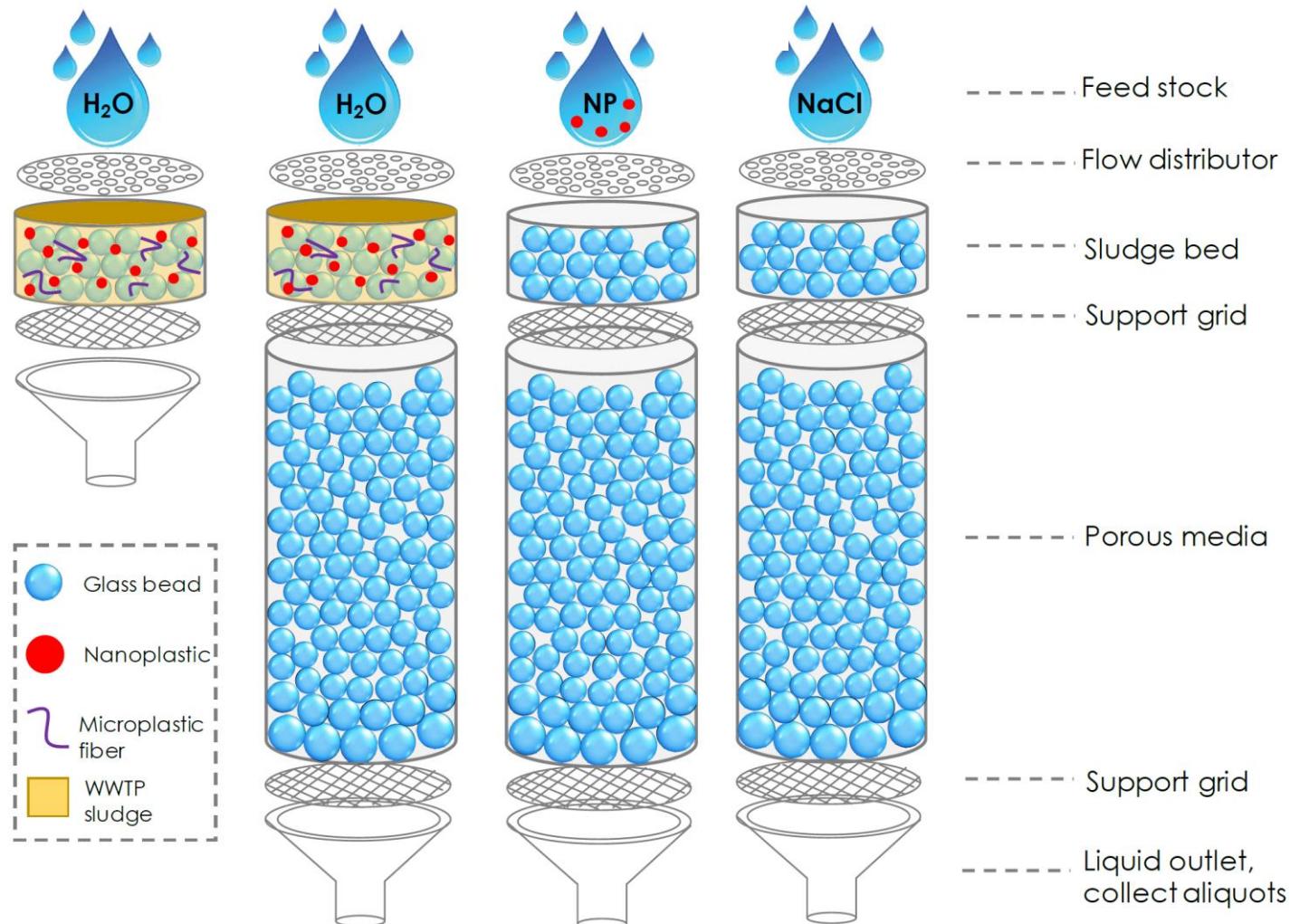
accumulation  
in the sewage sludge



use  
as fertilizer

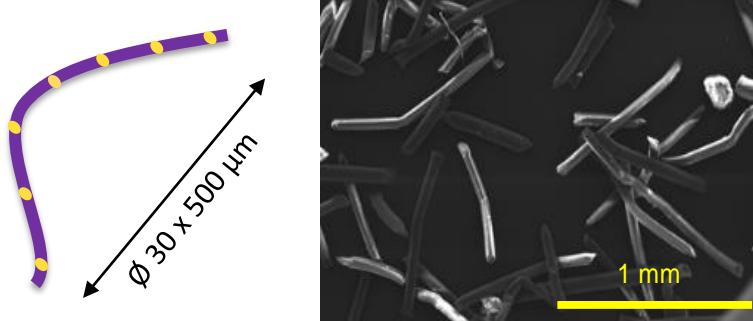


# Leaching from sludge and transport through the soil column experiments

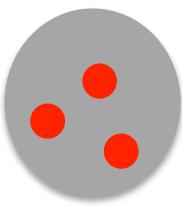


# Metal doped particulate plastic

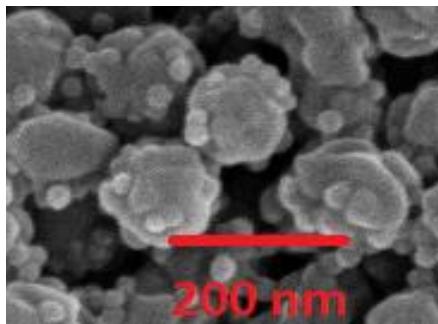
microplastic fibres – Indium



nanoplastics particles – Palladium

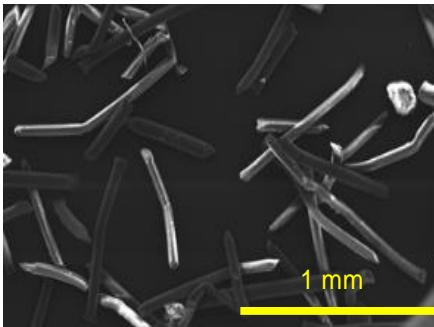
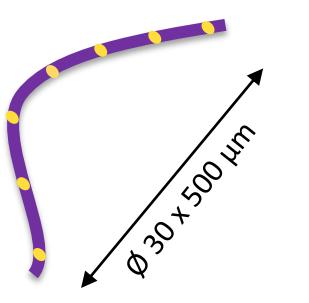


