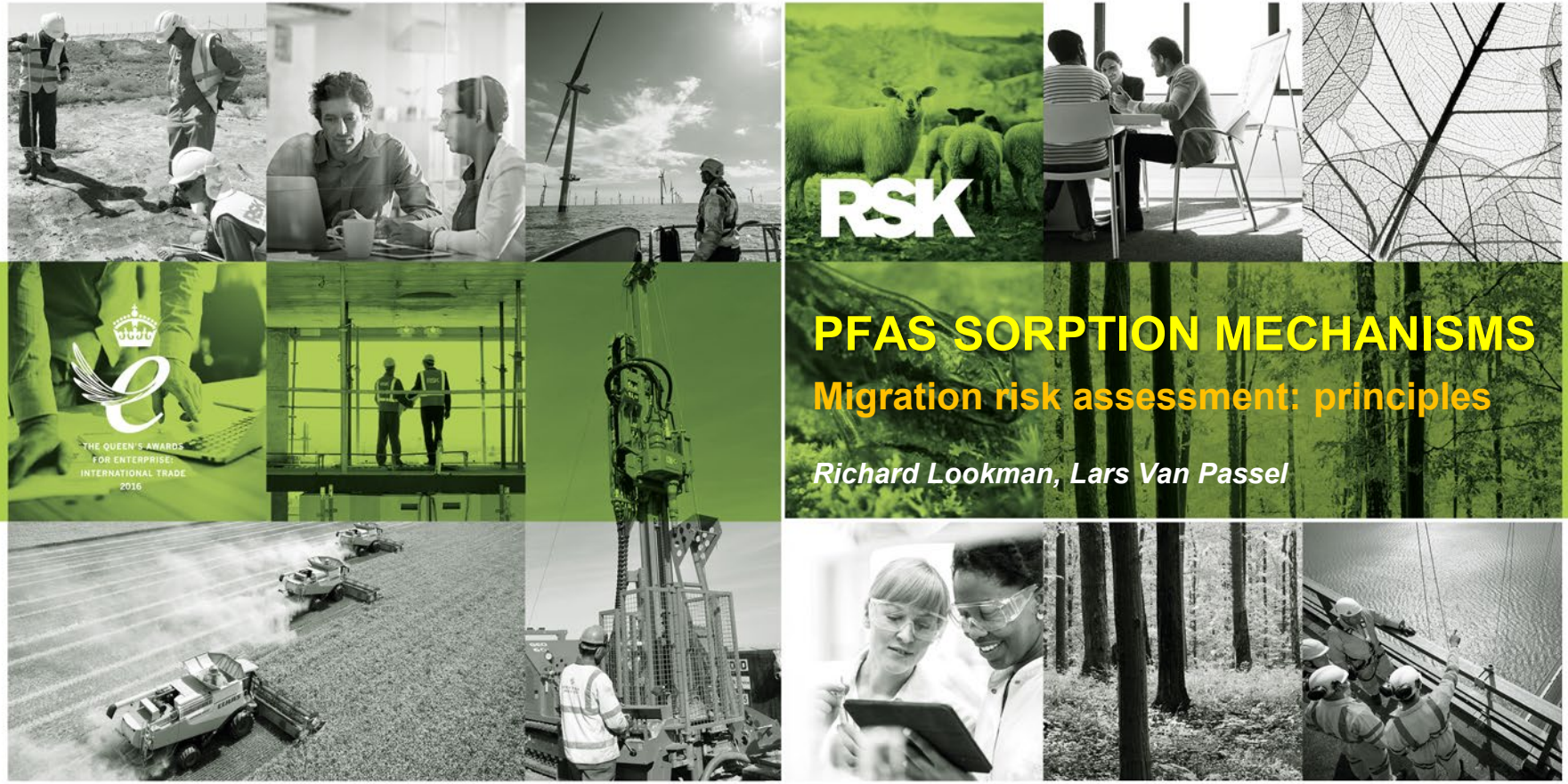
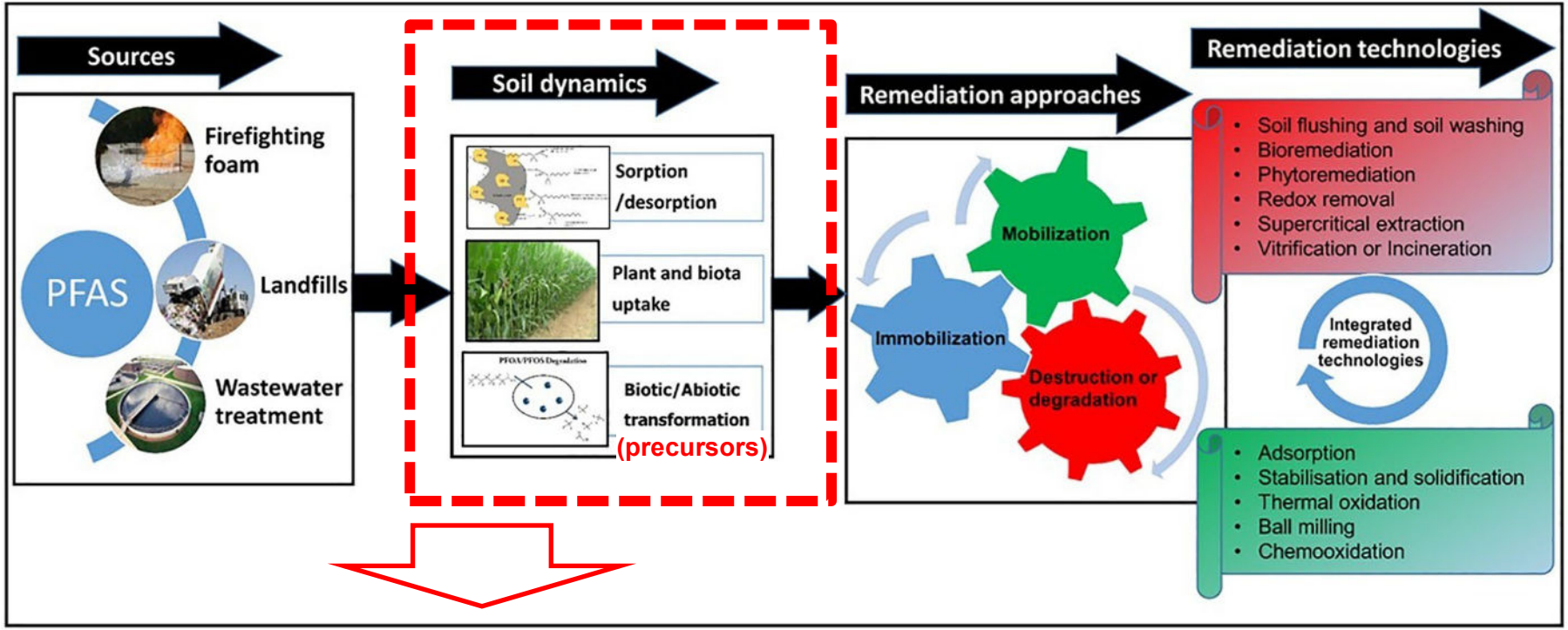



