

## PARTITIONING OF PERFLUORINATED ALKYLATED SUBSTANCES BETWEEN WATER AND SEDIMENT IN FIELD AND LABORATORY EXPERIMENTS

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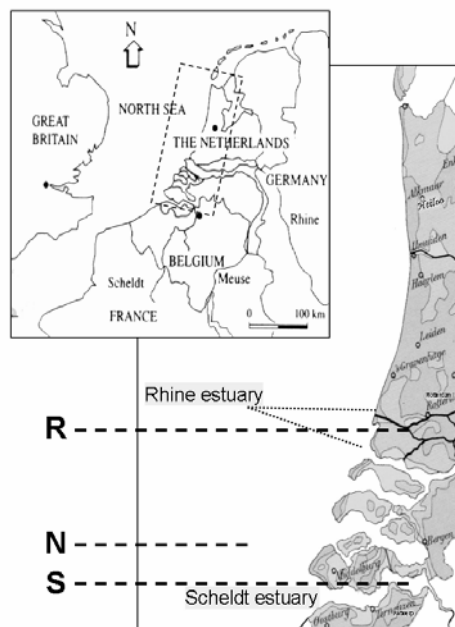
### Introduction

Perfluorinated alkylated substances (PFAS) consist of a perfluorinated carbon chain and a functional end group such as a sulfonic or carboxylic acid. PFAS are used in a wide variety of applications and products including sealants, fire fighting foams and surface coatings.<sup>1</sup> Although PFAS are measured in remote areas such as the Arctic, the sources of PFAS in the environment, their physical-chemical properties, and fate and transport are not well understood or described. It was recently suggested that a significant route for PFAS transport to the Arctic is discharge of the chemicals in surface waters and subsequent transport through river and ocean water.<sup>2</sup> A key process for this route is sorption to sediments, typically expressed as the sediment-water distribution coefficient  $K_d$  (L/kg). The very few available data are mostly on partitioning of PFAS between water and soils and suggest moderate sorption<sup>2,3</sup>, but a mechanistic understanding of the process is lacking. The aim of this study was to measure  $K_d$  values of PFAS as a function of carbon chain length ( $6 \leq \#C \leq 14$ ), functional group (carboxylates versus sulfonates) and temperature ( $T = 4, 10, 20^\circ\text{C}$ ). The  $K_d$  values were measured for three sediments originating from the Rhine and Scheldt estuaries and the North Sea by fitting the sorption isotherms with the Freundlich equation. The  $K_d$  values were compared to the distribution of PFAS between water and sediment in field samples collected from various locations in the Rhine and Scheldt estuaries and the North Sea.

### Materials and Methods

Sediment and water samples were collected from various locations in the Rhine and Scheldt estuaries and the North Sea (Figure 1). The locations indicated with R, S and N are for the sediments used in the laboratory experiments. Water samples were filtered directly after sampling (pore diameter =  $1.2 \mu\text{m}$ ). Water and sediment samples were stored in glass bottles at  $T = 4^\circ\text{C}$  and  $T = -20^\circ\text{C}$ , respectively.

For the sorption isotherms, approximately 2.5 g wet sediment and 12 ml water in centrifuge tubes was spiked with different amounts (range 10 – 5000 ng) of a PFAS mixture and allowed to equilibrate on a shaker for three days. The PFAS mixture contained the carboxylates with 7 (PFHpA), 8 (PFOA), 9 (PFNA), 10 (PFDA), 11 (PFUnA), 12 (PFDoA) and 14 (PFTeA) carbon atoms and the sulfonates with 6 (PFHxS) and 8 (PFOS) carbon atoms. The sediment and water phases were separated by centrifugation (15 minutes, 2000 rpm). The water layer and wet sediment were extracted separately. Sediment concentrations were corrected for PFAS contributions from water remaining in the sediment after centrifugation. Sorption isotherms were



**Figure 1** Sampling locations. The R (Rhine), S (Scheldt) and N (North Sea) indicate the origin of the sediments used for the laboratory sorption experiments.

obtained by plotting the concentration in the sediment ( $C_{sed}$ ,  $\mu\text{g}/\text{kg}$ ) against the concentration in the water ( $C_{wat}$ ,  $\mu\text{g}/\text{L}$ ). The isotherms were fitted with the Freundlich isotherm:  $C_{sed} = K_d C_{wat}^n$ , where  $K_d$  and  $n$  are constants. When  $n = 1$ ,  $K_d$  has units of  $\text{L}/\text{kg}$ .

The field distribution coefficients were calculated as:  $K_d (\text{L}/\text{kg}) = C_{sed} / C_{wat}$ . Because PFAS concentrations were often below detection limits, the  $K_d$  values could only be calculated for some PFAS and a few locations. Average values for Rhine and Scheldt estuaries and North Sea will be presented here, concentrations for specific locations will be published elsewhere.

