



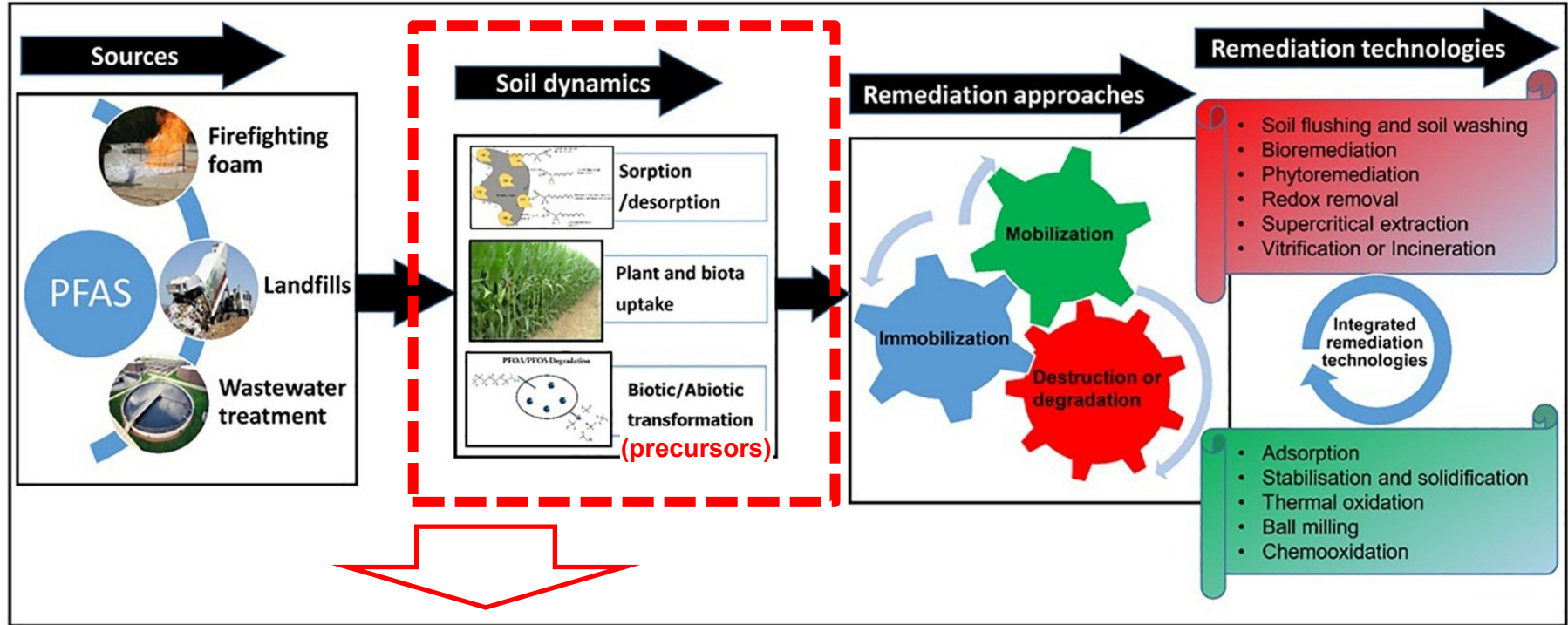
# PFAS SORPTION MECHANISMS

## Migration risk assessment: principles

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# PFAS: from source to remediation technologies



Migration risks?: SOURCE-PATH-RECEPTOR ANALYSIS

(Bolan et al., 2021)

## Determination of migration speed – distribution coefficient solid-liquid

$$K_d = C_s / C_l$$

$C_s$  = conc. sorbed (kg/kg soil)

$C_l$  = conc. in solution (kg/L solution)

Retardation due to sorption:

$$R = 1 + \rho_b K_d / n$$

$\rho_b$  = soil bulk density (kg/m<sup>3</sup>)

$n$  = total porosity

Groundwater velocity (Darcy)  $v_x = K_h \cdot i \cdot 1/n_e$

Migration velocity of the pollutant  $v = v_x / R$

With  $K_h$  the hydraulic conductivity (m/d);  $i$  the groundwater gradient (m/m) and  $n_e$  the effective porosity