# PFAS SORPTION MECHANISMS

## Migration risk assessment: principles

*Richard Lookman, Lars Van Passel*

# 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/m³)
$n$ = 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**: logKoc = 2.57 L/kg (Koc = 371)

**PFOA**: logKoc = 2.06 L/kg (Koc = 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[b] (20 - 25 °C) [g/L] | Melting Point[a] [°C] | Boiling Point[a] [°C] | Vapor Pressure[b] [Pa] | Henry-Coefficient [Pa·m³·mol⁻¹] | log Kow[b] [-] | log $K_{OC}$ [L/kg] | Kd (pH 7) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Perfluoroalkyl Carboxylates / Perfluoroalkyl Carboxylic Acids** | **PFCAs** | | | | | | | | | | | |
| Perfluorobutanoic Acid | PFBA | 375-22-4 | $F(CF_2)_3COOH$ | 214.04 | Miscible | -17.5 | 121 | 1307 | -- | 2.82 | 1.88 | -- |
| Perfluoropentanoic Acid | PFPeA | 2706-90-3 | $F(CF_2)_4COOH$ | 264.05 | 112.6 | -- | 124.4 | 1057 | -- | 3.43 | 1.37 | -- |
| Perfluorohexanoic Acid | PFHxA | 307-24-4 | $F(CF_2)_5COOH$ | 314.05 | 21.7 | 14 | 143 | 457 | -- | 4.06 | 1.91 | -- |
| Perfluoroheptanoic Acid | PFHpA | 375-85-9 | $F(CF_2)_6COOH$ | 364.06 | 4.2 | 30 | 175 | 158 | -- | 4.67 | 2.19 | 0.4 - 1.1 |
| Perfluorooctanoic Acid | PFOA | 335-67-1 | $F(CF_2)_7COOH$ | 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 | $F(CF_2)_8COOH$ | 464.08 | 9.50 | 59 - 66 | 218 | 1.3 | -- | 5.92 | 2.39 | 2.6 - 5.9 |
| Perfluorodecanoic Acid | PFDA | 335-76-2 | $F(CF_2)_9COOH$ | 514.09 | 9.50 | 77 - 88 | 218 | 0.2 | -- | 6.50 | 2.76 | 2.0 - 31 |
| Perfluoroundecanoic Acid | PFUnA | 2058-94-8 | $F(CF_2)_{10}COOH$ | 564.09 | 0.004 | 83 - 101 | 160 - 230 | 0.1 | -- | 7.15 | 3.30 | 12 - 103 |
| Perfluorododecanoic Acid | PFDoA | 307-55-1 | $F(CF_2)_{11}COOH$ | 614.10 | 0.0007 | 107 - 109 | 245 | 0.01 | -- | 7.77 | – | 24 - 269 |
| Perfluorotridecanoic Acid | PFTrdA | 72629-94-8 | $F(CF_2)_{12}COOH$ | 664.11 | 0.0002 | -- | | 0.3 | -- | 8.25 | – | -- |
| Perfluorotetradecanoic Acid | PFTeDA | 376-06-7 | $F(CF_2)_{13}COOH$ | 714.12 | 0.00003 | -- | 276 | 0.1 | -- | 8.90 | – | -- |
| Perfluoropentadecanoic Acid | PFPeDA | 141074-63-7 | $F(CF_2)_{14}COOH$ | 764.12 | – | -- | -- | -- | -- | – | – | -- |
| Pentadecafluorooctanoic Acid Ammonium Salt (Ammonium Pentadecafluorooctanoate) | APFO | 3825-26-1 | C8 H4 NF15 NO2 | 445.11 | 14.2 | 157 - 165 | -- | 0.01 | -- | – | – | -- |
