Appendix 6.1
PFAS: Definitions, deposition and sorption to the air-water interface

1 Introduction

The fate of Per- and Polyfluoroalkyl Substances (PFAS) above and below ground can be simulated by Daisy, as of Daisy 7.1. This appendix describes the definition of PFAS in Daisy (section 2), how these can be added to the system (section 3), and sorption to the air-water interface (section 4). The focus is on a key subgroup of PFAS, perfluoroalkyl acids (PFAAs), which are known for their high persistence in the environment and surface-active properties. The transport of PFAS is modelled in Daisy the same way as other solutes, as described in Chapter 6 'Solute Transport'. Thus, for common functions for solute transport, we refer to Chapter 6 for further details.

2 Defining PFAS

The file 'PFAS.dai' in the "lib" folder distributed with Daisy includes parameterizations of selected PFAS.

First, PFAS is defined as a group with common properties for all PFAS. This group is based on the default chemical parent group, and if nothing else is defined, it inherits the default parameters (see Chapter 6, section 2). The defined PFAS compounds are assumed to be stable (i.e., the final degradation products), so the decomposition rate is zero. Dissipation from the canopy is also zero (due to their low volatility), and everything is washed off the canopy, with no retention on the leaf surface. Although some PFAS can be taken up by plants, the current modelling work has only focused on transport and adsorption processes. Therefore, plant uptake is not included in this example. Based on the common PFAS parameterization, individual PFAS compounds are defined. This requires compound-specific adsorption models, which are explained in section 4.

Defining PFAS as a group (base):

```
(defchemical PFAS default
  (decompose_rate 0.0 [h^-1]) ; not degraded (stable)
  (canopy_dissipation_rate 0.0 [h^-1]) ; no canopy dissipation
  (canopy_washoff_coefficient 1.0 []) ; all is washed off
  (crop_uptake_reflection_factor 1.0 [])) ; not taken up
```

3 Adding PFAS to the field

PFAS can be added to the field via irrigation water, using the spray function, or as wet deposition. These functions are described in Chapter 11 'System management model'. The following gives some examples of how to add PFAS as wet deposition, as PFAS-contaminated pig slurry, and as PFAS-contaminated irrigation water. These examples can also be found in 'PFAS-sample.dai' in the "sample" folder distributed with Daisy.

In Daisy, a fixed chemical concentration in precipitation (rain and snow) can be defined for individual chemicals, along with the specific period during which this concentration is applied. In the example below, two periods are defined: *high* with a concentration of $1 \cdot 10^5$ ppm between 1950 and 2000 and *low* with concentration of $1 \cdot 10^{-6}$ ppm between 2000 and 2050 for four different PFAS compounds. The PFAS deposition is added to the simulated soil column under the *Bioclimate* module. In the example below, the depositions by *high* and *low* are combined with the wet and dry deposition of N given in the weather file (See Chapter 2 and 7) by adding *&old.* Alternatively, it can be added as (Bioclimate original (deposition weather high low)).

```
(defdeposition high const
   (before 2000 1 1)
   (after 1950 1 1)
   (wet
   (PFOS 1e-5 [ppm])
   (PFOA 1e-5 [ppm])
   (PFHxA 1e-5 [ppm])
   (PFBA 1e-5 [ppm])))

(defdeposition low const
    (before 2050 1 1)
    (after 2000 1 1)
    (wet
    (PFOS 1e-6 [ppm])
    (PFOA 1e-6 [ppm])
    (PFHxA 1e-6 [ppm])
    (PFBA 1e-6 [ppm])))

(defcolumn Sand Jyndevad
   "A sand soil with free drainage."
   (Chemistry original  (combine PFAS &old))
   (AWI Brusseau2023) ; default
   (Bioclimate original (deposition high low &old)))
```

4 Adsorption models

Individual PFAS compounds can be defined, inheriting all the base parameters defined from the group definition *PFAS*. For each compound, adsorption to the soil is specified. As with other solutes in Daisy, PFAS adsorption can be modelled using the *Linear, Freundlich,* or *Langmuir* isotherms, and requires sorption parameters K_{OC} or K_{clay}. Additionally, adsorption to the air-water interface (AWI) can be added. For compounds with high surface activity, this extra retention mechanism may result in significant retention in the unsaturated zone (Brusseau et al., 2019). Its contribution is calculated by adding an extra term to the linear sorption model (Eq 1):

$$M = \rho_s \cdot K_{ld} \cdot C + \theta \cdot C + A_{AWI} \cdot K_{AWI} \cdot C \qquad \text{(Eq. 1)}$$

Where

M = the chemical mass per volume of water, soil, and air at equilibrium [g cm^{-3}],

C = the chemical equilibrium soil water concentration [g cm^{-3}],

ρ_s = the soil bulk density [g cm^{-3}],

K_{ld} = the soil distribution coefficient [cm^3 g^{-1}],

θ = the volumetric water content [ ].