Frequently used for **organic compounds**:

$$K_d = K_{oc} \cdot f_{oc}$$

$K_{oc}$  = distribution coeff. org. matter / water

$f_{oc}$  = fraction organic carbon in soil

$$f_{oc} = 0,0058 \cdot OM (\%)$$

OM = soil organic matter (in %)

**“TOETSINGSWAARDEN VOOR PFOS EN PFOA IN BODEM EN VOOR PFAS IN GRONDWATER - AANVULLING BIJ BASISINFORMATIE VOOR RISICO-EVALUATIES” (OVAM - 4 APRIL 2022):**

**PFOS:**  $\log K_{oc} = 2.57$  L/kg ( $K_{oc} = 371$ )

**PFOA:**  $\log K_{oc} = 2.06$  L/kg ( $K_{oc} = 114,82$ )

## **HOWEVER: PFAS not only “organic” but also (an)ionic and surfactant!**

- **Calculating Kd from Koc** therefore is not **correct**
- PFAS also sorb to **positively charged soil constituents** – e.g. amorphous or (micro-)crystalline iron and aluminium (hydr)oxides and/or clay/humic complexes
- In the unsaturated zone, PFAS “sorb” to the **water-air interphase**
- Kd’s in the saturated zone can be experimentally determined in labtest (column or batch)
- Alternatively, measured groundwater concentrations in monitoring wells can be used with measured soil concentration at filter depth
- Or Kd’s (ranges!) can be taken from literature
- NB!: (1) every single PFAS compound has **its own Kd**;  
(2) **spatial variability of Kd’s** thus of R’s