| **Perfluoroalkyl Sulfonates / Perfluoroalkyl Sulfonic Acids** | **PFSAs** | | | | | | | | | | | |
| Perfluorobutane Sulfonate | PFBS | 375-73-5 | $F(CF_2)_4SO_3H$ | 300.10 | 46.2 - 56.6 | 76 - 84 | 211 | 631 | -- | 3.90 | 1.00 | -- |
| Perfluorohexane Sulfonate | PFHxS | 432-50-8 | $F(CF_2)_6SO_3H$ | 400.11 | 2.3 | -- | -- | 58.9 | -- | 5.17 | 1.78 | 0.6 - 3.2 |
| Perfluoroheptane Sulfonate | PFHpS | 357-92-8 | $F(CF_2)_7SO_3H$ | 450.12 | – | -- | -- | -- | -- | – | – | -- |
| Perfluorooctane Sulfonate | PFOS | 1763-23-1 | $F(CF_2)_8SO_3H$ | 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 | $F(CF_2)_{10}SO_3H$ | 600.14 | 0.002 | | | 0.71 | -- | 7.66 | 3.53 | -- |
| **Perfluoroalkyl Phosphonic Acids** | **PFPAs** | | | | | | | | | | | |
| Perfluorobutyl Phosphonic Acid | PFBPA | 52299-24-8 | $F(CF_2)_4P(O)(OH)_2$ | 350.02 | 14259.1 | -- | -- | 0.18 | -- | 2.19 | – | -- |
| Perfluorohexyl Phosphonic Acid | PFHxPA | 40143-76-8 | $F(CF_2)_6P(O)(OH)_2$ | 400.03 | 515.3 | -- | -- | 0.04 | -- | 3.48 | – | -- |
| Perfluorooctyl Phosphonic Acid | PFOPA | 40143-78-0 | $F(CF_2)_8P(O)(OH)_2$ | 500.05 | 24.5 | -- | -- | 0.01 | -- | 4.73 | – | -- |
| Perfluorodecyl Phosphonic Acid | PFDPA | 52299-26-0 | $F(CF_2)_{10}P(O)(OH)_2$ | 600.06 | 0.5 | -- | -- | 0.0002 | -- | 5.98 | – | -- |
| **Perfluorooctane Sulfonamide and Derivatives** | | | | | | | | | | | | |
| Perfluorooctane Sulfonamide | PFOSA | 754-91-6 | $F(CF_2)_8SO_2NH_2$ | 499.14 | - | 154 - 155 | -- | -- | -- | - | 2.5 - 2.62 | 35 - 56 |
| Perfluorooctane Sulfonamidoethanol | FOSE | 10116-92-4 | $F(CF_2)_8SO_2NH(CH_2)_2OH$ | 543.19 | 0.0009 | -- | -- | 0.00 | -- | 5.78 | – | -- |
| N-Methyl-Perfluorooctane Sulfonamide | N-MeFOSA | 31506-32-8 | $F(CF_2)_8SO_2NHCH_3$ | 513.17 | 0.0002 | -- | -- | 0.30 | -- | 6.07 | 3.14 | -- |
| N-Ethyl-Perfluorooctane Sulfonamide | N-EtFOSA | 4151-50-2 | $F(CF_2)_8SO_2NHCH_2CH_3$ | 527.20 | 0.0001 | -- | -- | 0.12 | -- | 6.71 | 3.23 | -- |
| N-Methyl-Perfluorooctane Sulfonamidoethanol | N-MeFOSE | 24448-09-7 | $F(CF_2)_8SO_2N(CH_3)(CH_2)_2OH$ | 557.22 | 0.0003 | -- | -- | 0.0004 | -- | 6.00 | – | -- |
| N-Ethyl-Perfluorooctane Sulfonamidoethanol | N-EtFOSE | 1691-99-2 | $F(CF_2)_8SO_2N(CH_2CH_3)(CH_2)_2OH$ | 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 ($m^2/m^3$)

