Results and Discussion

The 8:2 fluorotelomer alcohol (CF$_3$-(CF$_2$)$_7$-(CH$_2$)$_2$-OH) (8:2 FTOH), one of the confirmed precursors of perfluorooctanoic acid was selected as the probe compound to elucidate the sorption mechanisms of FTOHs in soils. Solubility and sorption by five soils of 8:2 FTOH were measured from water and cosolvent/water solutions. Aqueous solubility and soil-water distribution coefficients ($K_{d,w}$, L/kg) were extrapolated from cosolvent data using a log-linear cosolvency model and compared to direct aqueous measurements. Liquid chromatography tandem mass spectrometry with electrospray ionization was employed to analyze the 8:2 FTOH in solutions and soils. The cosolvent-extracted aqueous solubility is 0.224 mg L$^{-1}$ in good agreement with the measured value of 0.194 mg L$^{-1}$. All sorption isotherms were generally linear regardless of cosolvent composition or soil organic carbon (OC) content. $K_{d,w}$ values extrapolated from cosolvent data were similar, but consistently higher than those measured in aqueous solutions. The latter was hypothesized to be due to dissolved OC (DOC) in the aqueous slurries. An average log $K_{d,w}$ of 5.30 was estimated and supported by DOC and $K_{d,w}$ measurements at two soil-water ratios. Sorption appeared to be driven by hydrophobic partitioning with a log $K_{d,w}$ of 4.13 ± 0.16. Irreversible sorption was also observed and appeared related to OC content with extraction efficiency reduced from 85% to 45% with increasing contact time from 3 h to 72 h for the highest OC soil.

**Experimental Scheme**

- Measure solubility in binary solvents
- Select the cosolvent with most linear behavior
- Measure sorption coefficients in cosolvent/water solutions
- Estimate water solubility by extrapolation
- Estimate aqueous-based sorption coefficients by extrapolation
- Directly measure aqueous-based sorption coefficients

**Materials and Methods**

Log-linear Cosolvency Models

- Log-linear cosolvency models for solubility (Yakovlev, 1972) and sorption (Rao et al., 1985) are:

  \[ \log S = - \log 10^{-1/2} - \sigma - \sigma_f \cdot f \cdot \log K_{d,w} \]

where $S$ is solubility, $K_{d,w}$ is the sorption coefficient (L/kg), $f$ is the volume fraction of cosolvent, and $\sigma$ is the cosolvency power, $\alpha$ is an empirical constant reflecting solubility-solvent interactions.

**Sample Analysis**

- LC/MS/MS (Shimatzu LC; Applied Biosystem 3000 MS) in the negative ionization mode (see Szostek et al., 2004).
- Deuterated 8:2 (1D,1D,2D,2D, 313C-perfluorodecanol) was used as the internal standard.
- Dissolved organic carbon (DOC) of aqueous supernatants was analyzed using a Shimadzu TOC-VCSH Analyzer.

**Reduction of Matrix Effects**

(a) acidic soil supernatants: 10-fold increase in response by adding 5 mM ethanolamine to mobile phase.
- (b) soil extracts: 2-fold increase in response after cleanup with SupelClean ENV-2C bulk packing.

**Correlation with OC content**

- Aqueous sorption coefficients are best correlated with soil OC
- Average log $K_{d,w}$ = 4.13 ± 0.16 and 3.84 ± 0.16 estimated by extrapolation from cosolvents and measured directly, respectively.

**Irreversible Sorption**

- Reversible sorption equilibrium was established within 24 h; $K_{d,w}$ values
- Irreversible sorption increased with time: increasing contact times from 3 h to 72 h decreased soil extraction efficiency from 85% to 45%.

**Effects of Temperature**

- 8:2 FTOH solubility is exothermic; $K_{d,w}$ increased with increasing temperature.
- Log-linear cosolvency models for solubility (Yalkowsky, 1972) and sorption (Rao et al., 1985) are:

  \[ \log S = \log 10^{-1/2} - \sigma - \sigma_f \cdot f \cdot \log K_{d,w} \]

where $S$ is soil (permeability, pH, OC, CEC), $\sigma$ is the sorption coefficient, and $\sigma_f$ is the cosolvency power.

**Soil Properties**

- **Soil Texture**
  - *pH (isotherm)*
  - **Sand (%)**
  - **Clay (%)**
  - **OC (%)**
  - **CEC**

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References