(Concawe 2021)												
Name	Acronym	CAS Registry Number	Molecular Formula	Molecular Weight [g/mol]	Water Solubility <sup>b</sup> (20 - 25 °C) [g/L]	Melting Point <sup>c</sup> [°C]	Boiling Point <sup>c</sup> [°C]	Vapor Pressure <sup>b</sup> [Pa]	Henry-Coefficient [Pa·m <sup>3</sup> ·mol <sup>-1</sup> ]	log Kow <sup>b</sup> [-]	log K <sub>oc</sub> [L/kg]	K <sub>d</sub> (pH 7)
<b>Perfluoroalkyl Carboxylates / Perfluoroalkyl Carboxylic Acids</b>	<b>PFCAs</b>											
Perfluorobutanoic Acid	PFBA	375-22-4	F(CF <sub>2</sub> ) <sub>3</sub> COOH	214.04	Miscible	-17.5	121	1307	--	2.82	1.88	--
Perfluoropentanoic Acid	PFPeA	2706-90-3	F(CF <sub>2</sub> ) <sub>4</sub> COOH	264.05	112.6	--	124.4	1057	--	3.43	1.37	--
Perfluorohexanoic Acid	PFHxA	307-24-4	F(CF <sub>2</sub> ) <sub>5</sub> COOH	314.05	21.7	14	143	457	--	4.06	1.91	--
Perfluoroheptanoic Acid	PFHpA	375-85-9	F(CF <sub>2</sub> ) <sub>6</sub> COOH	364.06	4.2	30	175	158	--	4.67	2.19	0.4 - 1.1
Perfluorooctanoic Acid	PFOA	335-67-1	F(CF <sub>2</sub> ) <sub>7</sub> COOH	414.07	3.4 - 9.5	37 - 60	188 - 192	4 - 1300	0.04 - 0.09	5.30	1.31 - 2.35	0 - 3.4
Perfluorononanoic Acid	PFNA	375-95-1	F(CF <sub>2</sub> ) <sub>8</sub> COOH	464.08	9.50	59 - 66	218	1.3	--	5.92	2.39	2.6 - 5.9
Perfluorodecanoic Acid	PFDA	335-76-2	F(CF <sub>2</sub> ) <sub>9</sub> COOH	514.09	9.50	77 - 88	218	0.2	--	6.50	2.76	2.0 - 31
Perfluoroundecanoic Acid	PFUnA	2058-94-8	F(CF <sub>2</sub> ) <sub>10</sub> COOH	564.09	0.004	83 - 101	160 - 230	0.1	--	7.15	3.30	12 - 103
Perfluorododecanoic Acid	PFDoA	307-55-1	F(CF <sub>2</sub> ) <sub>11</sub> COOH	614.10	0.0007	107 - 109	245	0.01	--	7.77	--	24 - 269
Perfluorotridecanoic Acid	PFTTrA	72629-94-8	F(CF <sub>2</sub> ) <sub>12</sub> COOH	664.11	0.0002	--	--	0.3	--	8.25	--	--
Perfluorotetradecanoic Acid	PFTeDA	376-06-7	F(CF <sub>2</sub> ) <sub>13</sub> COOH	714.12	0.00003	--	276	0.1	--	8.90	--	--
Perfluoropentadecanoic Acid	PFPeDA	141074-63-7	F(CF <sub>2</sub> ) <sub>14</sub> COOH	764.12	--	--	--	--	--	--	--	--
Pentadecafluorooctanoic Acid Ammonium Salt (Ammonium Pentadecafluorooctanoate)	APFO	3825-26-1	C <sub>8</sub> H <sub>4</sub> NF <sub>15</sub> NO <sub>2</sub>	445.11	14.2	157 - 165	--	0.01	--	--	--	--
<b>Perfluoroalkyl Sulfonates / Perfluoroalkyl Sulfonic Acids</b>	<b>PFSAs</b>											
Perfluorobutane Sulfonate	PFBS	375-73-5	F(CF <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> H	300.10	46.2 - 56.6	76 - 84	211	631	--	3.90	1.00	--