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

  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 Kd'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

# Influence of pH

- Dissociation of PFAS - functional groups
- For example anions: $K_a = [anion^-]*[H^+]/[acid]$ or $pK_a = -\log_{10}(K_a)$
- Different physical & chemical properties for undissociated acid and anionic forms
- At environmental pH, most PFAS will be available in their anionic forms

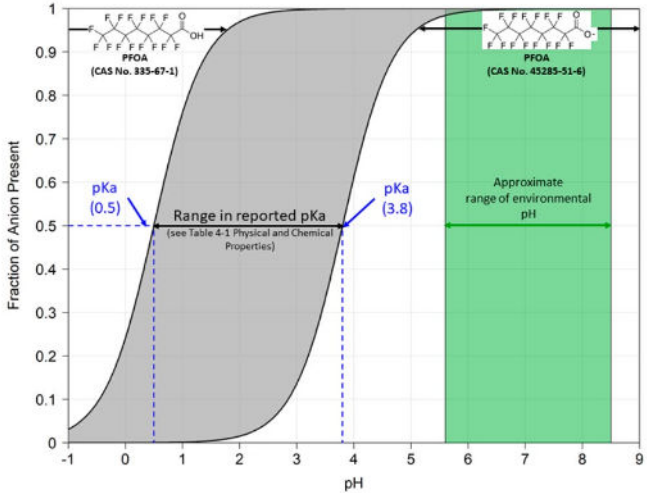
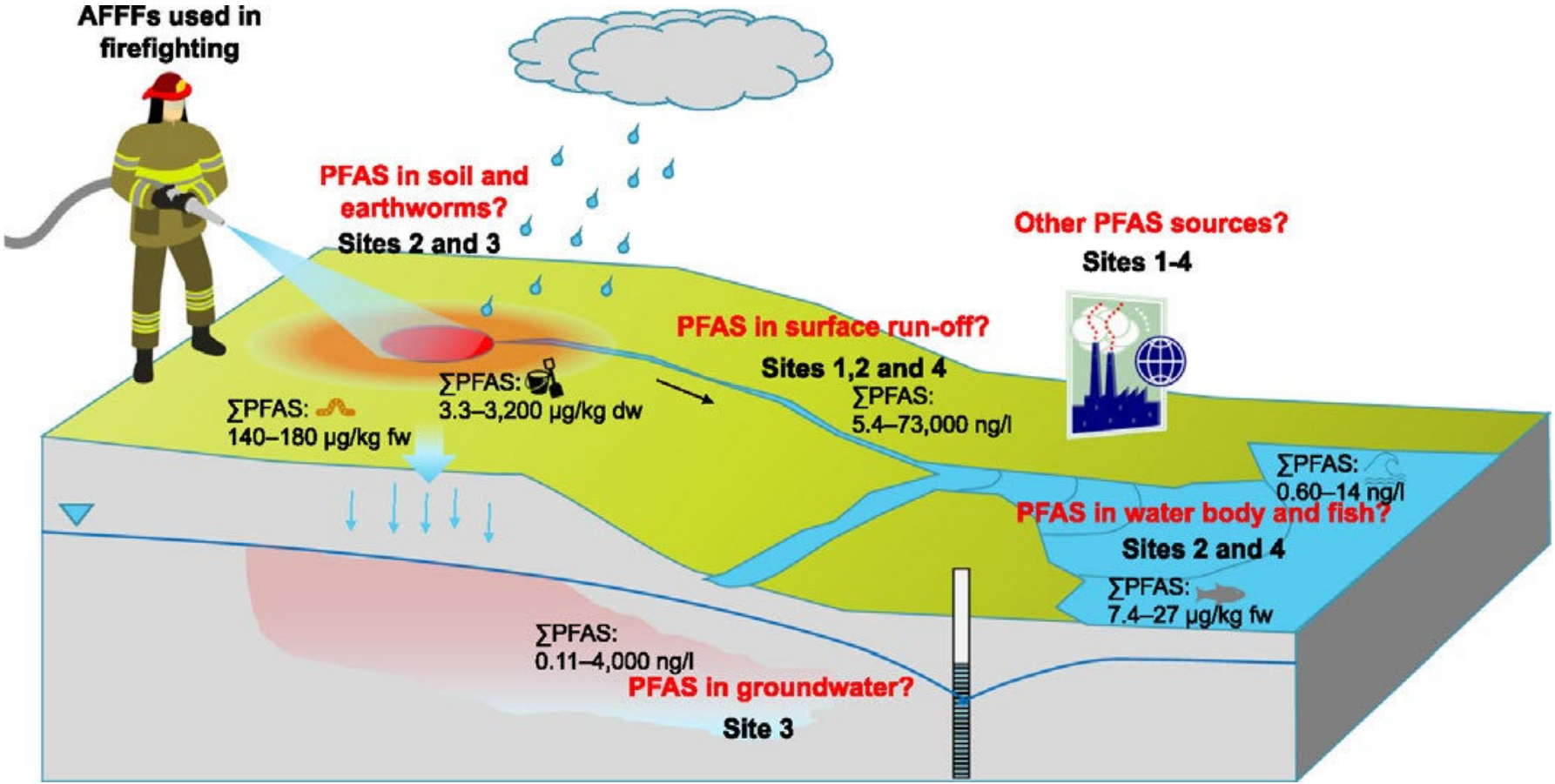