A_{AWI} = the area of the air-water-interface [cm^2 cm^{-3}], and

K_{AWI} = the distribution coefficient between soil water and the air-water interface at equilibrium [cm^2 cm^{-3}].

The last two parameters are new and described in detail below. This model assumes the chemicals reach instant equilibrium at each time step.

4.1 Air-water interface distribution coefficient K$_{AWI}$

There are two methods to define the air-water interface distribution coefficient, K_{AWI}. If not defined, K_{AWI} is by default zero. The first method is to define K_{AWI} as a constant parameter using the *linear* model, see example below.

```
(defchemical PFOS PFAS
  (molar_mass 550.13 [g/mol])
  (diffusion_coefficient 5.27e-6 [cm^2/s])
  (adsorption linear
    (K_AWI 1.51e-2 [cm^3/cm^2])
    (K_OC 606 [ml/g])
    (K_clay 54 [ml/g])))
```

The second method is using the adsorption model *Guo2020* (Eq. 2). In this model, K_{AWI}, is calculated as a function of concentration and temperature, and requires the compound *molar mass* and surface tension data a and b (Guo et al., 2020):

$$K_{AWI} = \frac{\sigma_0 b}{RT\left(\frac{C}{M} + a\right)} \qquad \text{(Eq. 2)}$$

Where

R = the universal gas constant = 8.3145 [J K^{-1} mol^{-1}],

σ_0 = the surface tension in pure water = 7.28·10^{-6} [J cm^{-2}],

T = temperature [K],

M = the molar mass of the compound [g/mol] and

a [molcm^{-3}] and b [-] are fitting parameters in the Szyszkowski equation (Brusseau and Van Glubt, 2021; Szyszkowski, 1908) and are compound-specific. The *Guo2020* model is applied in Daisy as:

```
(defchemical PFOS_Guo PFOS
  (adsorption Guo2020
    (a 3.4e-03 [umol/cm^3])
    (b 0.107 [])))
```

Below a certain concentration of PFAS, K_{AWI} defined by the *Guo2020* model approaches a maximum limit. This concentration is often many magnitudes lower than found in the environment; thus, it is reasonable to assume a constant K_{AWI} when simulating PFAS transport from diffuse contamination (Brusseau, 2021). However, when simulating point source contamination of PFAS, Eq. 2 may be relevant.

PFOS content in two soil profiles (JB1 and JB7, according to the Danish soil classification) was simulated for 10 years with three different input concentrations, using the two methods to estimate K_{AWI} (Figure 4.1).

K_{AWI} = 9.73 $\cdot 10^{-2}$ cm^3 cm^{-2} was used for the *linear* model, and a = 3.4$\cdot 10^{-3}$ μmol cm^{-3} and b = 0.107 were used in the *Guo2020* model (Guo et al, 2020). The PFOS input concentrations in precipitation were: 1 ng L^{-1}, 1 μg L^{-1}, and 1 mg L^{-1}, respectively. At the highest input level (1 mg L^{-1}), the two methods to estimate K_{AWI} yield slightly different results for the JB1 soil profile, as indicated by differences between the dark blue and dark orange curves. At the lower input concentrations, K_{AWI} was constant, and there was no difference between the two methods.
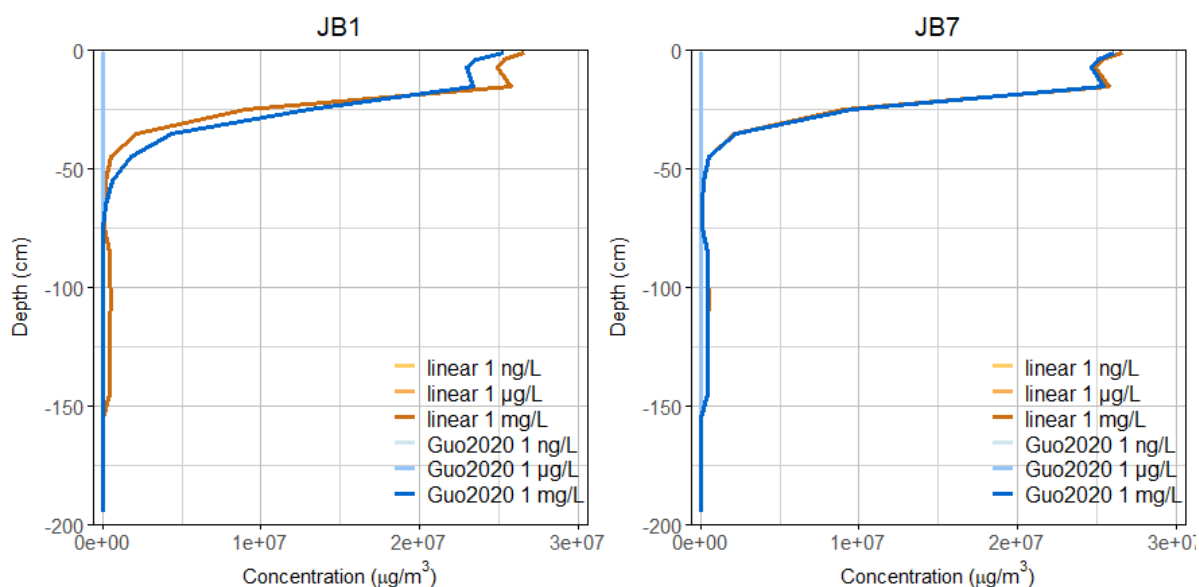