Perfluorohexane Sulfonate	PFHxS	432-50-8	F(CF <sub>2</sub> ) <sub>6</sub> SO <sub>3</sub> H	400.11	2.3	--	--	58.9	--	5.17	1.78	0.6 - 3.2
Perfluoroheptane Sulfonate	PFHpS	357-92-8	F(CF <sub>2</sub> ) <sub>7</sub> SO <sub>3</sub> H	450.12	--	--	--	--	--	--	--	--
Perfluorooctane Sulfonate	PFOS	1763-23-1	F(CF <sub>2</sub> ) <sub>8</sub> SO <sub>3</sub> H	500.13	0.52 - 0.57	54	> 400	6.7	<2e-6 to 3e-4	6.43	2.5 - 3.1	0.1 - 97
Perfluorodecane Sulfonate	PFDS	333-77-3	F(CF <sub>2</sub> ) <sub>10</sub> SO <sub>3</sub> H	600.14	0.002	--	--	0.71	--	7.66	3.53	--
<b>Perfluoroalkyl Phosphonic Acids</b>	<b>PFPA</b>											
Perfluorobutyl Phosphonic Acid	PFBPA	52299-24-8	F(CF <sub>2</sub> ) <sub>4</sub> P(O)(OH) <sub>2</sub>	350.02	14259.1	--	--	0.18	--	2.19	--	--
Perfluorohexyl Phosphonic Acid	PFHxPA	40143-76-8	F(CF <sub>2</sub> ) <sub>6</sub> P(O)(OH) <sub>2</sub>	400.03	515.3	--	--	0.04	--	3.48	--	--
Perfluorooctyl Phosphonic Acid	PFOPA	40143-78-0	F(CF <sub>2</sub> ) <sub>8</sub> P(O)(OH) <sub>2</sub>	500.05	24.5	--	--	0.01	--	4.73	--	--
Perfluorodecyl Phosphonic Acid	PFDPA	52299-26-0	F(CF <sub>2</sub> ) <sub>10</sub> P(O)(OH) <sub>2</sub>	600.06	0.5	--	--	0.0002	--	5.98	--	--
<b>Perfluorooctane Sulfonamide and Derivatives</b>												
Perfluorooctane Sulfonamide	PFOSA	754-91-6	F(CF <sub>2</sub> ) <sub>8</sub> SO <sub>2</sub> NH <sub>2</sub>	499.14	-	154 - 155	--	--	--	-	2.5 - 2.62	35 - 56
Perfluorooctane Sulfonamidoethanol	FOSE	10116-92-4	F(CF <sub>2</sub> ) <sub>8</sub> SO <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> OH	543.19	0.0009	--	--	0.00	--	5.78	--	--
N-Methyl-Perfluorooctane Sulfonamide	N-MeFOSA	31506-32-8	F(CF <sub>2</sub> ) <sub>8</sub> SO <sub>2</sub> NHCH <sub>3</sub>	513.17	0.0002	--	--	0.30	--	6.07	3.14	--
N-Ethyl-Perfluorooctane Sulfonamide	N-EtFOSA	4151-50-2	F(CF <sub>2</sub> ) <sub>8</sub> SO <sub>2</sub> NHCH <sub>2</sub> CH <sub>3</sub>	527.20	0.0001	--	--	0.12	--	6.71	3.23	--
N-Methyl-Perfluorooctane Sulfonamidoethanol	N-MeFOSE	24448-09-7	F(CF <sub>2</sub> ) <sub>8</sub> SO <sub>2</sub> N(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> OH	557.22	0.0003	--	--	0.0004	--	6.00	--	--
N-Ethyl-Perfluorooctane Sulfonamidoethanol	N-EtFOSE	1691-99-2	F(CF <sub>2</sub> ) <sub>8</sub> SO <sub>2</sub> N(CH <sub>2</sub> CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> OH	571.25	0.0001	55 - 60	--	0.002	--	6.52	--	--