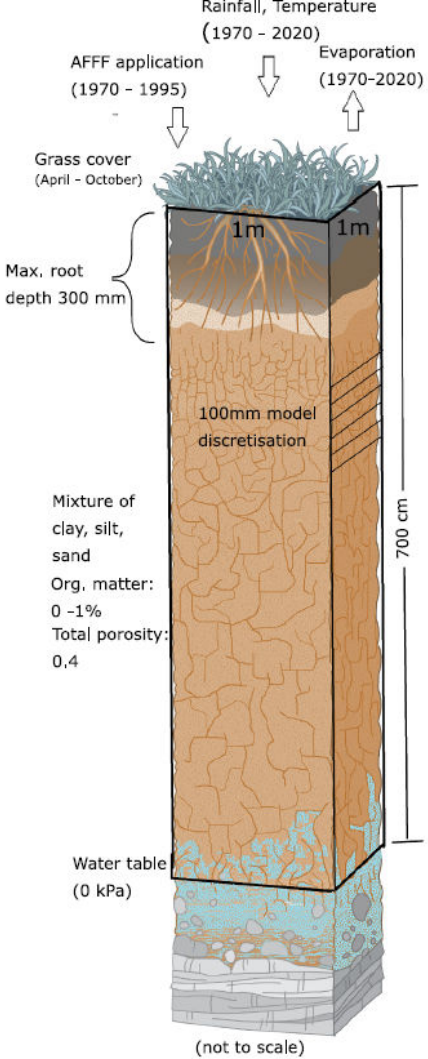

Figure 4-2. Titration curve for PFOA—relation of pKa to environmental pH.

