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INSTITUTE OF CHEMICAL ENGINEERING SCIENCES

NUMERICAL SIMULATION OF DISSOLVED PFAS TRANSPORT IN UNSATURATED SOIL COLUMNS

Transport Phenomena and Porous Media Laboratory

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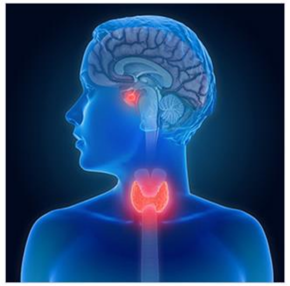
PFAS

≡ CNN health Life, But Better Fitness Food Sleep More Aud

Synthetic chemical in consumer products linked to early death, study finds

By Sandee LaMotte, CNN

Updated 2034 GMT (0434 HKT) October 12, 2021



NIH National Institute of Environmental Health Sciences

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Endocrine Disruptors

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Introduction

Many chemicals, both natural and man-made, may mimic or interfere with the body's hormones, known as the endocrine system. Called endocrine disruptors, these chemicals are linked with developmental, reproductive, brain, immune, and other problems.

Endocrine disruptors are found in many everyday products, including some plastic bottles and containers, liners of metal food cans, detergents, flame retardants, food, toys, cosmetics, and pesticides.

Some endocrine-disrupting chemicals are slow to break-down in the environment. That characteristic makes them potentially hazardous over time.

Endocrine disrupting chemicals cause adverse effects in animals. But limited scientific information exists on potential health problems in humans. Because people are typically exposed to multiple endocrine disruptors at the same time, assessing public health effects is difficult.

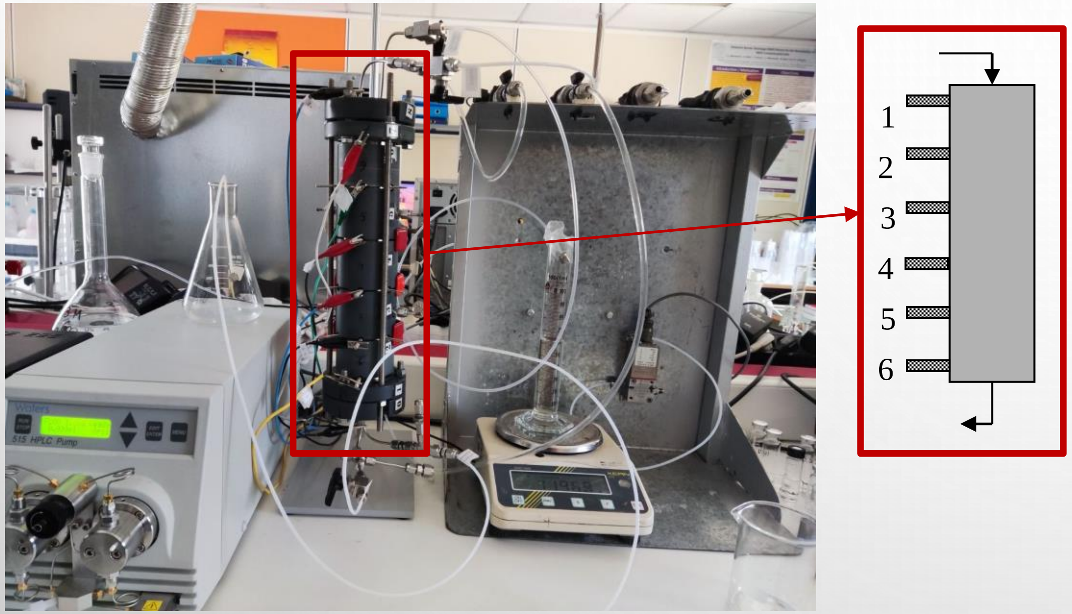
European Chemicals Agency

In addition, the Stockholm Convention regulates the global elimination of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. PFOA has been banned under the POPs Regulation since 4 July 2020.

Perfluorohexane sulfonic acid (PFHxS), its salts and related compounds as well as perfluorinated carboxylic acids (C9-14 PFCAs) are being considered for inclusion in the Stockholm Convention and consequent global elimination.