## In the unsaturated zone PFAS stick to the **water-air interphase**

- The **retardation coefficient R** thus becomes:
- **$R = 1 + \rho_b K_d/n + K_{aw} A_{aw}/n$**  with  $A_{aw}$  : air-water surface area per unit soil volume ( $\text{m}^2/\text{m}^3$ )

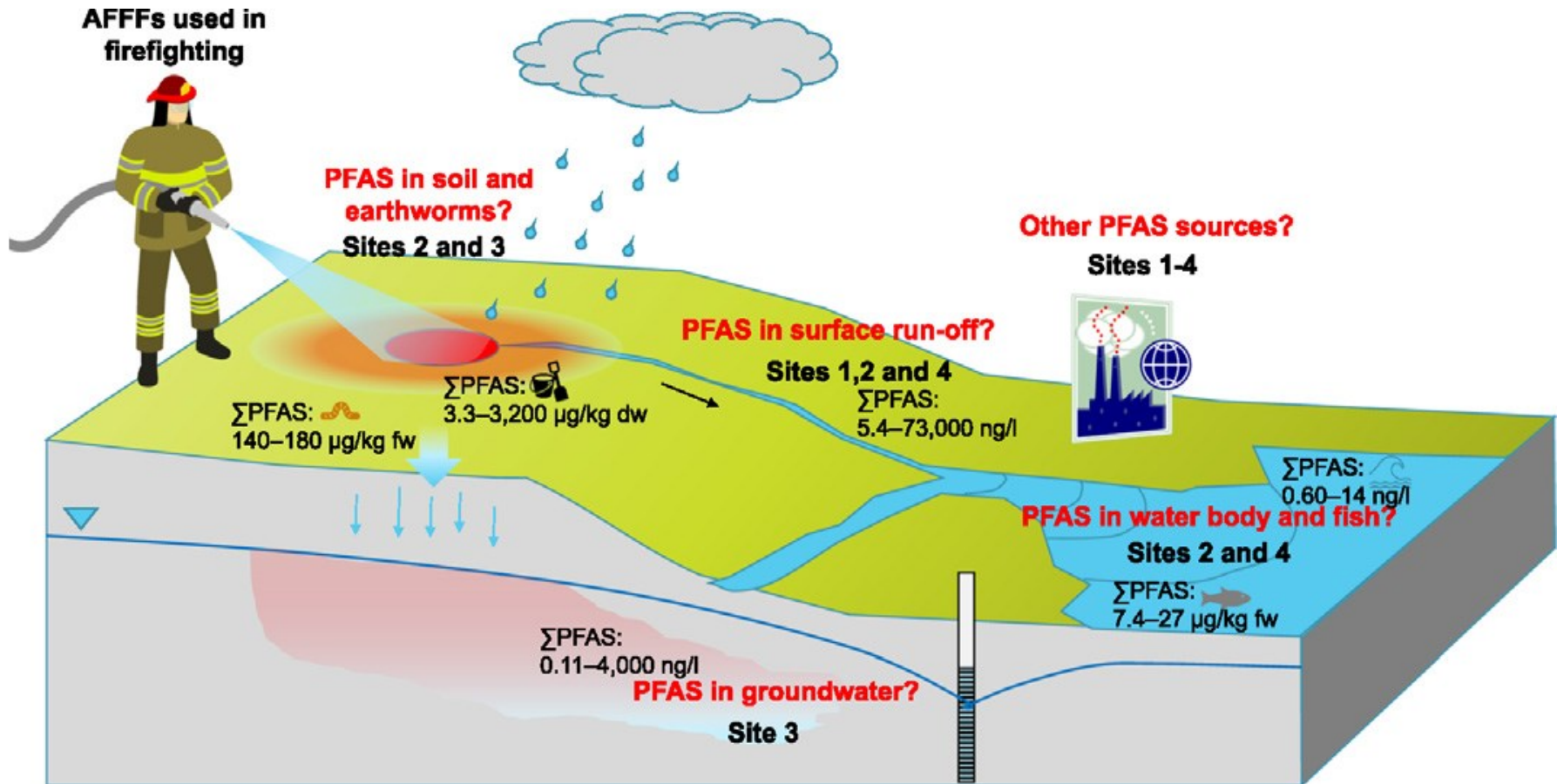
$A_{\max}$  = specific surface area of dry bulk soil ( $\text{m}^2/\text{m}^3$ )