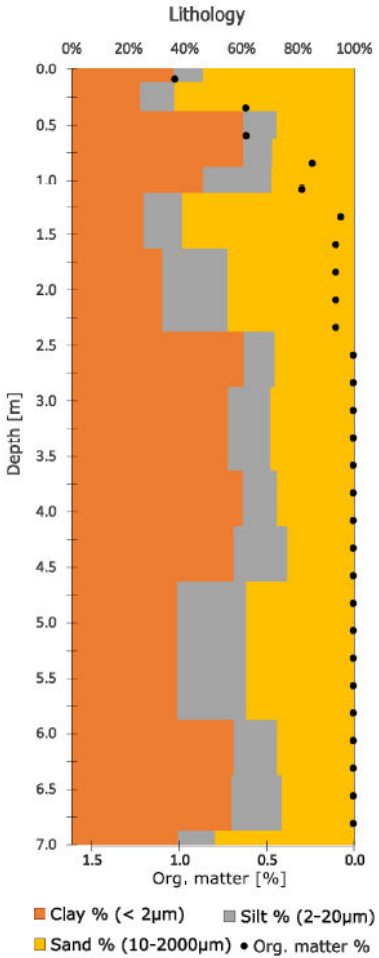
Source: https://pfas-1.itrcweb.org

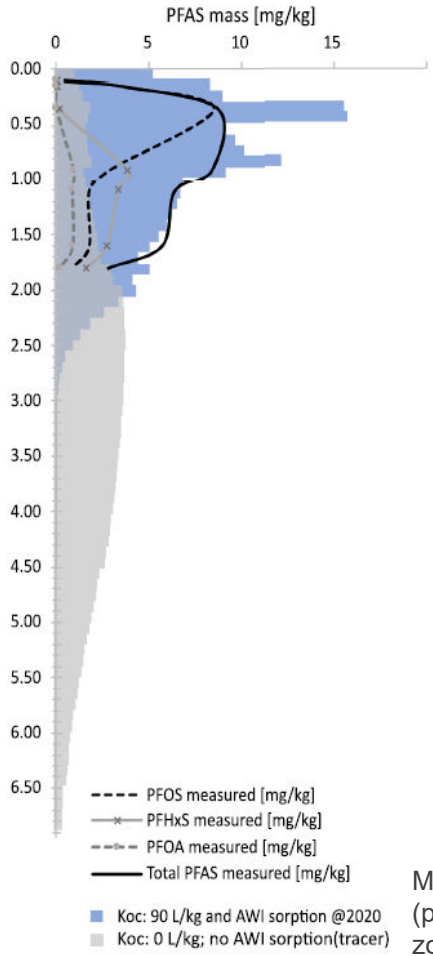
- All sorption characteristics are determined by PFAS-type / chain length, ionic strength, pH, valence of cations present, temperature,…
- If **NAPL is present** (oils, CAHs), PFAS can also accumulate at the water/NAPL and air/NAPL interphases
- PFAS can migrate when attached to **mobile soil particles/colloids**
- PFAS can migrate through **superficial runoff** (unpaved surfaces)
- Diffusion of PFAS into low permeability materials: zwitterionic/cationic > anionic
- **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)*