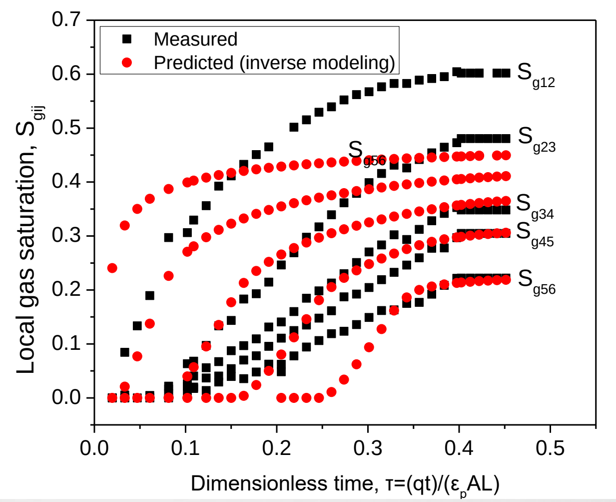
EXPERIMENTAL SETUP & PRELIMINARY RESULTS

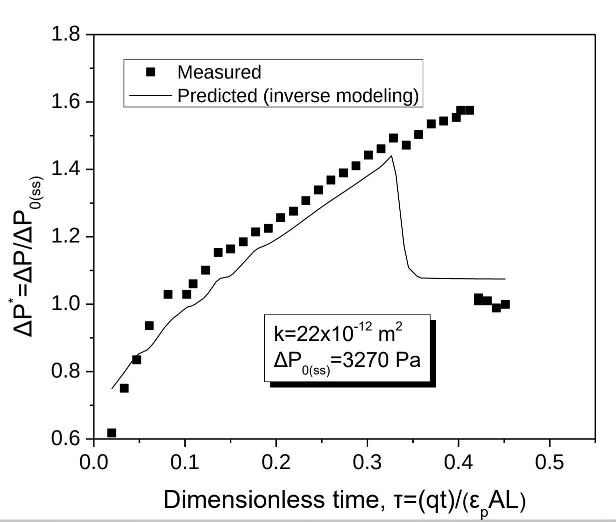
ESTIMATION OF THE WATER/GAS RELATIVE PERMEABILITIES



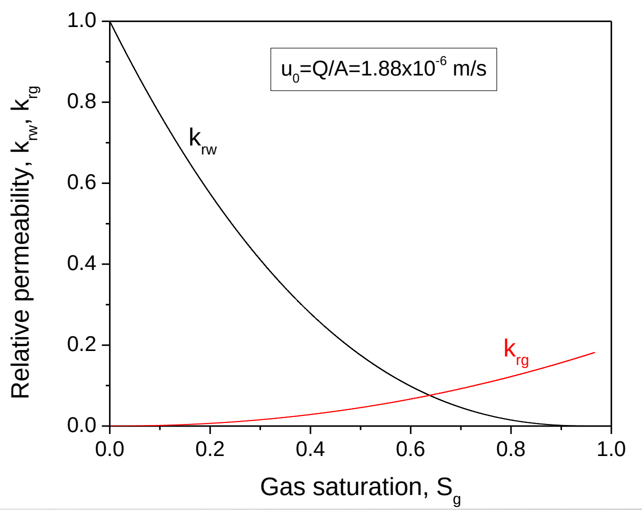
Transient immiscible displacement tests on soil columns

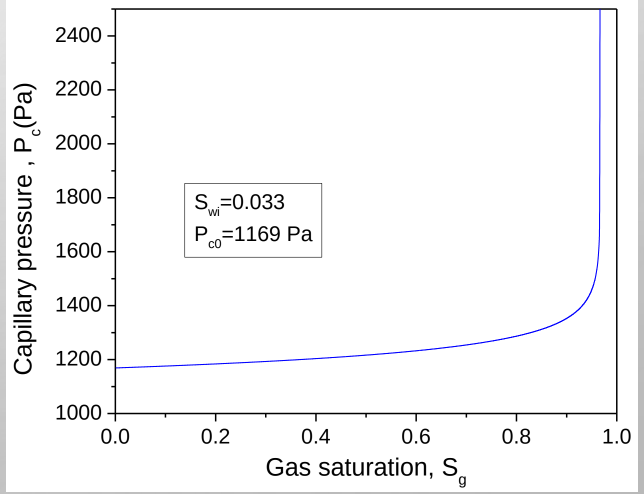
Air injection through a water-saturated sand column





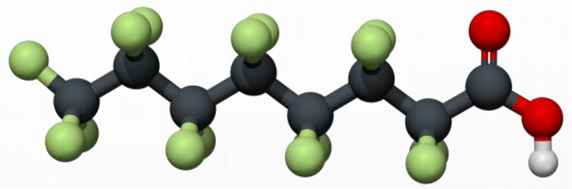
Estimated relative permeability and capillary pressure curves





NUMERICAL MODELS

C8 :PFOA



Case 1: 3D Model simulates the Forced imbibition (two-phase flow) process (without PFOA)

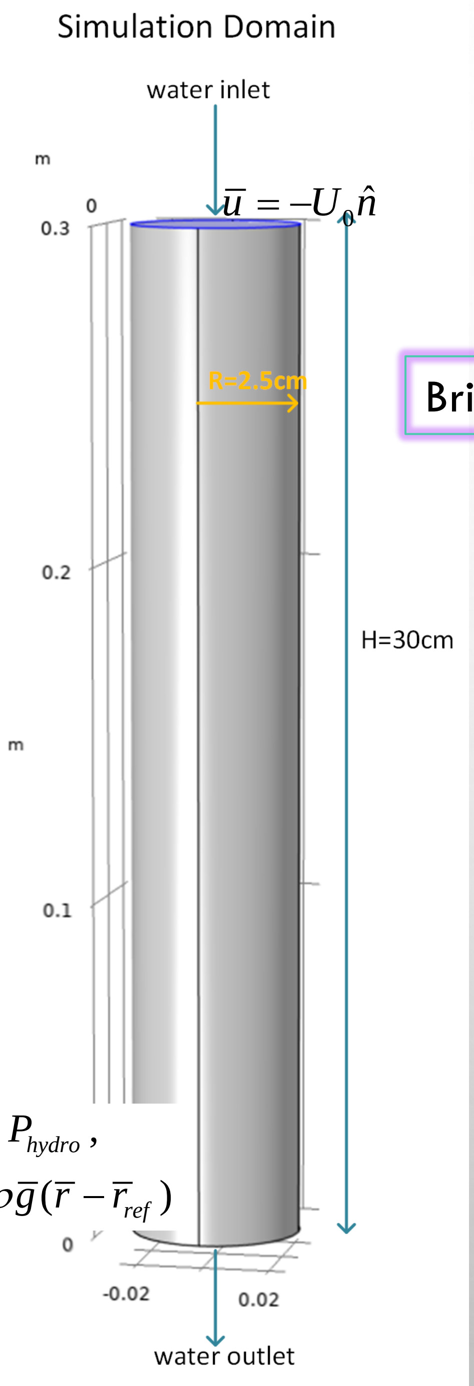
Results: 1. Figure presentation of water volume fraction vs time
2. Flow field