Ø 200 nm

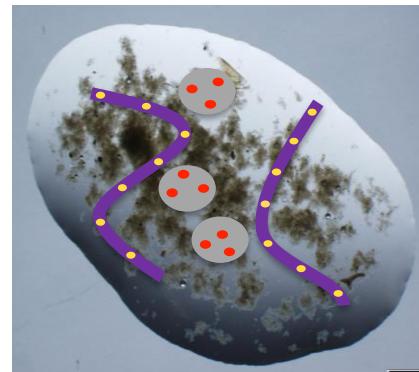


# Metal doped particulate plastic

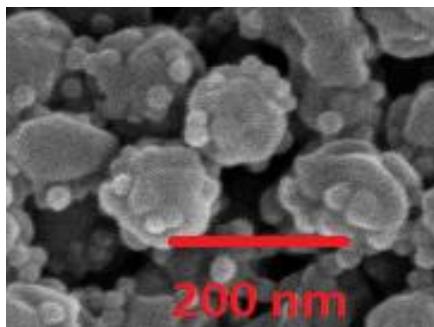
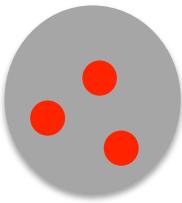
microplastic fibres – Indium



spiking in  
complex matrix

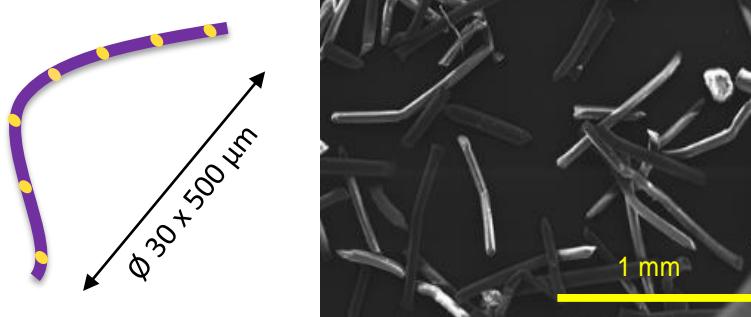


nanoplastics particles – Palladium



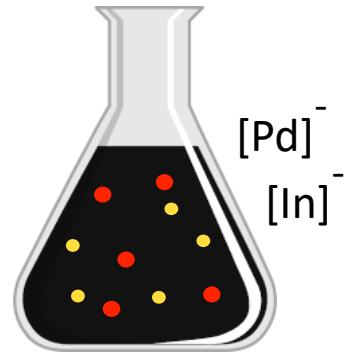
# Metal doped particulate plastic

microplastic fibres – Indium

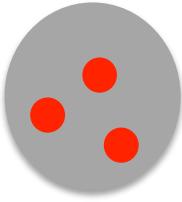


spiking in  
complex matrix

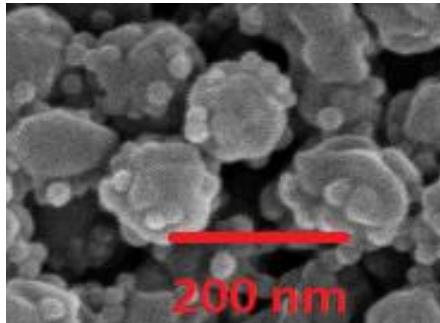
analysis by  
Acid Microwave Digestion  
ICP-MS