And:  $A_{aw} = A_{\max} (1 - S)$        $S$  = fraction of water filled pores

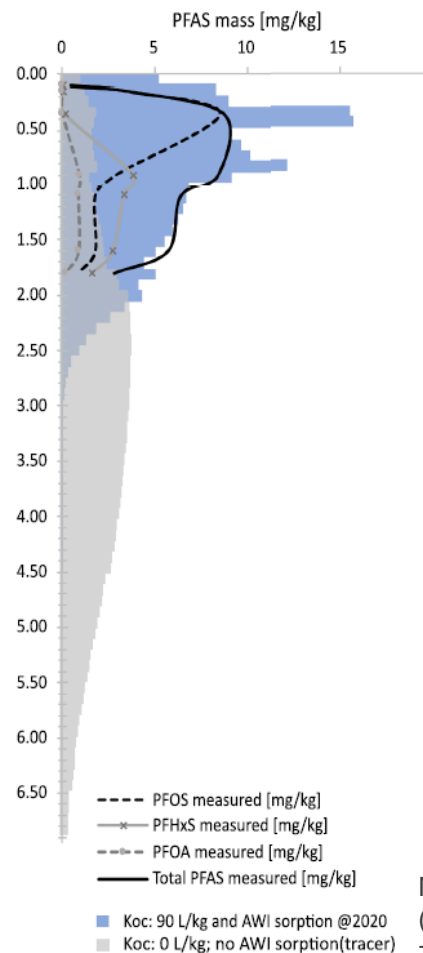
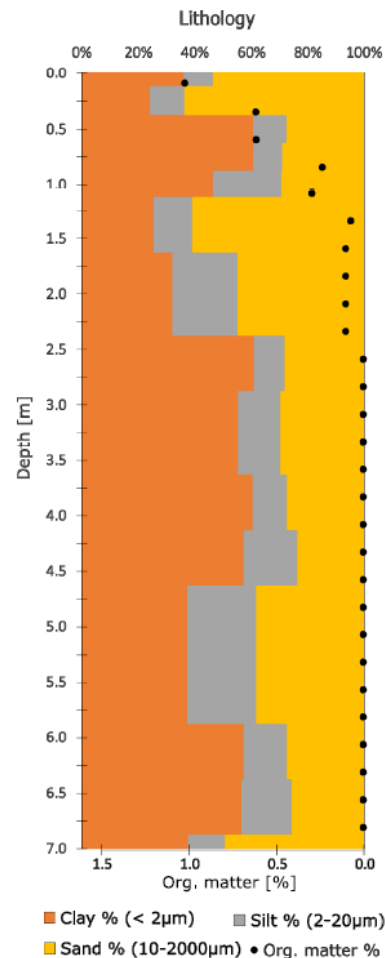
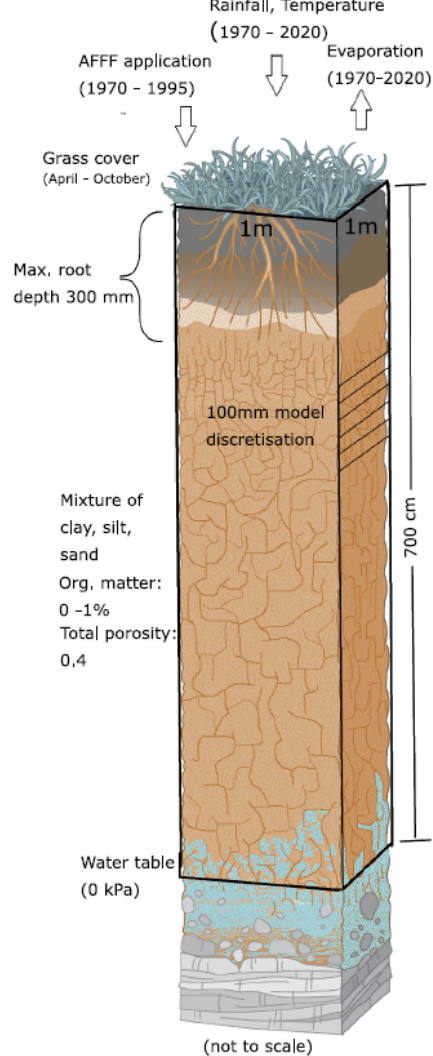
- **Surface coverage (recharge)? Precipitation amount/frequency? Plants (evapotranspiration)?**
- **“Measure to know”**: e.g. median lab-measured  $K_d$ ’s for PFOS, PFOA, PFHxS and PFHxA were 15.49 – 1.48 – 0.95 and 0.26 L/kg, respectively (Li *et al.*, 2018).
- **Also**: compare plume length and age of the pollution source: further migration speed can then be extrapolated