Case 2: 2D PFOA transport (convection, diffusion, dispersion, adsorption)

Results: 1. Figure presentation PFOA concentration distribution over time
2. Figure presentation PFOA vs time at various soil properties

3D-COLUMN MODEL: FORCED IMBIBITION

Model 1 : FLOW FIELD



$$P = P_0 + P_{hydro} \,,$$

$$P_{hydro} = \rho \bar{g}(\bar{r} - \bar{r}_{ref})$$

The purpose of this model is to calculate the volumetric water content over time

Brinkman- Darcy Equation for calculating velocity field inside porous medium

$$\frac{1}{\varepsilon_p}\rho\frac{\partial \bar{u}}{\partial t} = \nabla\left[-P\bar{I} + \bar{k}\right] - \left(\mu k^{-1} + \frac{Q_m}{\varepsilon_p{}^2}\right)\bar{u} + \rho\bar{g}$$

Phase changes according to Level Set method

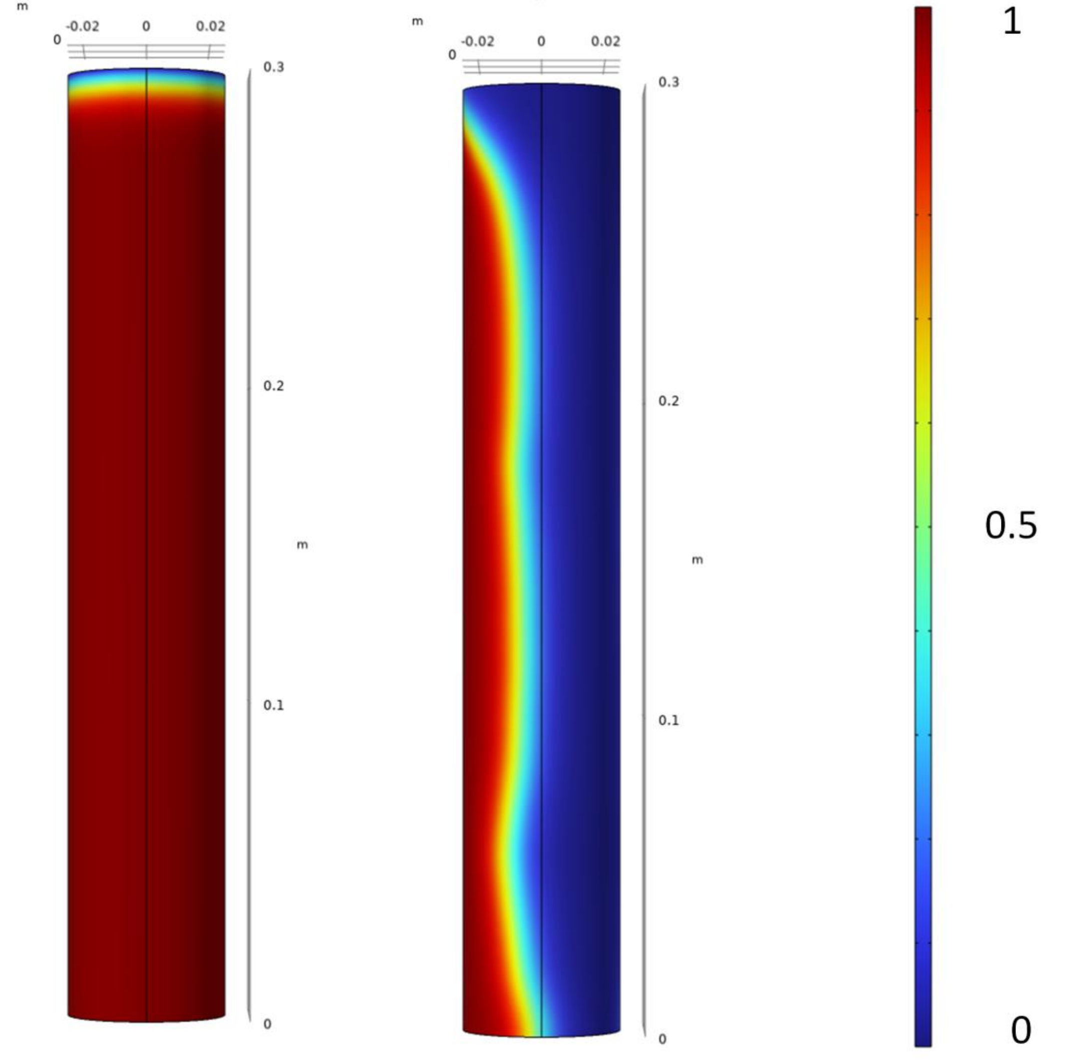
$$\frac{\partial \phi}{\partial t} + \bar{u}\nabla\phi = \gamma\nabla\left(\varepsilon_{ls}\nabla\phi - \phi(1-\phi)\frac{\nabla\phi}{|\nabla\phi|}\right)$$