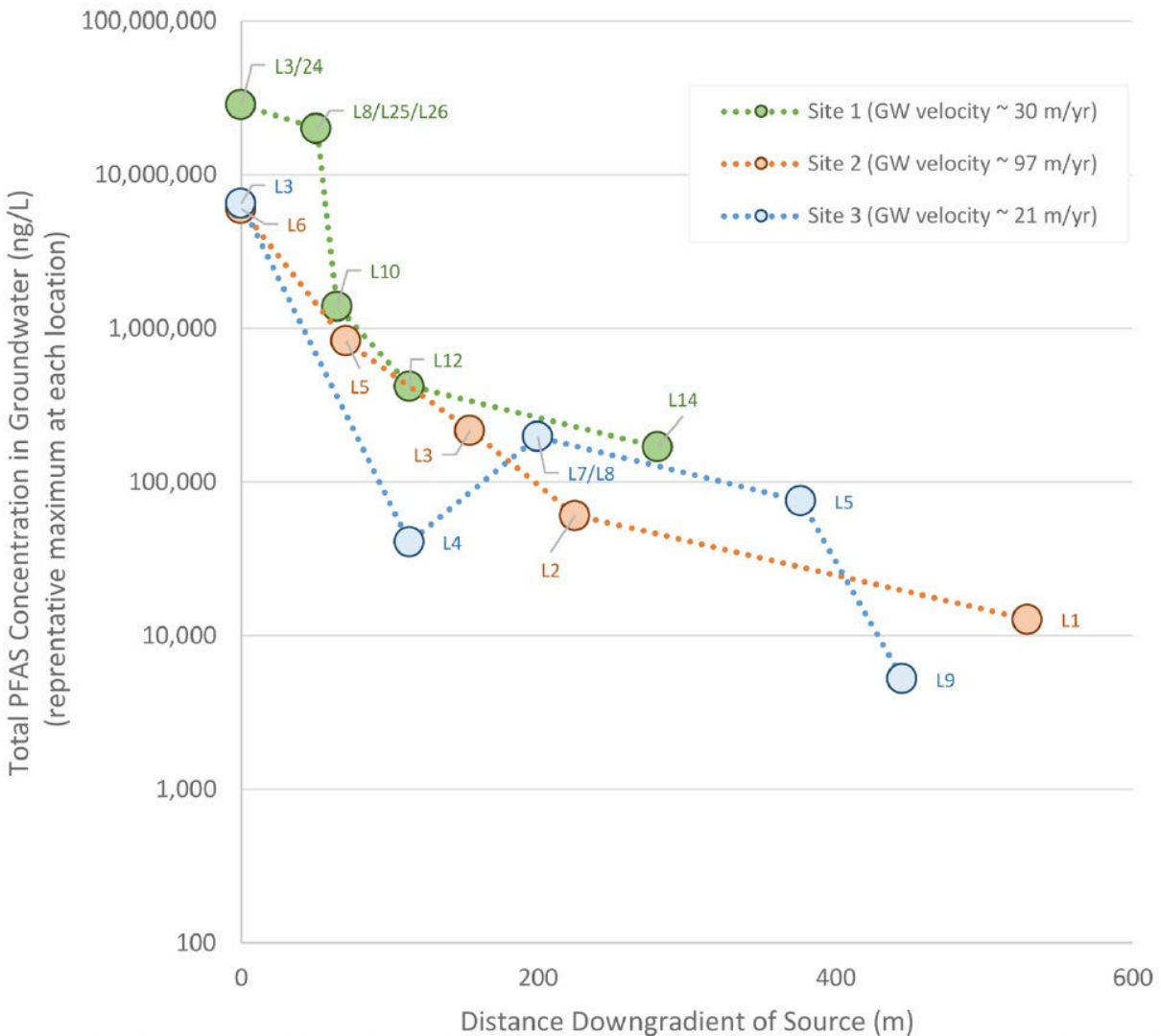


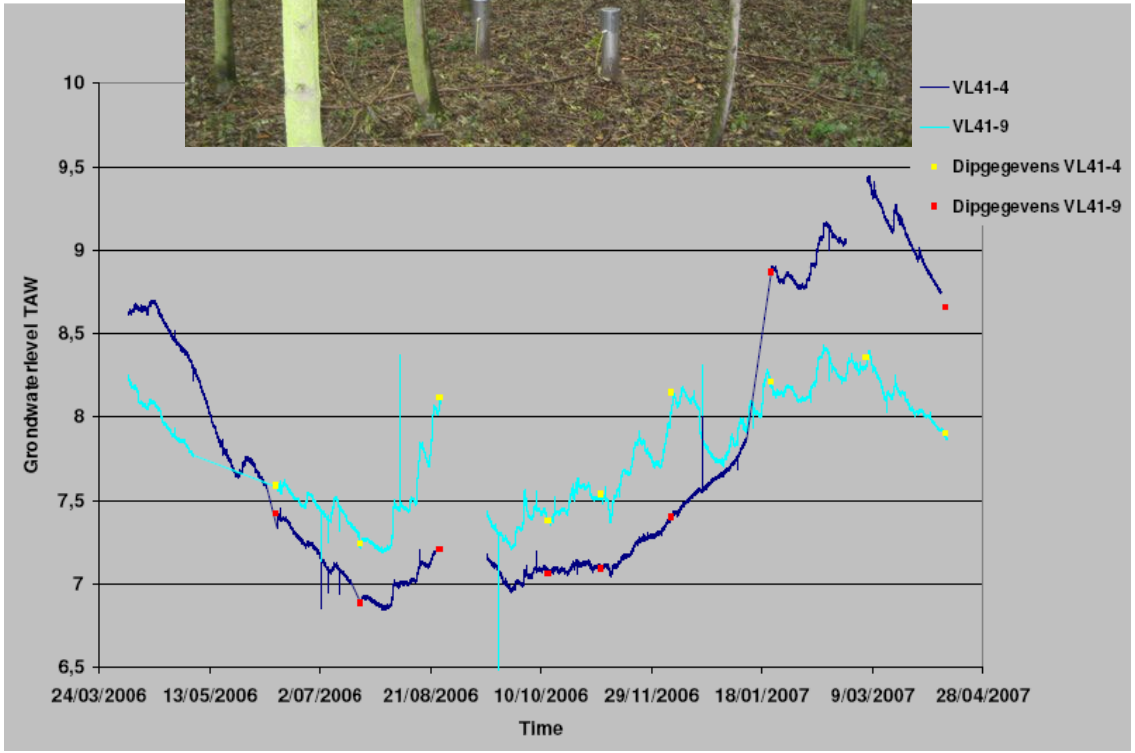




(Wallis et al., 2022)