Figure 4.1: The PFOS distribution in the soil profile of a JB1 and JB6 soil, after 10 years of atmospheric deposition with different precipitation concentration as input (1 ng/L, 1 ug/L, 1 mg/L), using two methods to model K$_{awi}$: Guo2020 or linear.

4.2 Air-water interface area (A$_{AWI}$)

In Daisy, there are two methods to estimate the air-water interface area, A_{AWI}: *Costanza2008x* or *Brusseau2023* (default) (Brusseau, 2023; Costanza-Robinson et al., 2008).

Which model to use is defined when parameterizing the column, see example below:

```
(defcolumn Jyndevad default
  (Chemistry original (combine PFAS &old))
  (AWI Costanza2008x)
  ;; Or
  (AWI Brusseau2023) ;; default
```

Brusseau2023 is an empirical model (Eq. 3) calculated as a function of relative water saturation and median grain size d_{50} [cm], and it is also referred to as "the corrected AQITT-based linear method", taking the particle surface roughness into account (Brusseau, 2023). This model is developed based on a training set consisting of three different media: Vinton soil (97% sand, 1.8% silt, 1.2% clay), 0.35 mm sand, and 1.2 mm sand.

$$A_{AWI} = \left(-2.85 \cdot \frac{\theta}{\theta_{sat}} + 3.6\right)\left(\left(1 - \frac{\theta}{\theta_{sat}}\right) \cdot 3.9 \cdot d_{50}^{-1.2}\right) \tag{Eq. 3}$$

Where

θ = the volumetric water content [cm^3 cm^{-3}],

θ_{sat} = the saturated water content [cm^3 cm^{-3}] and

d_{50} = the median grain size [cm], calculated as shown in Figure 4.2

Constanza2008x is based on X-ray microtomography measurements; thus, measured air-water interfaces are equivalent to smooth-surface areas (Brusseau, 2023), and consequently, the model assumes that all particles have a smooth surface area (Costanza-Robinson et al., 2008).

$$A_{AWI} = 6 \cdot \frac{(1 - \theta_{sat})}{d_{50}} \cdot \left(0.9031 - 0911 \cdot \frac{\theta}{\theta_{sat}}\right) \tag{Eq. 4}$$

The median grain size d_{50} is calculated from soil texture. The cumulative mass is calculated and plotted against the corresponding particle sizes on a semi-logarithmic scale (Figure 4.2). The value of d_{50} is determined by identifying the particle diameter at which 50 % of the sample mass is finer (orange point).

Texture class	Clay (> 2 µm)	Fine silt (2-20 µm)	Coarse silt (20-63 µm)	Fine sand (63-200 µm)	Coarse sand (200-2000 µm)
Amount (%)	4.6	1.2	2.8	23.9	67.5

Table 4.1: Particle size distribution of Jyndevad Ap from which d_{50} is calculated.
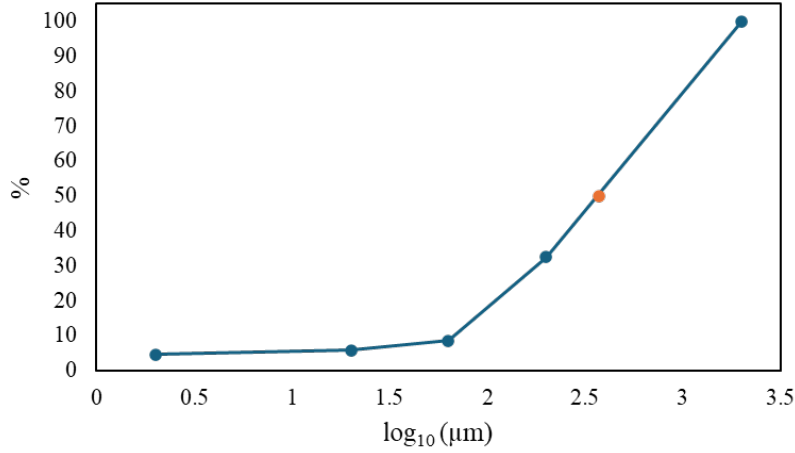
Figure 4.2: d$_{50}$ is determined as the particle diameter at which 50% (by mass) of the sample consists of particles of that size or smaller.