- All sorption characteristics are determined by PFAS-type / chain length, ionic strength, pH, valence of cations present, temperature,...
- If **NAPL is present** (oils, CAHs), PFAS can also accumulate at the water/NAPL and air/NAPL interphases
- PFAS can migrate when attached to **mobile soil particles/colloids**
- PFAS can migrate through **superficial runoff** (unpaved surfaces)
- **NB:** (unknown) **PFAS-precursors** may be present that are biotransformed to stable PFAS during transport in the groundwater plume, complicating concentration trend analysis!



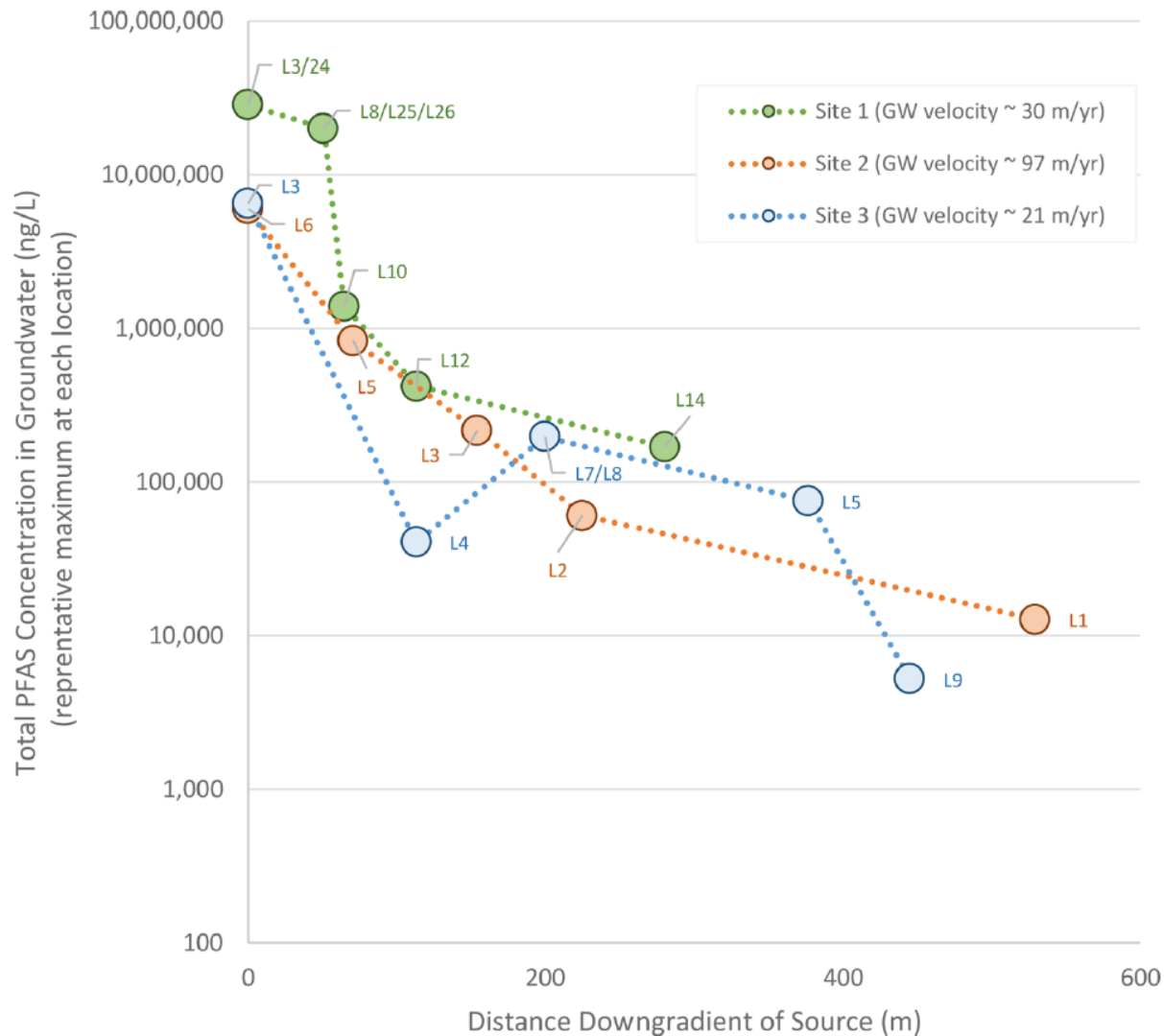


(Reinikainen et al., 2022)

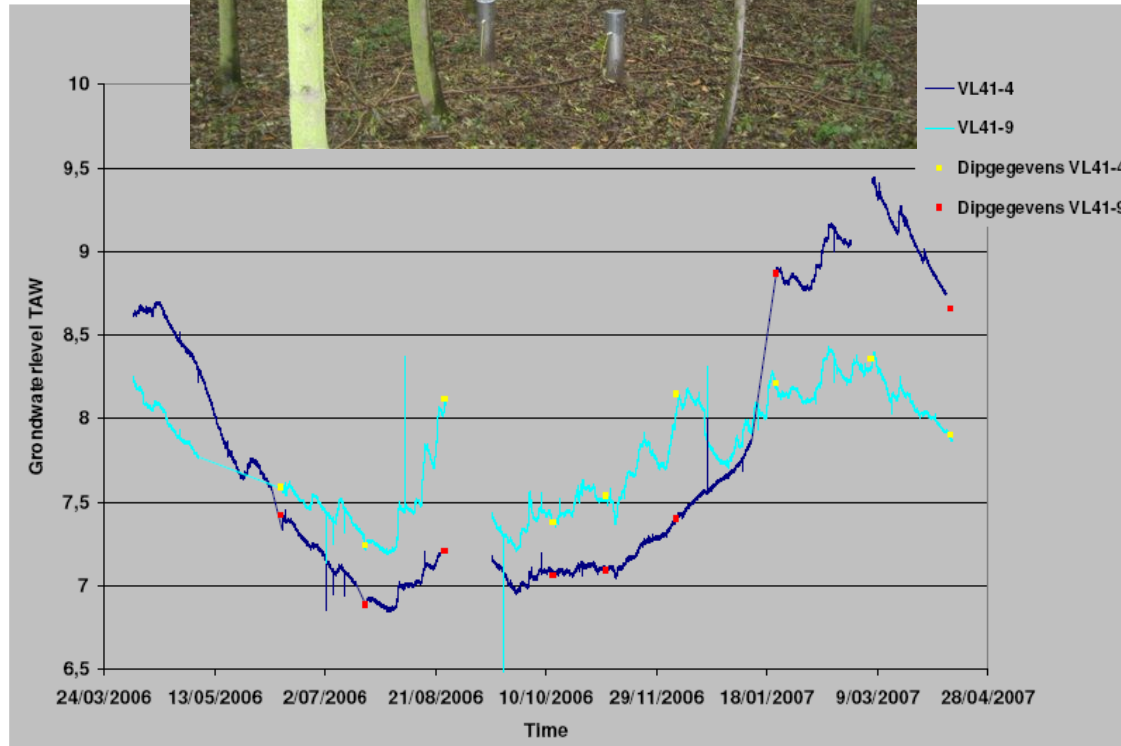


(Wallis et al., 2022)