nanoplastics particles – Palladium

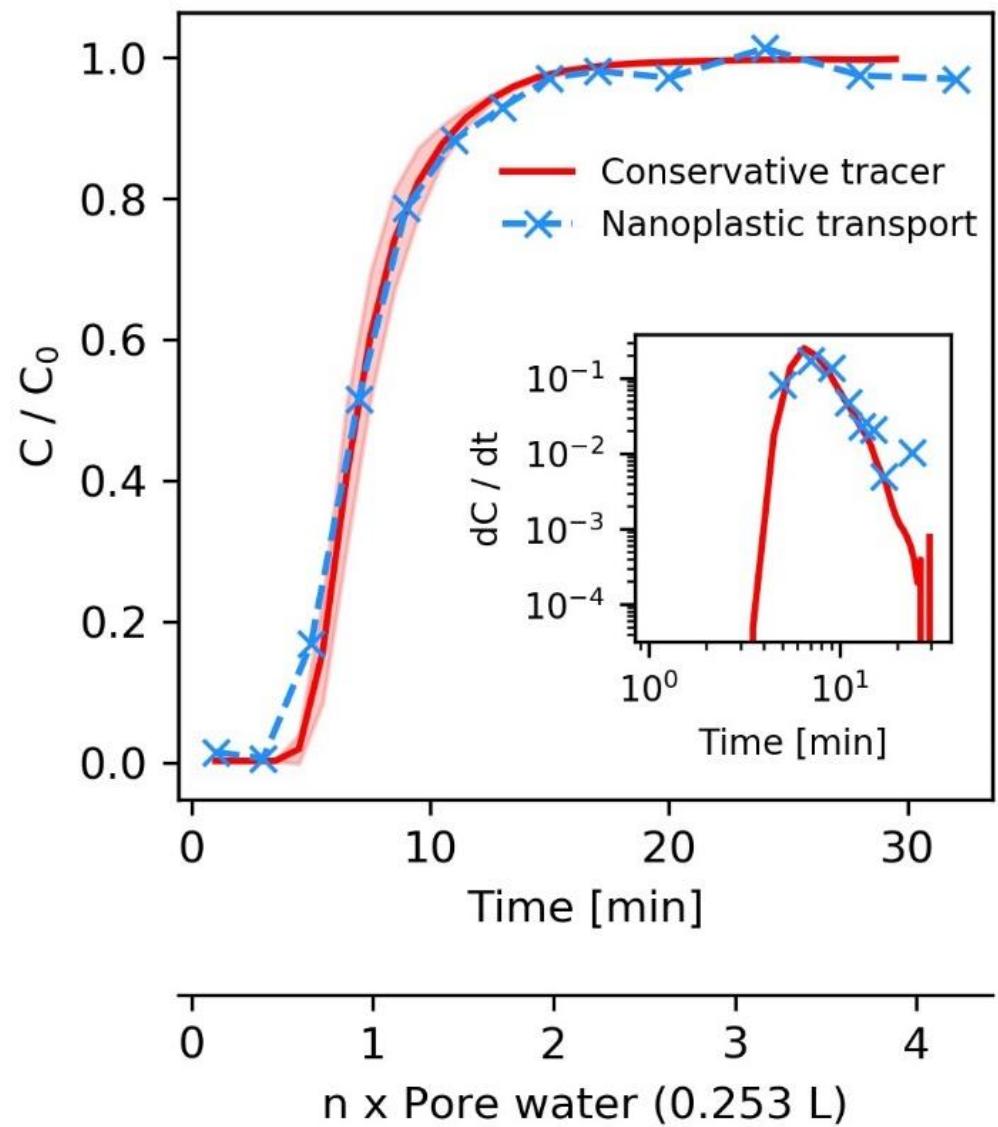


$\phi 200 \text{ nm}$



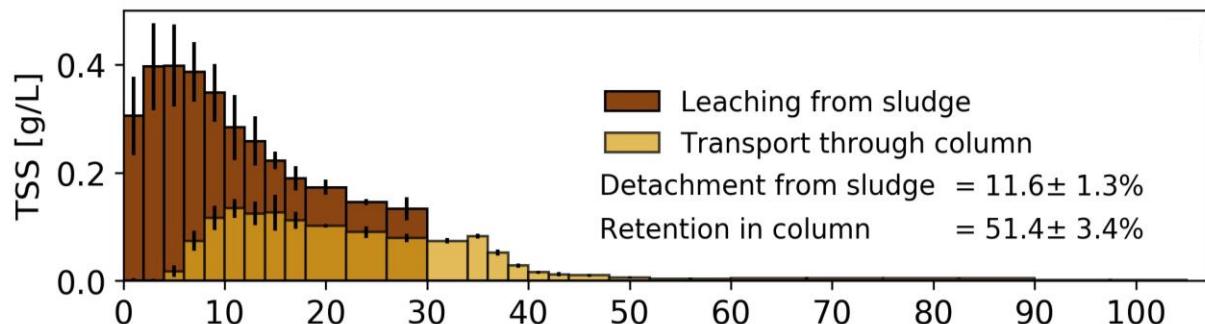
# Pristine nanoparticles and tracer transport