Before extraction, water and sediment samples were spiked with  $^{13}\text{C}$ -PFOA and  $^{18}\text{O}_2$ -PFOS to correct for losses during extraction of the carboxylates and sulfonates, respectively. Water samples were extracted by solid phase extraction (SPE, C18) and eluted with methanol. Sediment samples were extracted (ultrasonic bath, 15 minutes) with tert-butyl methyl ether (MTBE) after adding buffer ( $\text{pH} = 10$ ) and tetrapropylammoniumhydrogensulfate (TPA) as counter-ion. Liquid chromatographic separation was with a RP-C18 column (Lichrosphere) and a methanol/water (5 mM ammonium acetate) gradient. Analysis was with single quad MS (Thermoquest Navigator).

## Results and Discussion

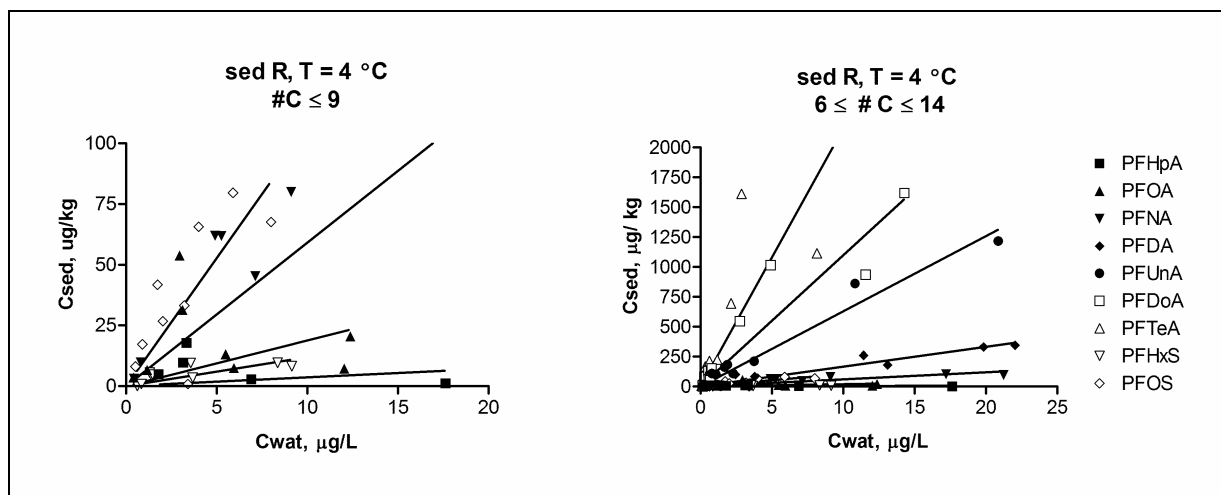
The sediment characterization data are summarized in Table 1. The organic carbon content is low or zero for the sediments from the Scheldt estuary and the North Sea.

**Table 1** Sediment composition. See Figure 1 for the origin of the sediments. Total, inorganic and organic carbon (C) content, nitrogen (N) and sulfur (S) contents and the Redfield ratio (C/N).

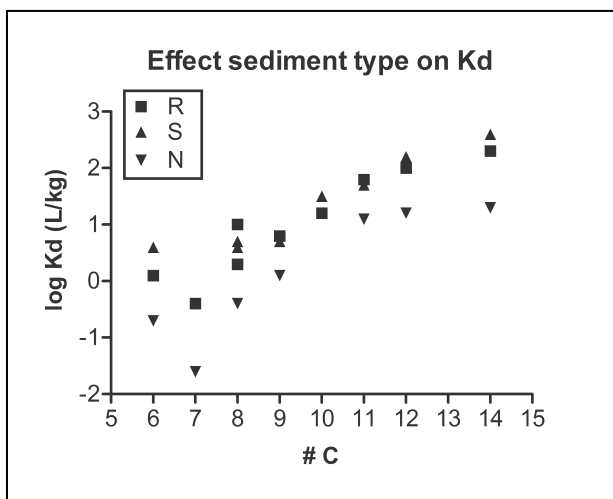
	%C			%N	%S	C/N [m/m]
	total	inorg	org			
R	4.2	0.00	4.2	0.16	0.23	27
S	0.33	0.34	0.000	0.005	0.05	71
N	0.50	0.49	0.002	0.009	0.06	56

Figure 2 shows the sorption isotherms for the selected PFAS in sediment R at  $T = 4^\circ\text{C}$ . Because the scatter in the data was rather high, a simple linear fit (i.e.  $n=1$  in the Freundlich equation) was applied to calculate  $K_d$ . Despite the rather high scatter in the data, the relationship between the logarithm of  $K_d$  versus PFAS size (expressed as the carbon chain length) in Figure 3 shows clear trends for the three sediments. The amount of sorption increased with increasing PFAS size. This increase seems to level off for larger PFAS and is most pronounced for the sediment from the North Sea. The higher values for C8 are for PFOS. Extrapolating the trend for the C7-C14 carboxylates to C6 indicates that  $K_d (\text{PFHxS}) > K_d (\text{PFHxA})$ . Thus, sorption is higher for sulfonates than for carboxylates. Figure 4 shows the effect of temperature on  $K_d$ . No clear temperature effect was observed. In Table 2 the data for  $T = 4^\circ\text{C}$  are summarized and compared to the field data.