The air-water interface area, A_{AWI}, calculated for a JB7 and JB1 soil using the *Brusseau2023* model (blue line) or the *Constanza2008x* model (orange line) at different relative saturation levels is shown in Figure 4.3. For both soils, the estimated A_{AWI} is higher at unsaturated conditions when using *Brusseau2023* compared to *Constanza2008x*, and the difference is more pronounced in the finer textured JB7 soil, compared to the sandy JB1 soil.
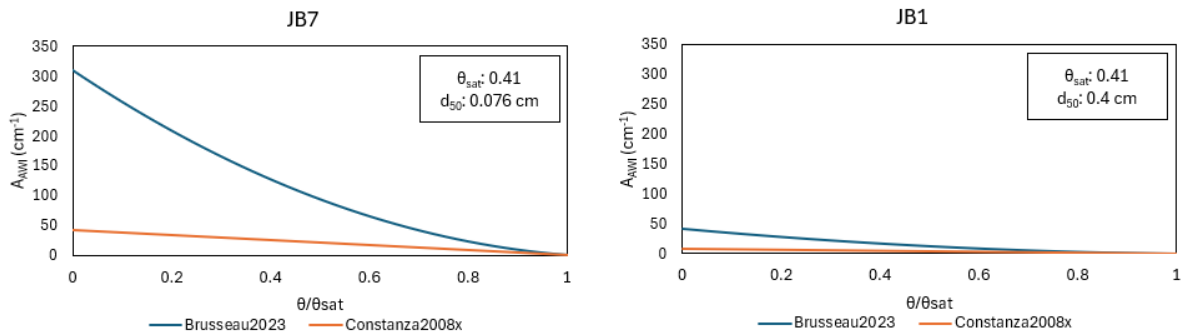

Figure 4.3: Calculated A$_{AWI}$ as a function of relative water saturation using the two methods Brusseau2023 and Constanza2008x, in a JB7 and JB1 soil.

5   Parameter overview

Name and explanation		Model (in Daisy)	Parameter name (Daisy reference manual)	Default	Default unit
K$_{AWI}$	Air-water interface distribution coefficient	linear	*K_AWI*	0	[cm^3 cm^{-2}]
a	Fitting parameter in the Szyszkowski Equation	Guo2020	*a*	User specified	[μmol cm^3]
b	Fitting parameter in the Szyszkowski Equation	Guo2020	*b*	User specified	[ ]

M	Molar mass	Guo2020	*molar_mass*	User specified	[g/mol]

Original text from	New text	
Updated by	Date	For Daisy version
Jakobsen, C.	2025 06 24	7.1.0

6 References

Brusseau, M.L., 2023. Determining air-water interfacial areas for the retention and transport of PFAS and other interfacially active solutes in unsaturated porous media. Sci. Total Environ. 884, 163730. https://doi.org/10.1016/j.scitotenv.2023.163730

Brusseau, M.L., 2021. Examining the robustness and concentration dependency of PFAS air-water and NAPL-water interfacial adsorption coefficients. Water Res. 190, 116778. https://doi.org/10.1016/j.watres.2020.116778

Brusseau, M.L., Van Glubt, S., 2021. The influence of molecular structure on PFAS adsorption at air-water interfaces in electrolyte solutions. Chemosphere 281, 130829. https://doi.org/10.1016/j.chemosphere.2021.130829

Brusseau, M.L., Yan, N., Van Glubt, S., Wang, Y., Chen, W., Lyu, Y., Dungan, B., Carroll, K.C., Holguin, F.O., 2019. Comprehensive retention model for PFAS transport in subsurface systems. Water Res. 148, 41–50. https://doi.org/10.1016/j.watres.2018.10.035

Costanza-Robinson, M.S., Harrold, K.H., Lieb-Lappen, R.M., 2008. X-ray Microtomography Determination of Air–Water Interfacial Area–Water Saturation Relationships in Sandy Porous Media. Environ. Sci. Technol. 42, 2949–2956. https://doi.org/10.1021/es072080d

Guo, B., Zeng, J., Brusseau, M.L., 2020. A Mathematical Model for the Release, Transport, and Retention of Per- and Polyfluoroalkyl Substances (PFAS) in the Vadose Zone. Water Resour. Res. 56, e2019WR026667. https://doi.org/10.1029/2019WR026667

Szyszkowski, B., 1908. Experimentelle Studien über kapillare Eigenschaften der wässerigen Lösungen von Fettsäuren. Z. Für Phys. Chem. 64, 385–414.