anomalous (*non-Fickian*)  
transport

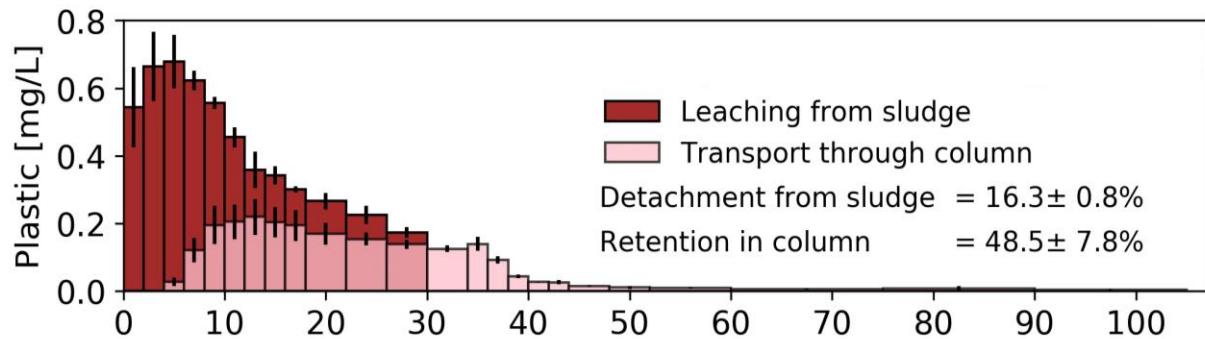


# Leaching from sludge and transport through the soil

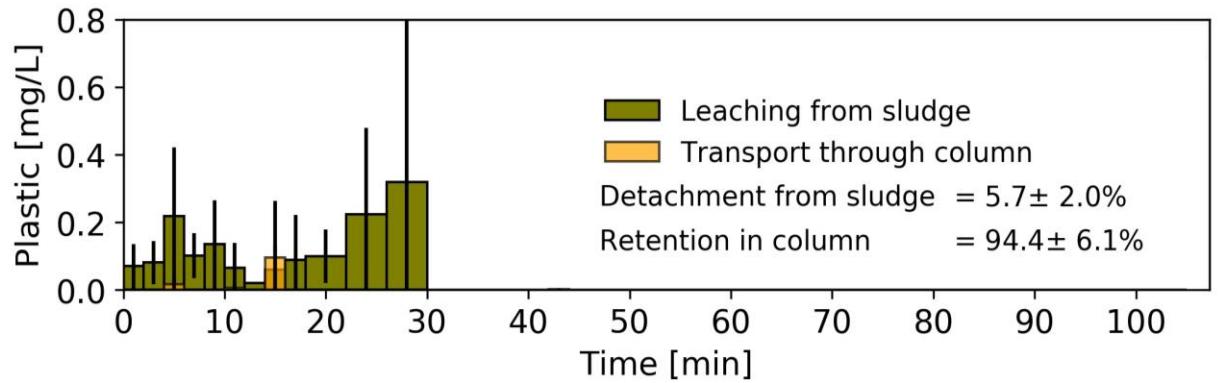
organic solids



nanoplastics

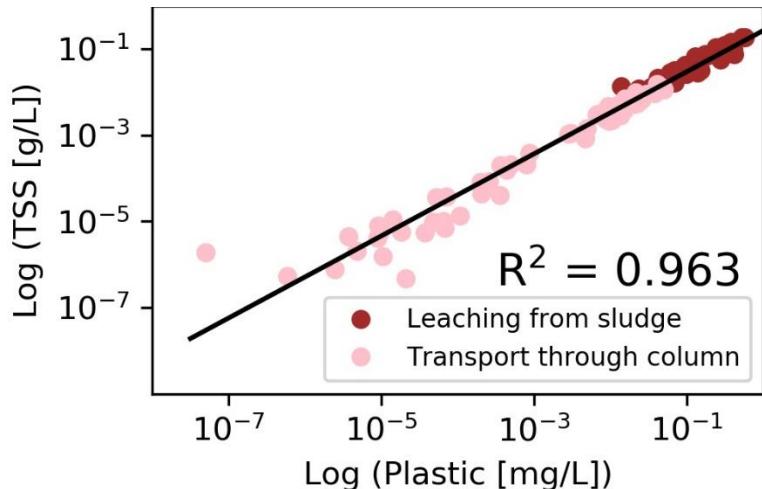


microplastics

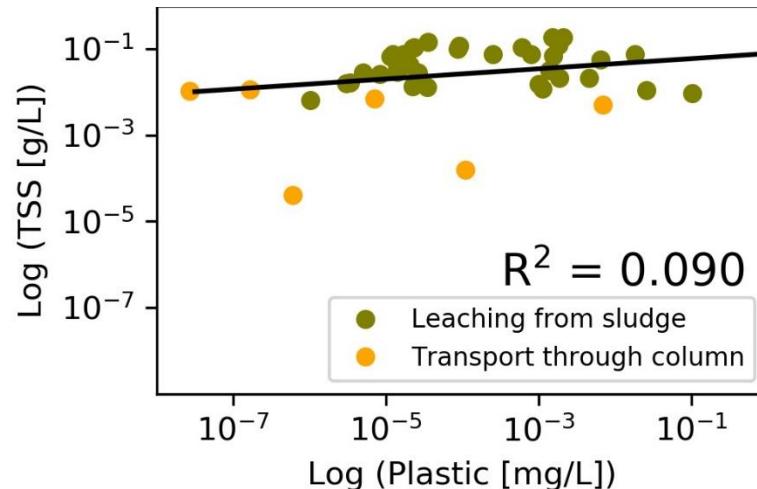


# Nanoplastics co-transport and microfibers straining

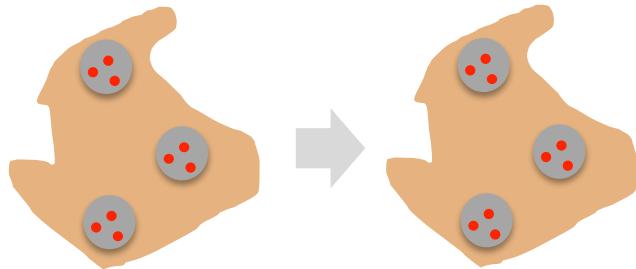
nanoplastic particles



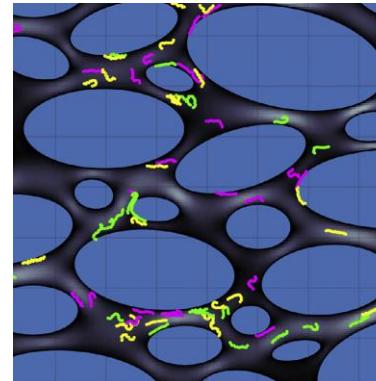
microplastic fibers



co-transport



straining



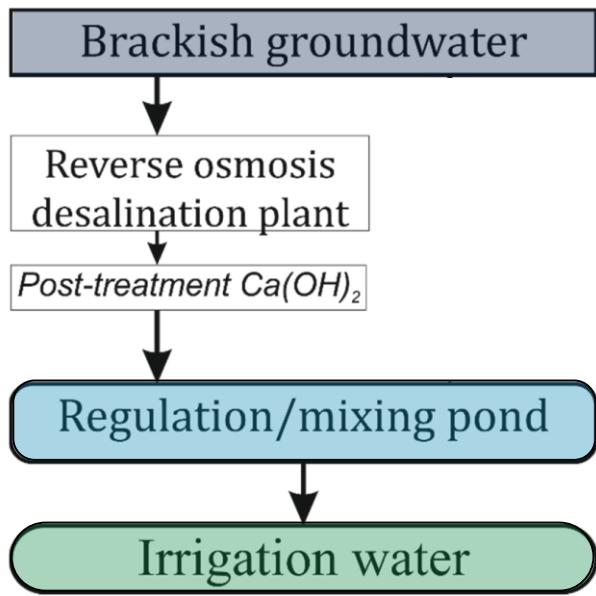
Engdhal AWR (2018)

ionic strength << hydrodynamics

e.g., Predelus et al. *JNP* (2017)