<u>List of symbols</u>

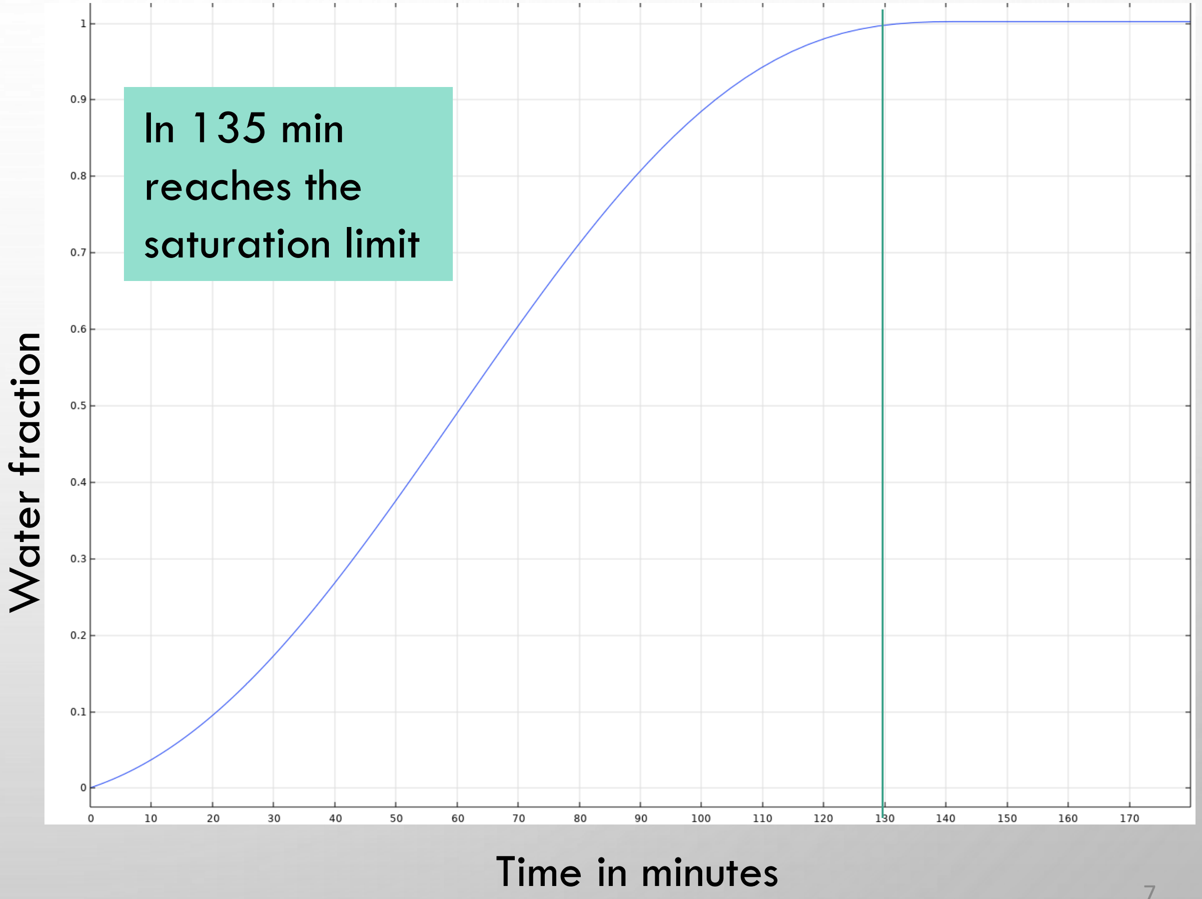
ε_p: porosity
ρ: density
υ: Darcy velocity
μ: dynamic viscosity
P: pressure
k: absolute permeability
g: gravity acceleration
ϕ: liquid phase
γ:term for numerical instabilities
ε_{ls}: interface thickness