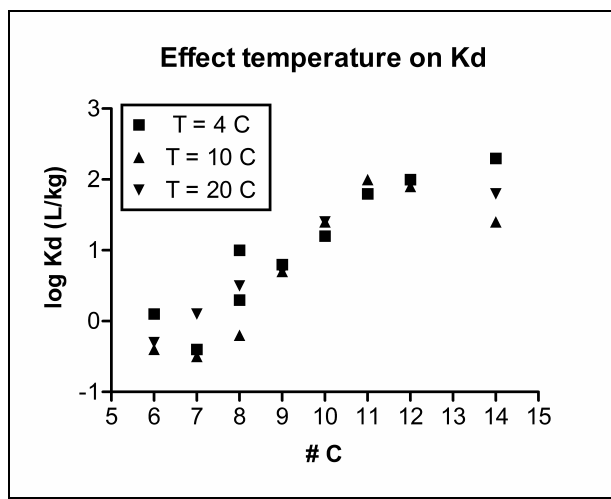
Because of the many variables in this study, a mechanistic explanation of the results is not straightforward. A PFAS molecule could interact with sediment by its perfluorinated carbon chain and / or by the functional group. Due to the low intermolecular (van der Waals) interactions of the perfluorinated tail, it is unlikely to interact strongly with sediment phases. Nevertheless, the linear fit of the sorption isotherm suggests an adsorption phenomenon. This would agree with the observation that sorption typically increases with the size of perfluorinated carbon chain (Figure 3). It is, however, unclear into what the PFAS molecules partition. Note that the amount of sorption in the sediment from the Scheldt estuary (no organic carbon) is similar or even higher than sorption in sediment from the Rhine estuary. Thus, the role of organic matter as a partitioning phase is unclear.



**Figure 2** Sorption isotherms of PFAS with different carbon chain length (#C). The lines are the fitted linear equation. The slope of this line is equal to the distribution coefficients (Kd).



**Figure 3** The distribution coefficient (Kd) as a function of carbon chain length (#C) and sediment type (R, S, N). The data are for T = 4 °C.



**Figure 4** The distribution coefficient (Kd) as a function of carbon chain length (#C) and temperature (T). The data are for sediment R.

Also the functional group of a PFAS molecule may interact with the sediment. Because PFAS molecules are strong acids, they are charged under environmental conditions and may form strong bonds in sediments via a chemisorption mechanism. The data suggest that the interaction of a sulfonate group with sediment is stronger than the interaction of a carboxylic acid with sediment. Unfortunately, no temperature effects were measured. From a measured temperature effect the energy associated with the sorption process can be calculated which may give clues about the sorption mechanism.

Field  $K_d$  values could be calculated for PFOA and PFOS for a few sampling sites (Table 2). The field  $K_d$  values for the Rhine estuary are similar to the laboratory data. The field  $K_d$  for PFOS in the Scheldt estuary are considerably higher than the laboratory data. A difference between laboratory and field  $K_d$  values point at the non-equilibrium conditions which typically prevail in the environment. A possible explanation for the higher field  $K_d$  values for PFOS is reduced water concentrations and a slow desorption of PFOS.

Another explanation for the observed differences is the influence of dissolved organic carbon (DOC) on the water concentrations. The water concentrations used to calculate  $K_d$  were the sum of the really dissolved and DOC associated PFAS. It is likely that the DOC type and concentration in the filtered water from the field experiments and the centrifuged water from the laboratory experiments was different.

**Table 2** Sediment-water distribution coefficients ( $K_d$ , L/kg) measured in laboratory experiments (linear fit of the Freundlich isotherm) and in field samples (ratio of concentrations in sediment and water).

	Laboratory experiments			Field experiments	
	R	S	N	R	S
PFHpA	0.4		0.0		
PFOA	2	4	0.5	0.4-2	
PFNA	6	5	1		
PFDA	17	31	16		
PFUnA	63	51	12		
PFDoA	110	175	17		
PFTeA	215	424	18		
PFHxS	1	4	0.2		
PFOS	11	5	2	3-10	8-97

In conclusion, PFAS sorption to sediment increases with the length of the perfluorinated carbon chain, is higher for sulfonates than for carboxylates, depends strongly on sediment type and shows no clear trends with temperature or sediment organic matter content.

### References

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2. Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. Environ Sci Technol 2006;40:32.
3. Beach SA, Newsted JL, Coady K, Giesy JP. Rev Environ Contam Toxicol 2006;186:133.