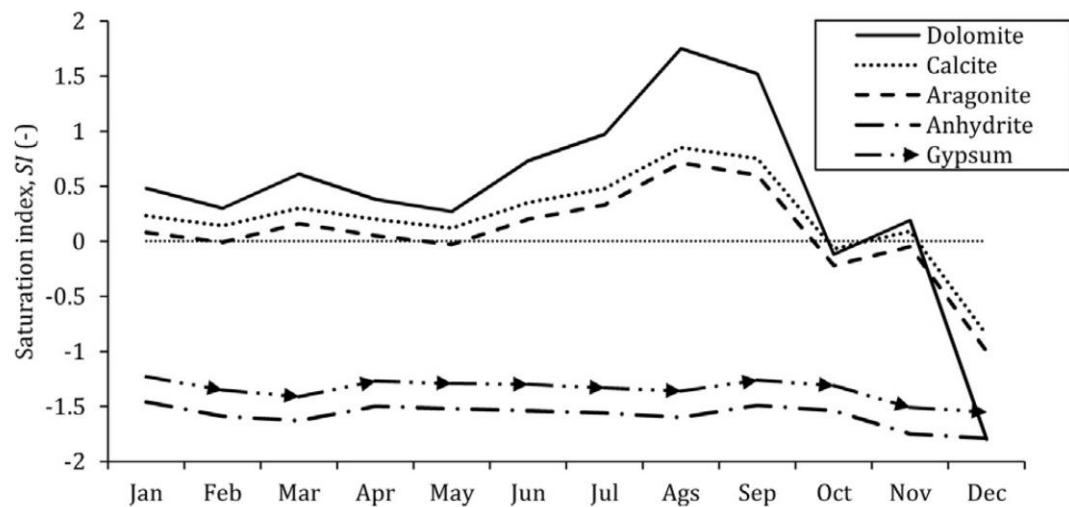
# Impact from desalinated water

## irrigation water production



## minerals saturation

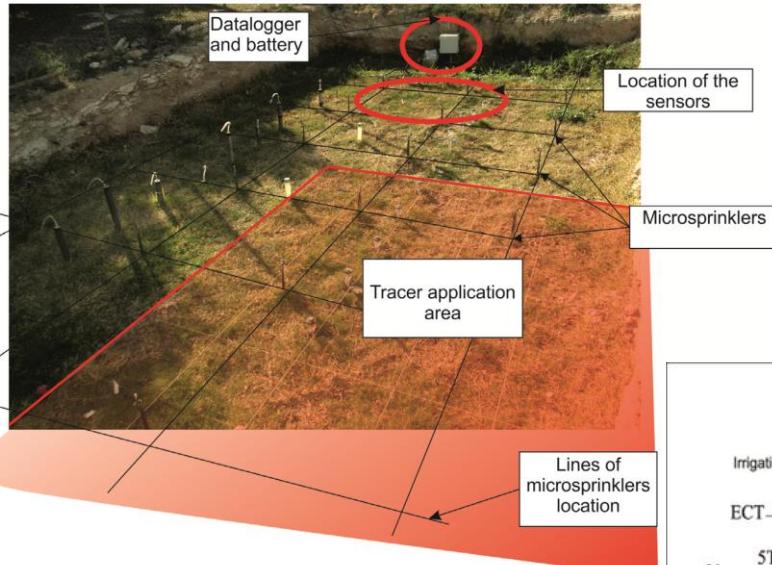
Dolomite	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$
Calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$
Aragonite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$
Anhydrite	$\text{CaSO}_4 = \text{Ca}^{2+} + \text{SO}_4^{2-}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$



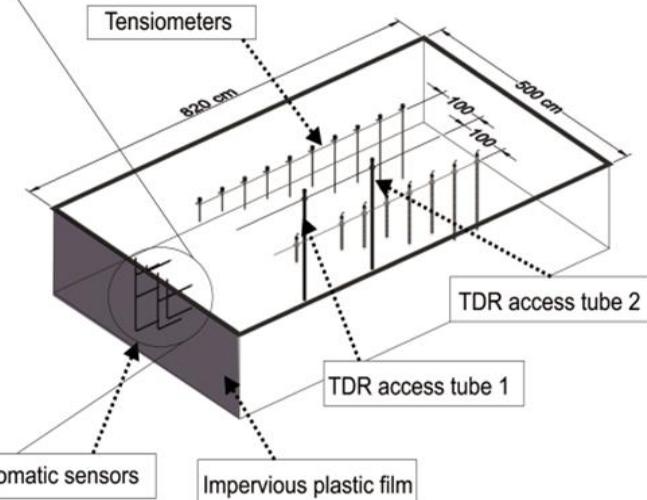
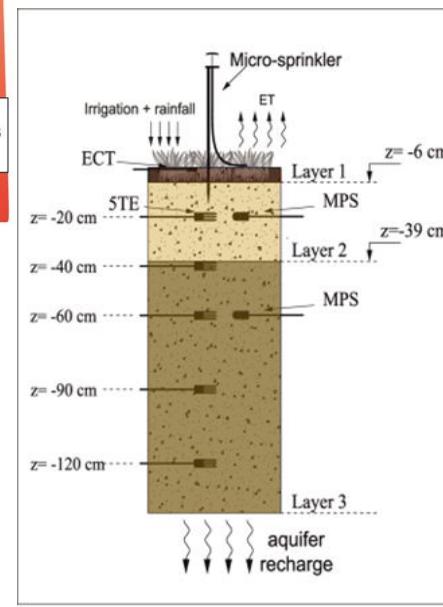
Valdes-Abellan et al. DWT (2013)