AIR & WATER SATURATION CURVE

Distribution of air volume fraction inside 3D-column



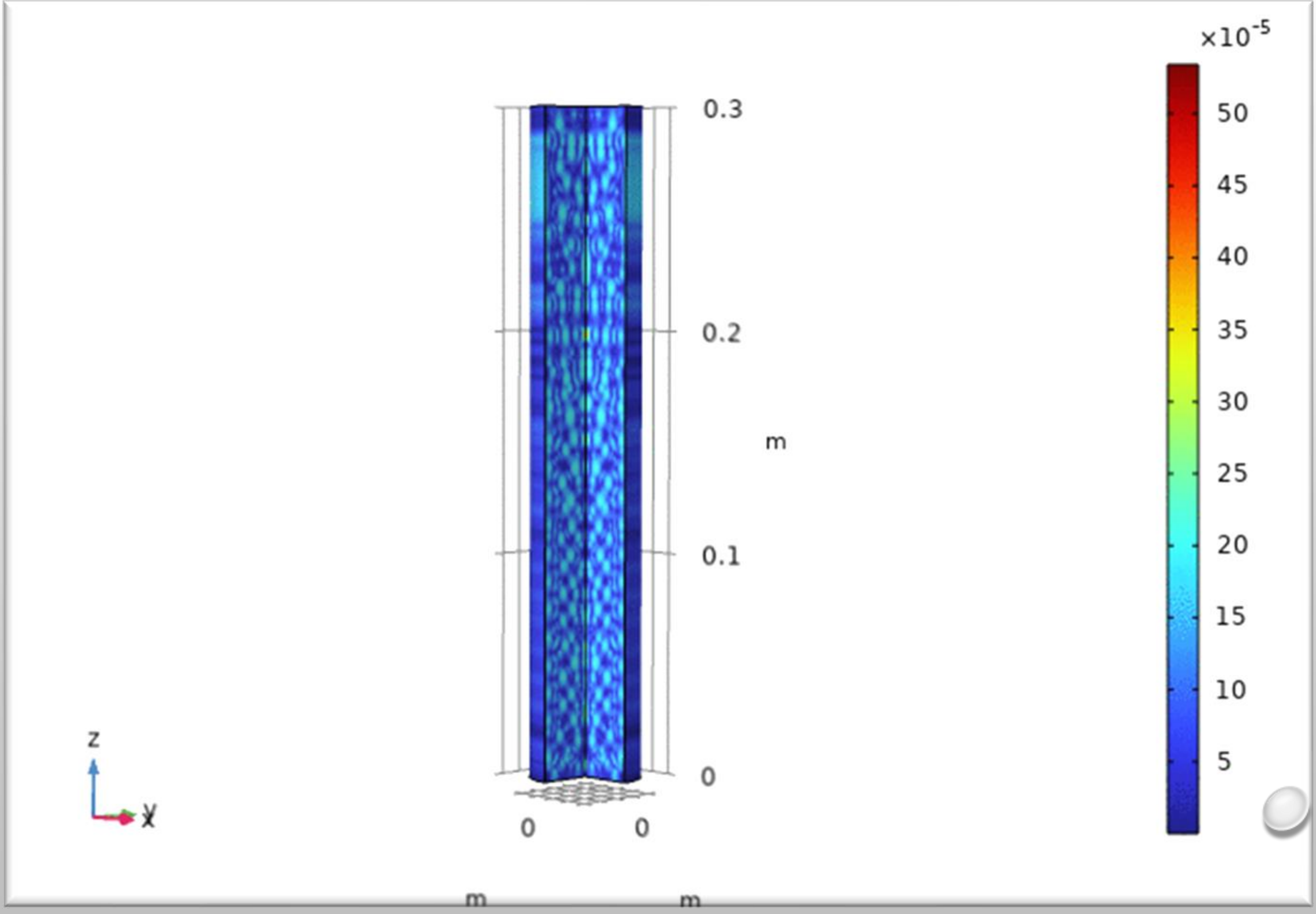
- WATER: SATURATION CURVE



VELOCITY FIELD VS TIME INSIDE UNSATURATED POROUS MEDIUM

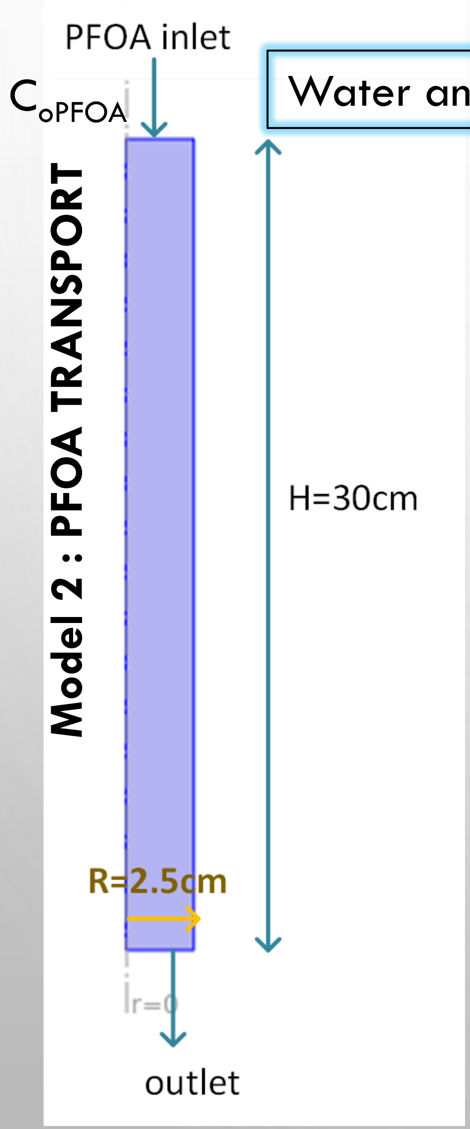
- 0.5 mm/s maximum velocity
- 0.04 mm/s minimum velocity

Velocity (in m/s) distribution inside 3D soil column



2D-COLUMN MODEL BASED ON HYDRAULIC PARAMETERS

The purpose of this model is to simulate the PFOA transport for various rheological properties i.e., hydraulic permeability, saturation curve, fluid compressibility, etc.



Water and dissolved PFOA transport equations in an unsaturated porous medium

$$\rho\left(S_e S_p + \frac{C_m}{\rho g}\right)\frac{\partial p}{\partial t} + \nabla(\rho u) = 0$$

$$u = -\frac{K}{\rho g}\nabla p$$

$$\frac{\partial(\varepsilon_p c_i)}{\partial t} + \frac{\partial(\rho c_{p,i})}{\partial t} + \nabla(D_D + D_e)\nabla c_i + u\nabla c_i = 0$$