Model result LEACHM (public domain unsaturated zone simulator)




*(Adamson et al., 2022)*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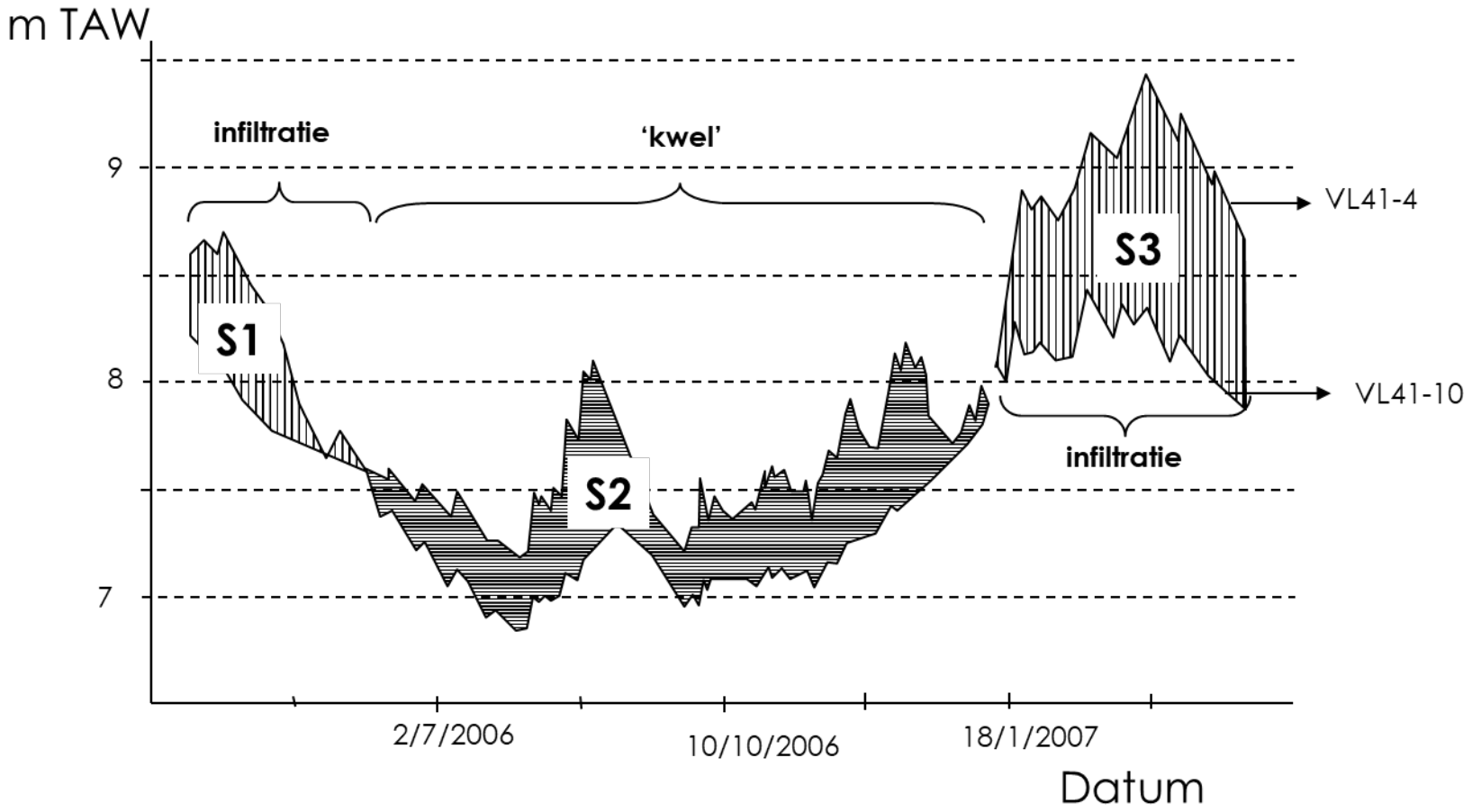
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