# Impact from desalinated water

## field experiment – experimental plot

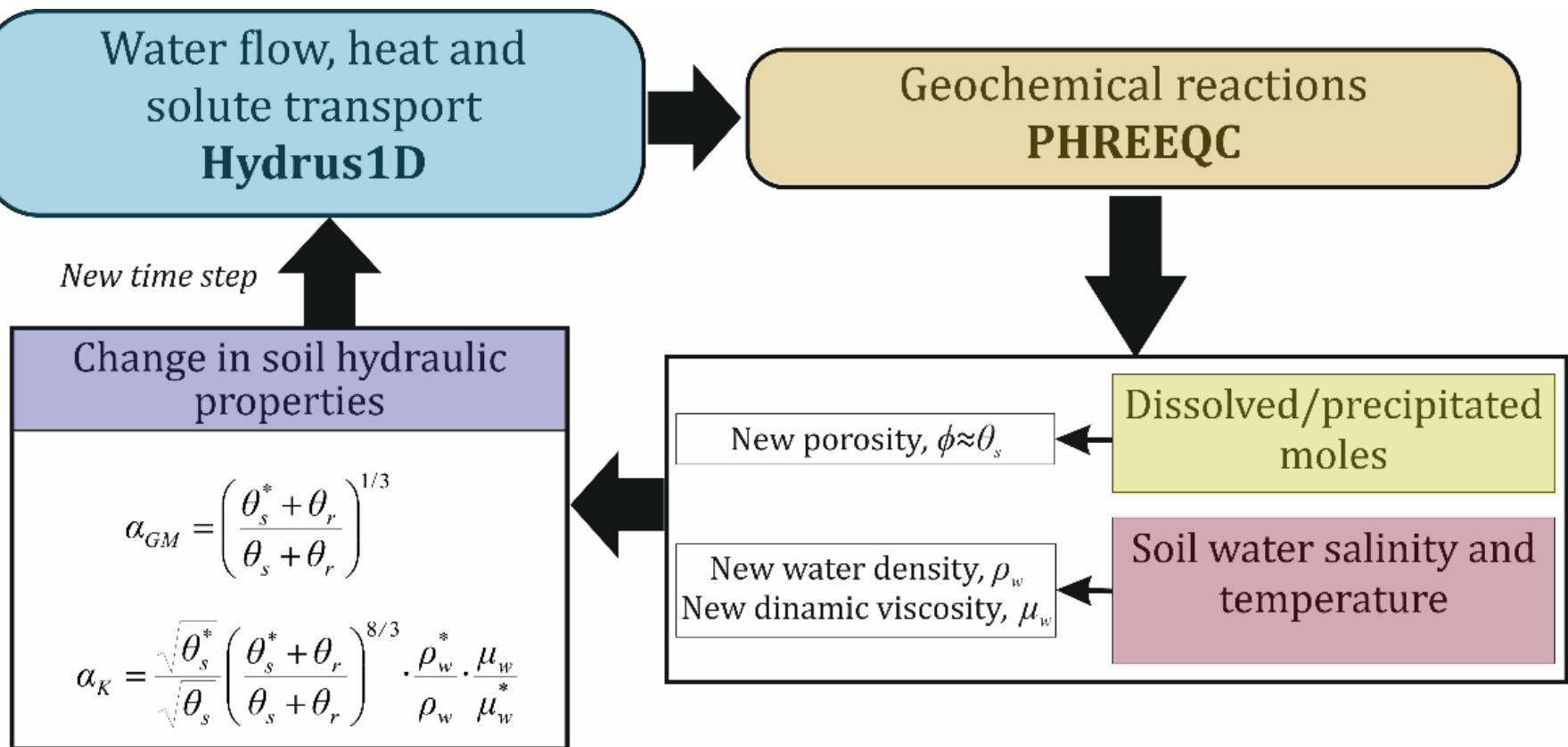


Valdes-Abellan et al. SS (2014)



Valdes-Abellan et al. SJAR (2015)

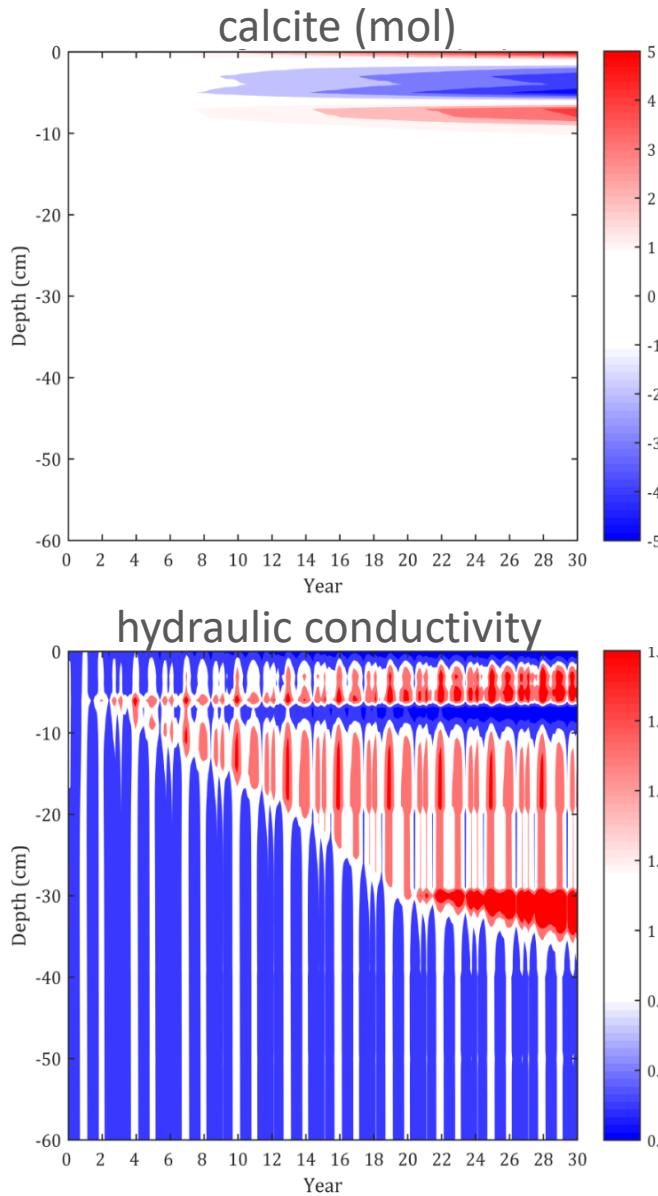
# Non-isothermal multicomponent reactive transport



Valdes-Abellan et al. JofH (2017)