Adsorption isotherm Langmuir

$$c_p = c_{p\max}\frac{K_L c}{1 + K_L c}$$

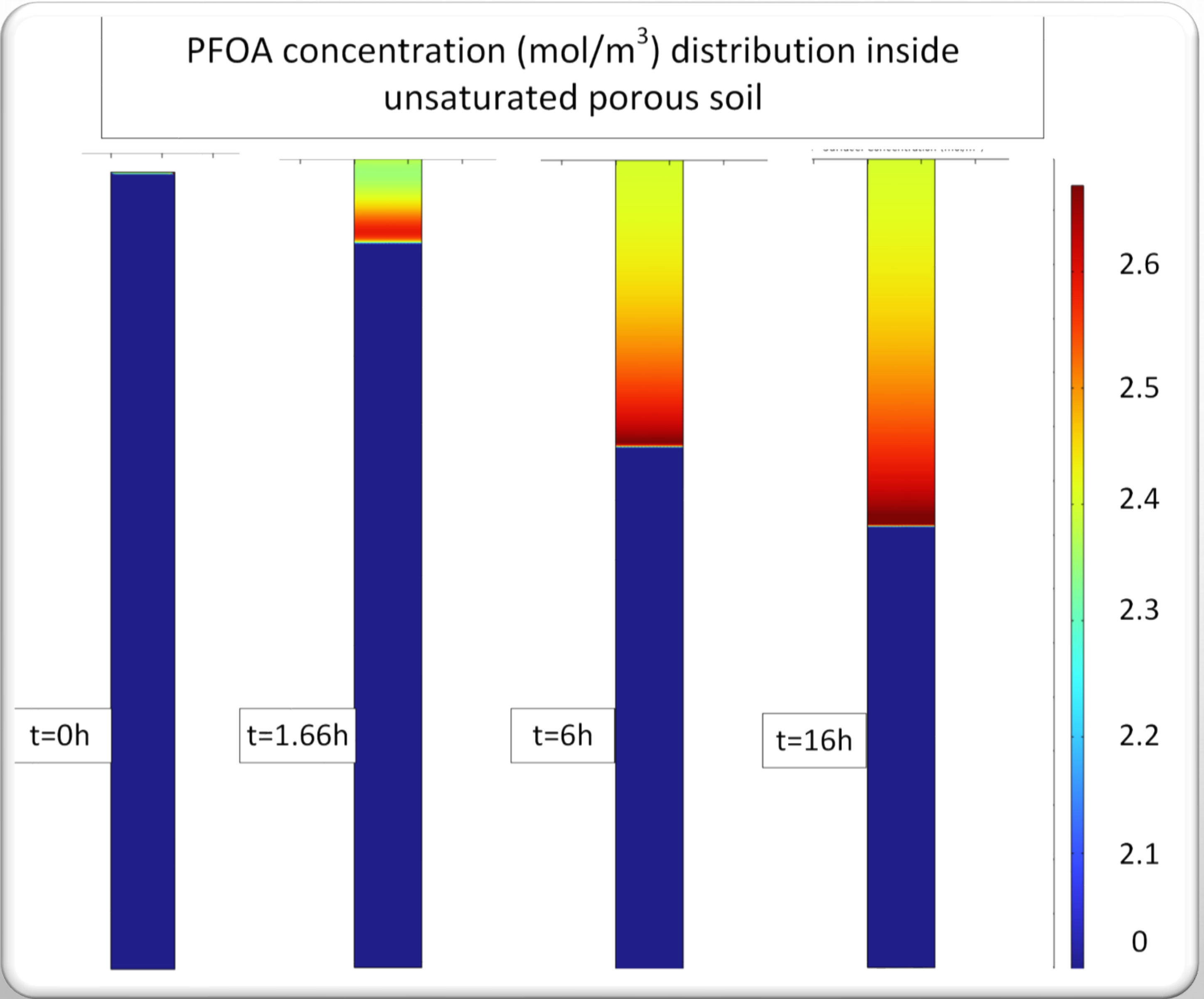
The link between 3D model and the 2D is the saturation term

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$$

$$K = K_s K_r S_e$$

Lists of Symbols

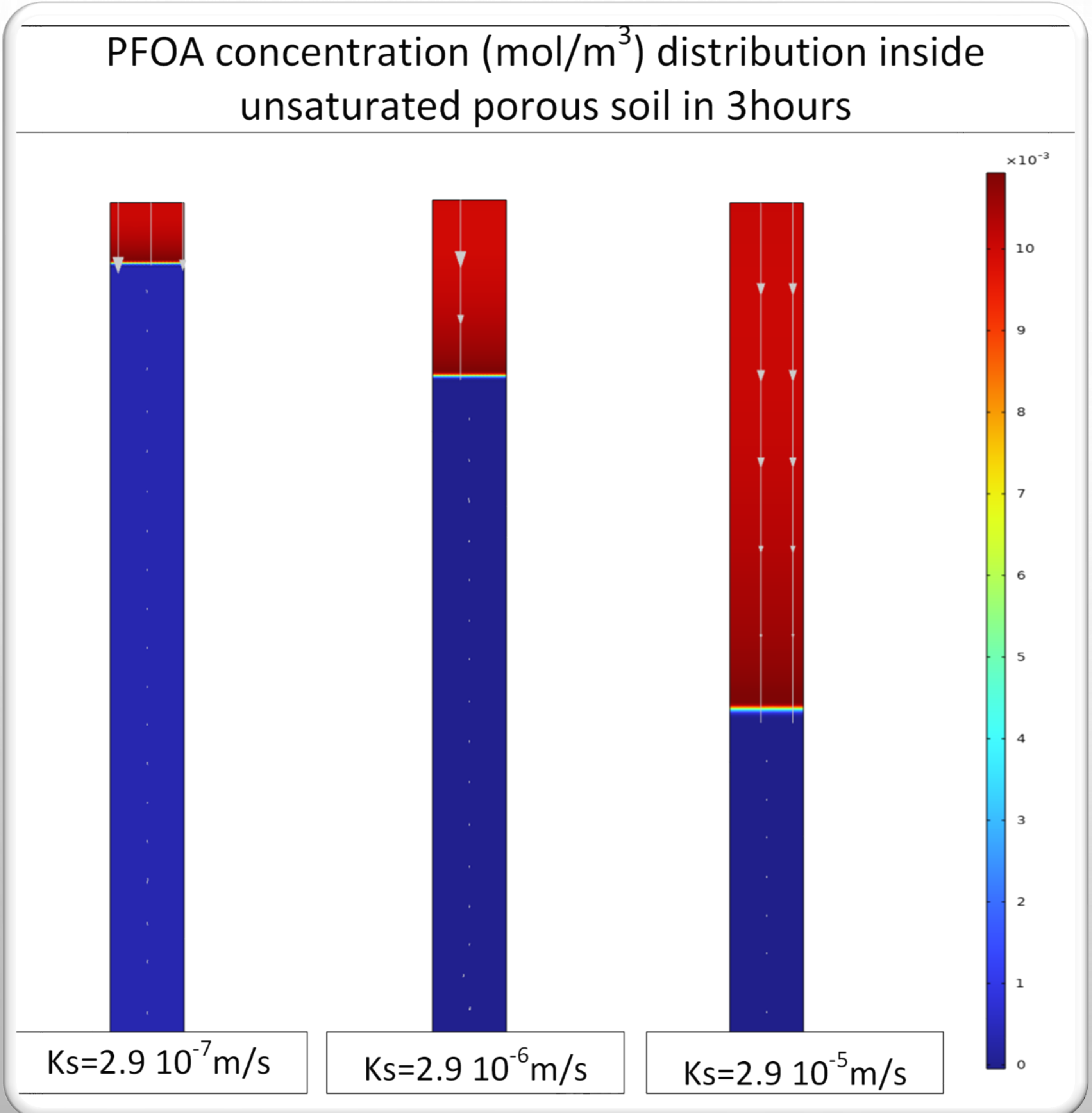
- ρ: fluid density
- S_e: effective saturation
- S_p: water storage
- ε_p: porosity
- u: Darcy velocity
- K: absolute permeability
- µ: dynamic viscosity
- P: pressure
- K_r: relative permeability
- K_s: hydraulic permeability
- θ: vol. water content
- θ_r: vol. residual water content
- θ_s: saturated vol. water content



