

# **Co-occurrence and correlations of PFASs and chlorinated volatile** organic compounds (cVOCs) in subsurface in a fluorochemical industrial park: Laboratory and field investigations

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## **Motivation**





A total of 13 groundwater samples and aquifer solids in 5 different depth of two sampling locations were collected from a FIP. All the samples were analyzed PFASs, cVOCs and other properties. Moreover, a Lab sorption experiment was conducted to investigate the effect of cVOCs in the form of DNAPL on the distribution of PFASs. This study also explore the impact of cVOCs on the log K<sub>d-field</sub> of PFASs at various aquifers in the field. Solid-water distribution coefficients  $(K_{d-field}, L/kg)$  for PFASs were calculated by the paired groundwater and aquifer solids according to Eq:

Fluorochemical industrial park (FIP) represents an important source of PFASs and cVOCs. However the effect of aquifer solids on PFAS fate in the presence of DNAPL are still unclear under natural conditions. Therefore, the occurrence and distribution of PFASs in groundwater and aquifer solid at various depths and their correlations were studied. And the influence of DNAPL on the occurrence and migration of PFASs in subsurface was explored in the field, which was further investigated via laboratory adsorption experiment under more controlled conditions.



Fig. 1. Map of the sampling locations for soil and groundwater (a and b) and cross-section (c).



### Results



aquifer solids (b).

Table. 1 Distributions of cVOCs in the shallow, middle, and deep aquifers ( $\mu g/L$ ).

Aquifers	Sample location	DCM	TCM	1,1,2-TCA	CCl <sub>4</sub>	TCE	PCE
Shallow aquifer	GW-1S	6030	>10,000	>10,000	>10,000	>10,000	>10,000
	GW-4S	8	>10,000	46.4	4510	2560	241
	GW-5S	>10,000	>10,000	1520	>10,000	>10,000	3450
Middle aquifer	GW-1M	1440	>10,000	>10,000	>10,000	>10,000	>10,000
	GW-2M	23.7	>10,000	653	>10,000	2220	677
	GW-3M	20.1	711	11.4	810	134	32.2
	GW-4M	6.2	>10,000	78.8	9220	2450	246
	GW-5M	8060	>10,000	434	>10,000	>10,000	1390
Deep aquifer	GW-1D	1260	>10,000	2100	>10,000	1120	1210
	GW-2D	5.1	>10,000	50.2	>10,000	5700	157
	GW-3D	14.1	>10,000	74.4	>10,000	378	184
	GW-4D	68.8	452	13	272	76.4	50.9
	GW-5D	>10,000	>10,000	1310	>10,000	>10,000	4160

The  $\sum_{17}$  PFASs concentrations in groundwater ranged from 0.48 µg/L to 249.21 µg/L, and PFOA was the most dominant PFASs, followed by short-chain PFCAs (C4-C7). In addition, HFPO-DA and HFPO-TA were detected frequently at high concentrations. HFPO-TA concentration (4,808 ng/L) was the highest concentration reported so far. The concentrations of  $\sum_{17}$  PFASs in soil were 7.49- 22.42 ng/L, and PFBA and PFOA were the dominant PFASs. The relative abundance of 6:2 FTS and 6:2 Cl-PFESAs were higher than those of HFPO oligomers. The usage of PFOA and PFOS shifted toward the applications of short-chain or emerging PFAS substitutes.



Fig. 3 Sorption isotherms of PFBA, PFOA, and HFPO-DA to solids collected from the shallow (a), middle (b), and deep (c) aquifers in the absence/presence of DNAPL. The log Kd-field values of individual PFAS in the shallow (d), middle (e), deep (f) aquifers.

The log K<sub>d</sub> values, determined in the laboratory, were found to increase in the presence of DNAPL. Specifically, PFOA had a higher potential to participate into DNAPL, which can migrate with DNAPL to the deep aquifer.

# Conclusions

The presence of DNAPL led to high concentrations of PFASs and relatively high abundance of PFOA in the deep aquifer, which was confirmed by the increased  $K_d$  values in the presence of DNAPL observed in the laboratory investigations. No significant correlations (p > 0.05) were found between log  $K_d$  values and chain-length of PFCAs at various depths in the field, even the log  $K_{d-field}$  values of PFBA and HFPO-DA were higher than that of PFOA, indicating that in the field, PFASs distributions were a result of composite factors, such as the presence of DNAPL, aquifer solids parameters, groundwater geochemistry properties, and PFASs structures.

#### Acknowledgement:

This work was supported by the National Natural Science Foundation of China (32061133001) and the National Natural Science Foundation of China (41771354). We acknowledge the cooperation between China and the EU through the EiCLaR project (European Union's Horizon 2020, N°965945).