# Main scenario

precipitation  
dissolution

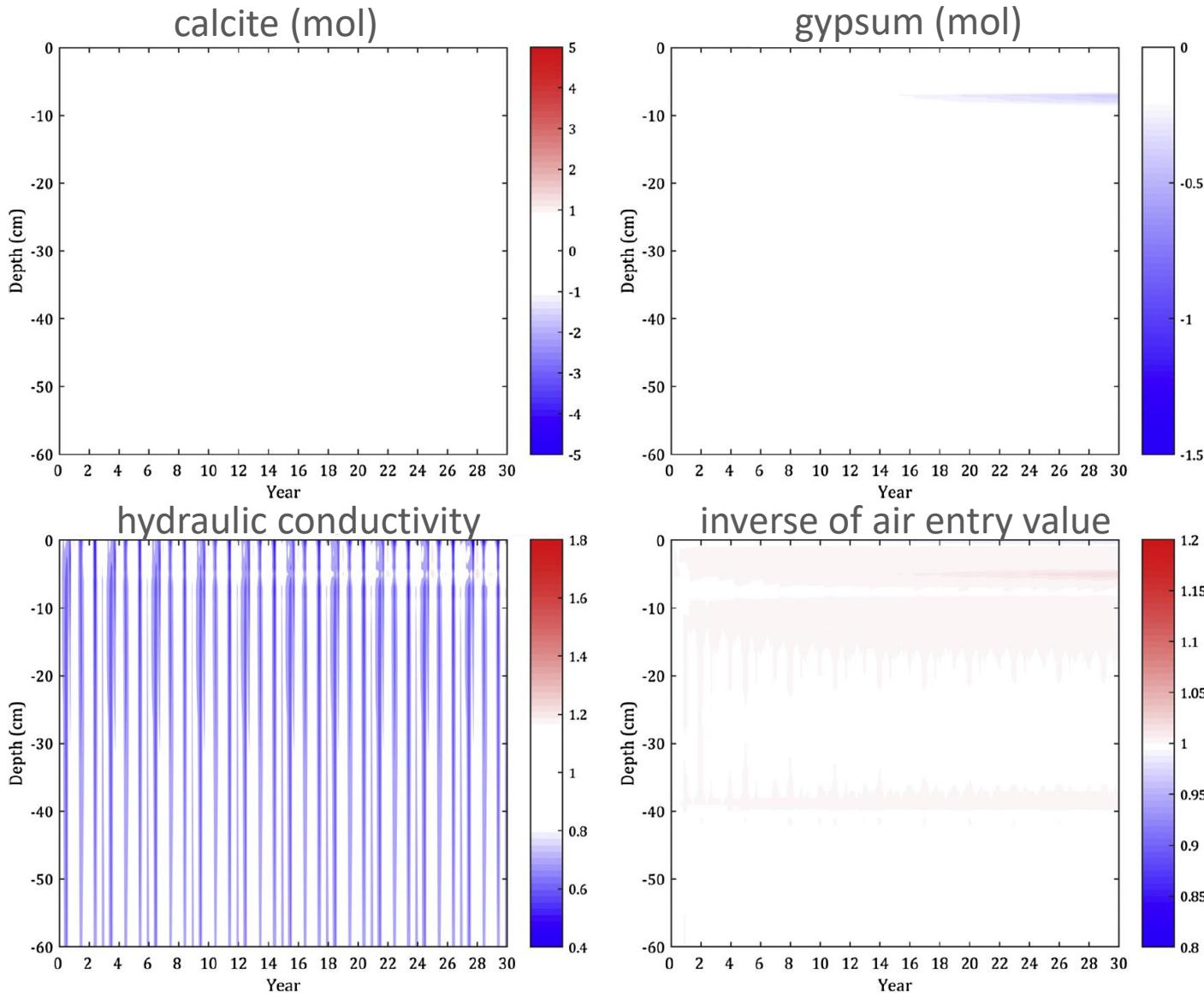


soil properties

# Rain-fed scenario

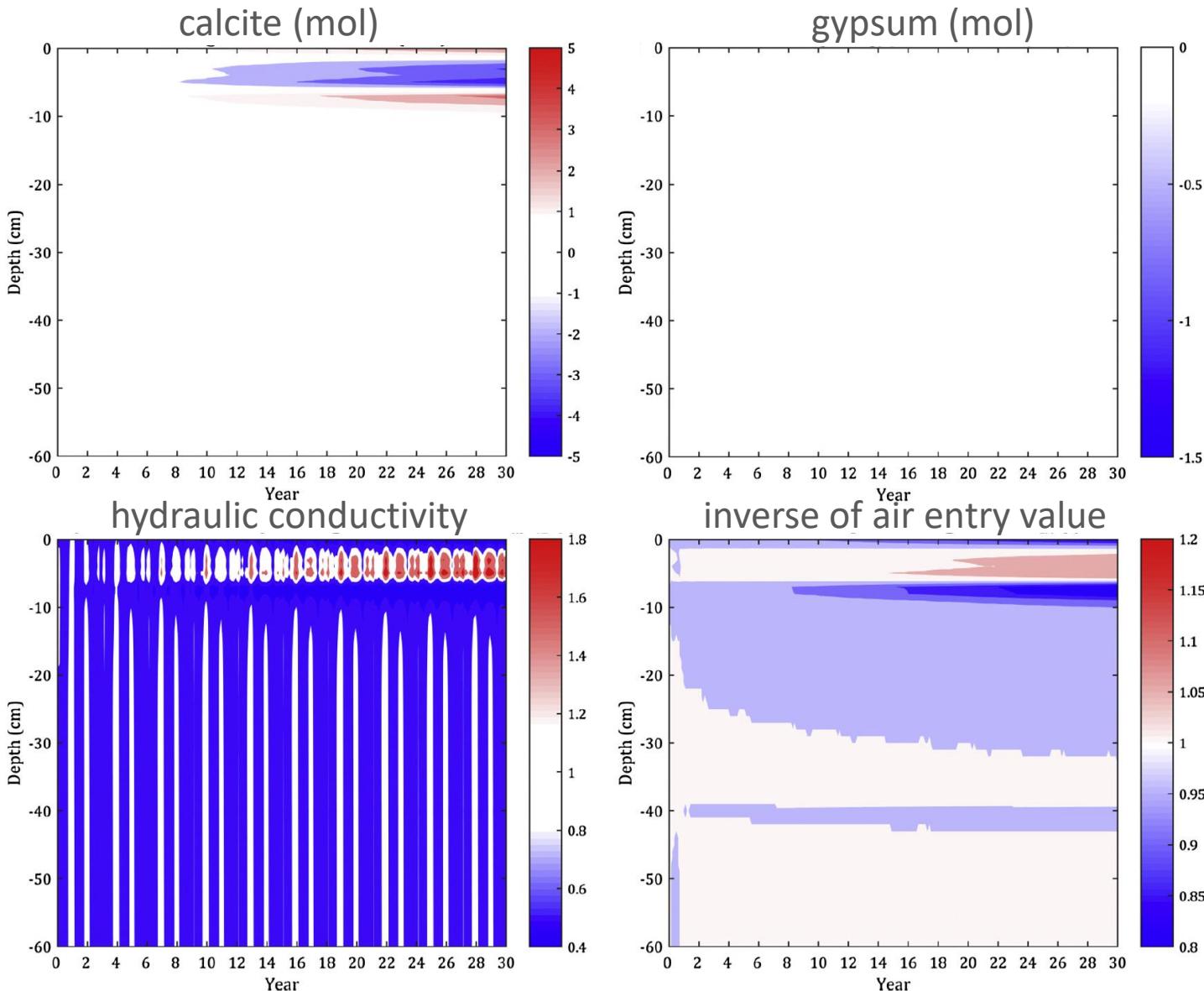
precipitation  
dissolution

soil properties



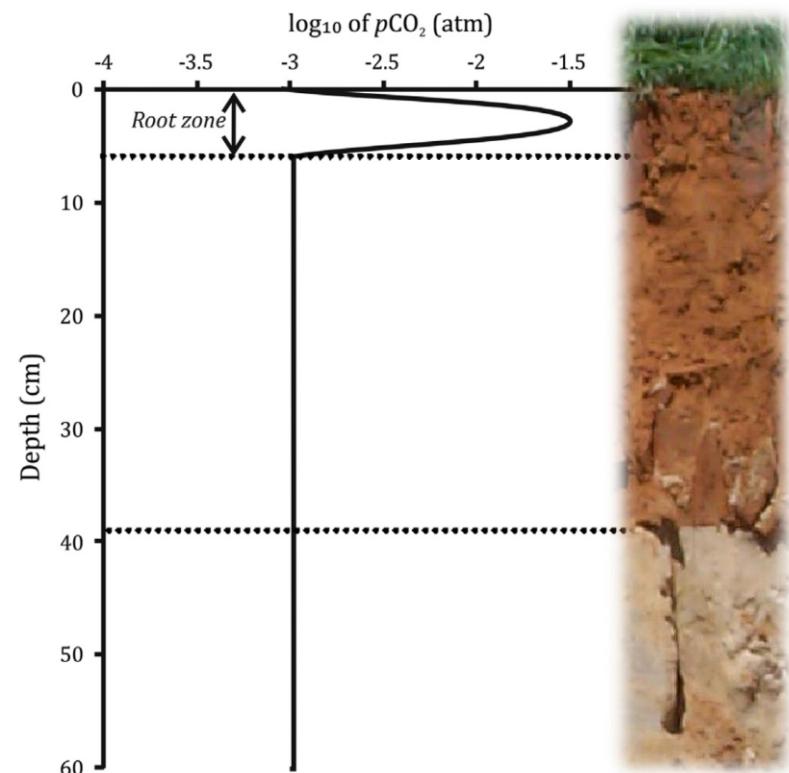
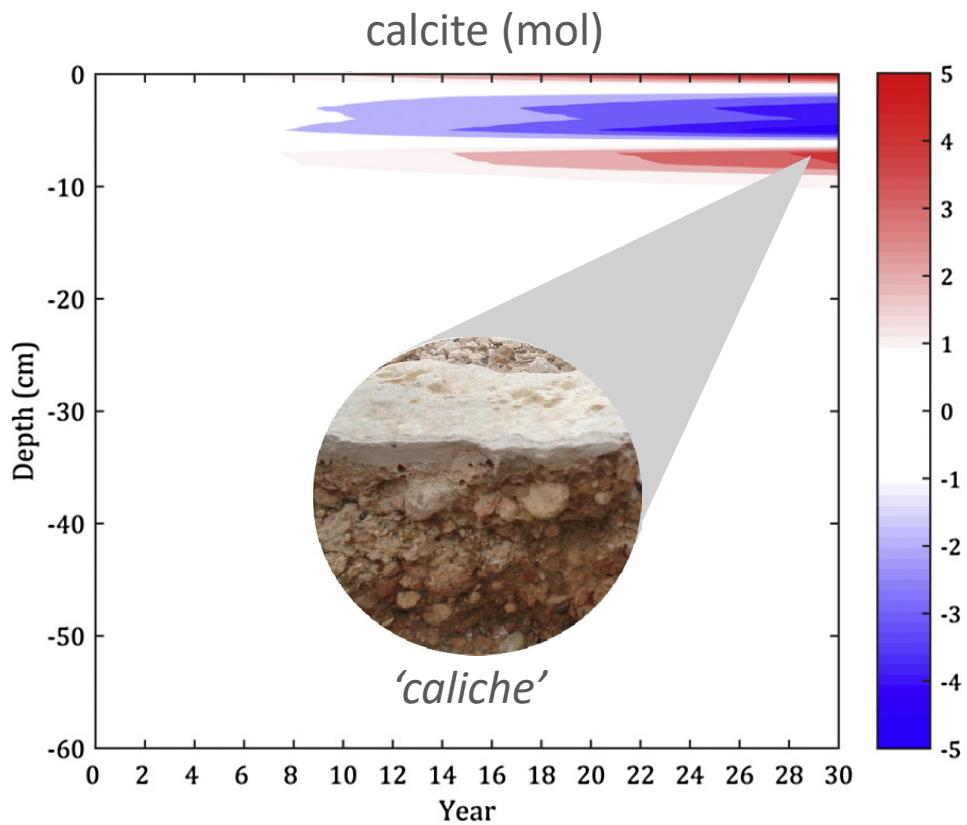
# Gypsum-free soil scenario

precipitation  
dissolution



soil properties

# Partial pressure of CO<sub>2</sub> in the root zone – soil respiration



# Concluding remarks

non-ionic surfactants – alcohol polyethoxylates (AEOs)

- Batch kinetics not reliable at environmental conditions
- at low concentrations and low clay and organic matter content, no differences between homologs

co-transport of nanoplastic particles and organic solids,  
and straining of microplastic fibers

soil respiration at the root zone plays a key role in the long-term  
carbonates precipitation



Botella-Espeso, M. (SEP group)

Keller, A.; Mitrano, D. (Eawag, Switzerland)

Corada-Fernandez, C.; Lara-Martin, P.; Gonzalez-Mazo, E. (University of Cadiz, Spain)

Valdes-Abellan, J. (University of Alicante, Spain)

Candela, L. (IMDEA, Spain)

Jacques, D. (SCK-CEN, Belgium)