VARIANCE OF PFOA CONCENTRATION

- input velocity u_0=3.4 10^{-5} m/s
- initial pfoa concentration c_0=2.4mol/m^3 or (1g/l)
- initial hydraulic permeability

  k_s=2.46 10^{-6} m/s
- dispersivity transverse α=10^{-5} m



DIFFERENT HYDRAULIC PERMEABILITIES AND POROSITIES

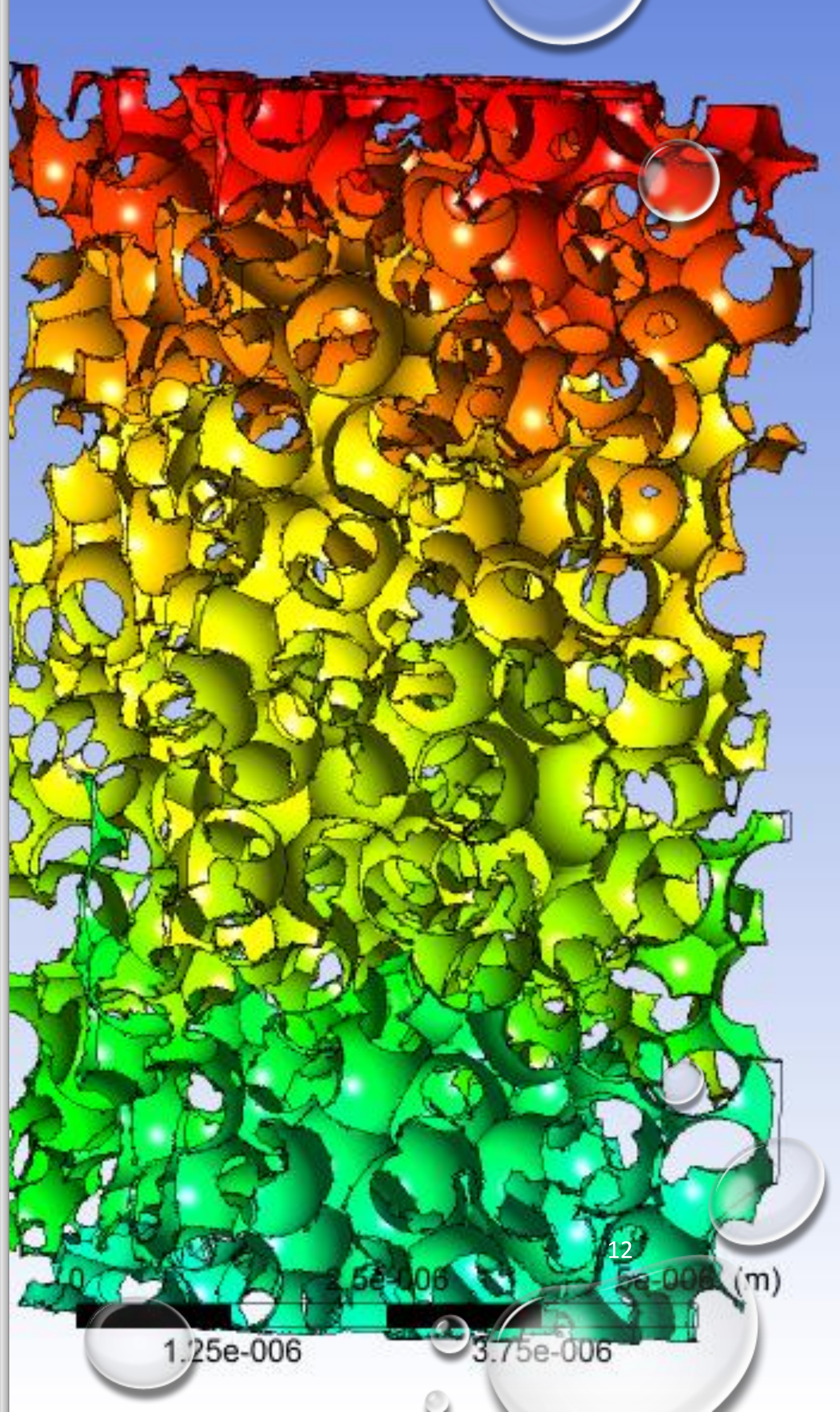
- input velocity u_0=3.4 10^{-5} m/s
- initial pfoa concentration c_0=2.4mol/m^3 or (1g/l)
- dispersivity transverse α=10^{-5} m

FUTURE WORK

- Calibration of the model based on experiments in column (surface tensions and contact angle with PFAS on the air/water interfaces, PFAS sorption parameters)