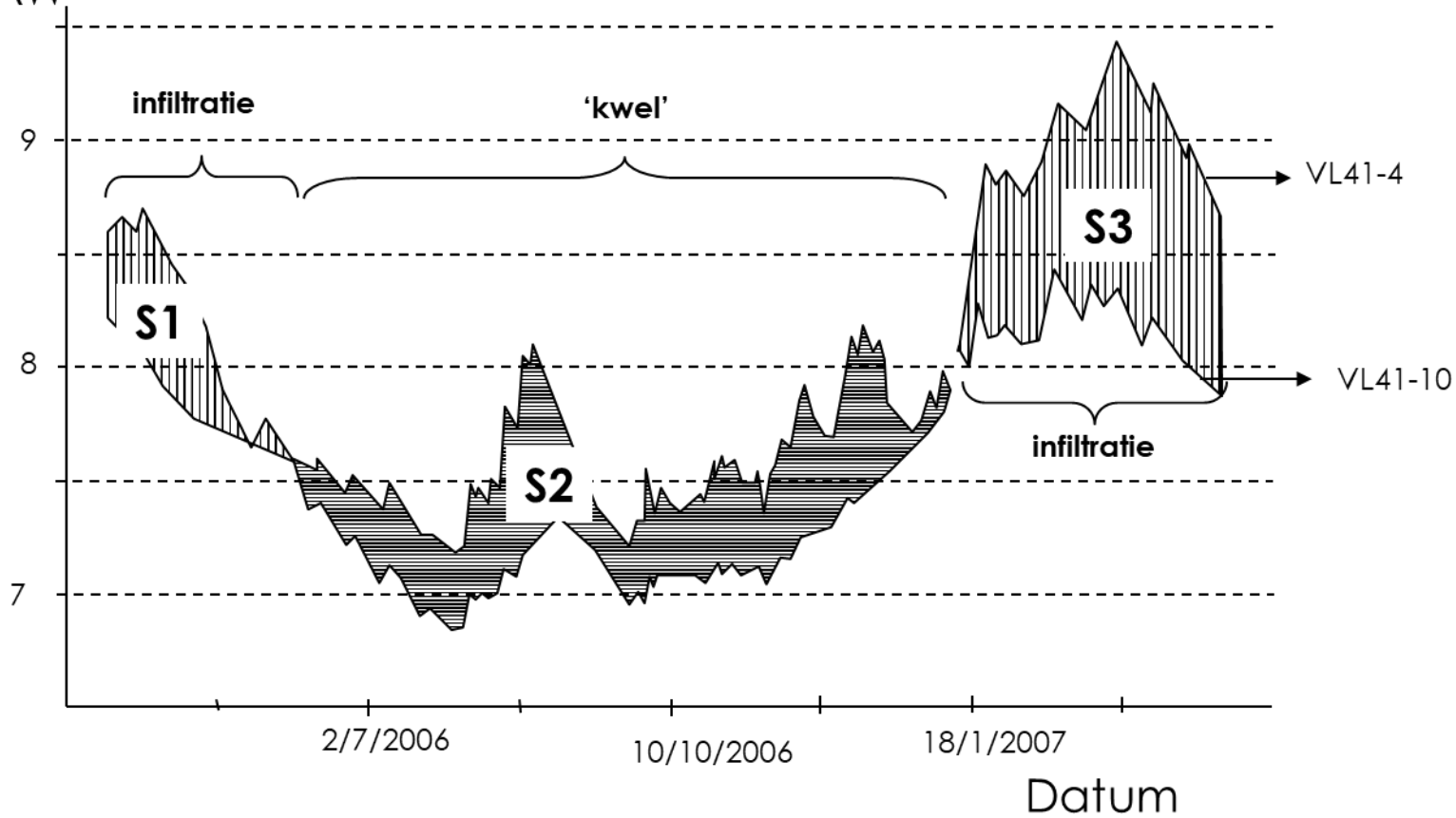
Model result LEACHM  
 (public domain unsaturated  
 zone simulator)



(Adamson et al., 2022)



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