↓

- Field scale application



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COMSOL MULTIPHYSICS®: MODULE CFD (2PHASE FLOW INSIDE POROUS MEDIUM WITH SOME MODIFICATIONS)

ACKNOWLEDGMENTS

This project has received funding from the H2020 programme under Grant Agreement No. 101037509

SCENARIOS

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THANKS

Flow-rate dependency of gas/water relative permeabilities

Capillary numbers

$$Ca_w = \mu_w q_w / (A\gamma_{gw})$$

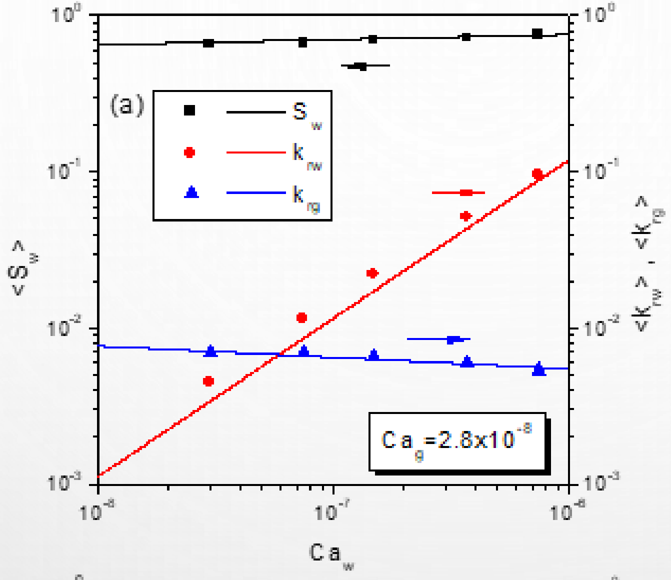
$$Ca_g = \mu_g q_g / (A\gamma_{gw})$$

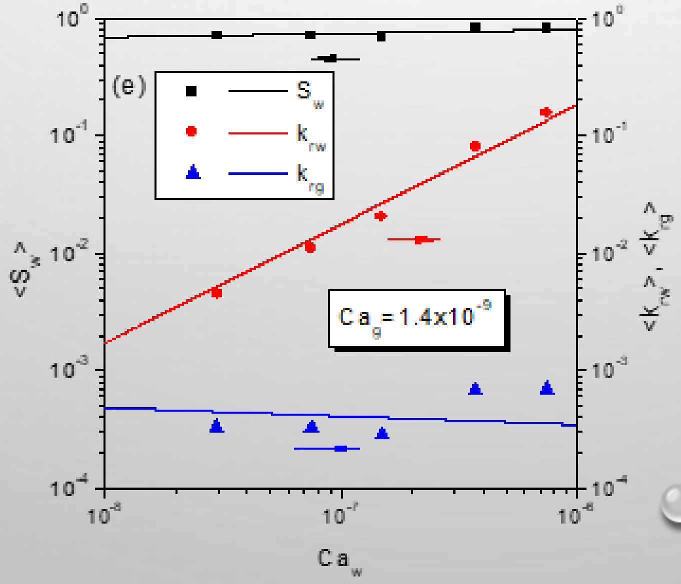
Power-law dependency

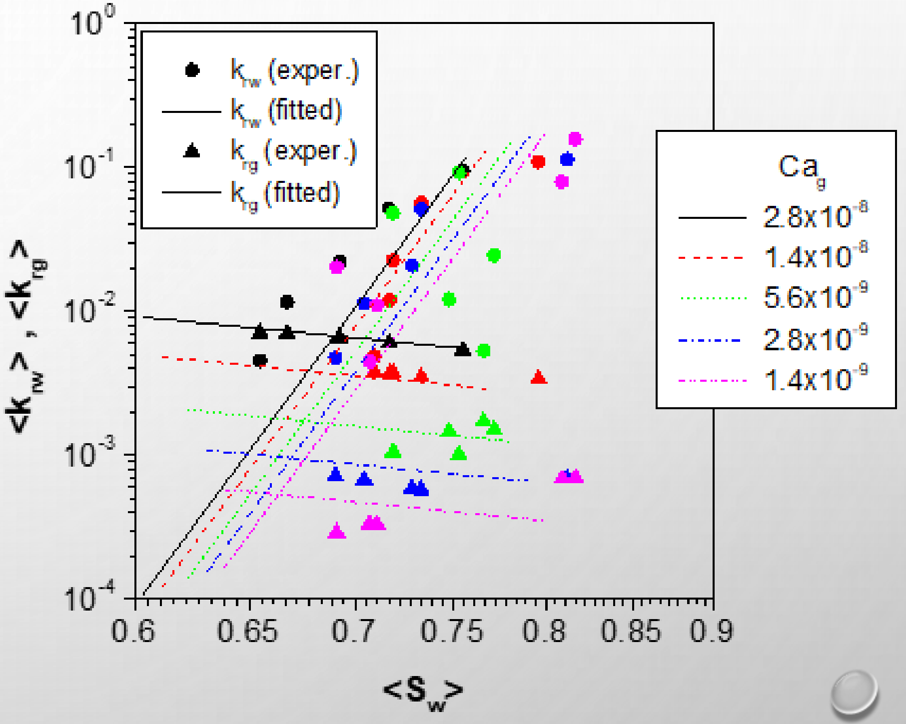
$$\langle k_{rg} \rangle = a_g Ca_w^{\,e_w} Ca_g^{\,e_g}$$

$$\langle k_{rw} \rangle = a_w Ca_w^{\,b_w} Ca_g^{\,b_g}$$

$$\langle S_w \rangle = a_s Ca_w^{\,c_w} Ca_g^{\,c_g}$$







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