



Estimating dry deposition and gas/particle partition coefficients of neutral poly-/perfluoroalkyl substances in northern German coast



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ABSTRACT

Dry deposition fluxes of 12 neutral poly-/perfluoroalkyl substances (PFASs) were estimated at Büsum located in northern German coast, and their gas/particle partition coefficients were predicted by employing the polyparameter linear free energy relationships (PP-LFERS). The gas deposition flux, particle deposition flux and total (gas + particle) flux of the 12 PFASs during sampling periods were 1088 ± 611 , 189 ± 75 and 1277 ± 627 pg/(m² d), respectively. The gas deposition of PFASs played a key role during deposition to marine ecosystem. Sensitivity analysis showed that wind speed was the most sensitive parameter for gas deposition fluxes. Good agreements (within 1 log unit) were observed between the measured gas/particle partitioning data of PFASs and the predicted partition coefficients using PP-LFERS, indicating the model can reliably predict the gas/particle partitioning behaviors of atmospheric neutral PFASs.

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1. Introduction

Poly-/perfluoroalkyl substances (PFASs) belong to a relatively new group of environmental contaminants and comprise a wide range of chemicals with different fluorocarbon chains (CF₃[CF₂]_n-) (Lindstrom et al., 2011). They are increasingly concerned because of their widespread presence in a variety of environmental compartments. Understanding their environmental behaviors in the atmosphere, for example, gas/particle partitioning, is of utmost importance (Paul et al., 2009). Several typical neutral PFASs, such as fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAs), perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs), are prone to release into the atmosphere and undergo long range atmospheric transport (LRAT) during their manufacture, use and disposal (Paul et al., 2009). These PFASs can degrade to, for example perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), under the condition of ·OH radicals initiated oxidation in the atmosphere (Butt et al., 2009; D'Eon et al., 2006).

For several typical semi-volatile organic compounds (SVOCs), such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), gas diffusive deposition is the predominant way from the atmosphere to the ocean over wet and dry particle deposition, except in rainy and with high atmospheric particulate matter level regions (Gigliotti et al., 2005). As to neutral PFASs, few data were reported on their gas and particle deposition to the surface water (Xie et al., 2013). Previous studies showed that gas deposition of SVOCs to the surface water are mainly driven by concentrations and wind speed (*v*) (Gigliotti et al., 2005). Since changes of *v* pose a nonlinear effect on the water-side mass transfer coefficient (Schwarzenbach et al., 2003), and temperature (*T*) would change Henry law constant (*H*), it is necessary to understand the combination effects of changes of *v*, concentration and *T* via sensitivity analysis. Furthermore, PFASs are commonly characterized with exceptionally weak van der Waals interactions compared to other hydrocarbon-based compounds of comparable sizes, and fluorinated organic compounds often exhibit special sorption and partition properties (Endo and Goss, 2014; Goss and Bronner, 2006), as a result, *H* values predicted by various existing models may be different considerably (Ding and Peijnenburg, 2013; Wang et al., 2011). Then, the variation of *H* value should be taken into account for PFASs during sensitivity analysis.

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Goss and Bronner (2006) found that the partition and adsorption behavior of fluorinated compounds, for example FTOHs and FOSEs, differs clearly from other compounds. The main reason is because these fluorinated compounds exhibit weaker van der Waals interactions compared to other compounds with comparable sizes or volumes (Endo and Goss, 2014; Goss and Bronner, 2006). Most existing models of estimating partition coefficients between different media are suitable for hydrocarbon-based compounds, however, which may not predict satisfactorily for fluorinated compounds (Arp et al., 2006; Ding et al., 2013). Moreover, for many fluorinated compounds with polar functional groups, they may be characterized with additional specific interactions, which also lead to unexpected deviations. Developing a model to predict the partitioning behaviors of fluorinated compounds is therefore important and urgently needed.

Polyparameter linear free energy relationships (PP-LFERs) have been often employed to predict physicochemical properties or partition coefficients of hydrocarbon-based compounds (Endo and Goss, 2014; Huang et al., 2004; Yan et al., 2005). It is a useful tool to describe the contributions toward free energy change from multiple kinds of molecular interactions of the phase transfer for neutral organic compounds (Arp et al., 2008; Endo and Goss, 2014; Goss, 2005). Recently, Endo and Goss (2014) successfully evaluated PP-LFERs for predicting partition coefficients, such as octanol–water and oil–water, of FTOHs and cyclic volatile methylsiloxanes (cVMS) employing three forms of PP-LFER equations. However, they did not investigate the gas/particle partitioning coefficients (K_{SA}) of typical neutral PFASs.

As stated above, atmospheric deposition of PFASs is influenced mainly by their gas/particle partitioning, however, to our knowledge, there are very few studies dealing with the relation of the partitioning behaviors to physicochemical properties of atmospheric PFASs and their dry deposition fluxes (Wang et al., 2014). Moreover, the existing models are not suitable for predicting the gas/particle partitioning of neutral PFASs (Endo and Goss, 2014; Goss and Bronner, 2006). It therefore becomes the purpose of this study to (1) estimate the diffusive gas deposition and dry particle deposition fluxes of atmospheric PFASs collected from a seaside village Büsum in northern German coast; and (2) develop a model to predict the gas/particle partition coefficients of neutral PFASs using PP-LFERs.

2. Materials and methods

2.1. Air sampling, pretreatment and analysis

Detailed information on air sampling, pretreatment, analysis and quality control are presented elsewhere (Wang et al., 2014). Briefly, 58 air samples were collected at Büsum (54.13°N, 8.88°E) from August 3, 2011 to October 2, 2012, using a high-volume air sampler with a self-packed polyurethane foam (PUF)/XAD-2 cartridge for gas phase and a glass fiber filter (GFF) for particle phase. PUF/XAD-2 and GFF were extracted with Soxhlet apparatus using dichloromethane separately. Extracts were concentrated to 200 μ L and spiked with 1 ng 9:1 FTOH as internal standard. The 12 PFASs were quantified with an Agilent 6890 GC – 5973 MS equipped with an SUPELCO WAX® 10 column in selective ion monitoring (SIM) mode with positive chemical ionization (PCI) mode. Methane was used as reagent gas and helium as carrier gas at a flow rate of 1.3 mL/min. The names of the 12 PFASs are listed in Table 1.

2.2. Calculation of gas diffusive deposition and dry particle deposition fluxes

Detailed calculation process of gas diffusive deposition fluxes is presented in Supplementary Information (SI). Briefly, the gas diffusive deposition flux (F_{gas} , $\text{pg}/(\text{m}^2 \text{d})$) between gas and coastal water is calculated according to the Whitman two-layer model:

$$F_{\text{gas}} = K_{\text{OL}} (C_{\text{gas}}/H') \quad (1)$$

where K_{OL} is the total mass transfer coefficient (m/d), C_{gas} is the concentration of gas-phase PFASs (pg/m^3) and H' is the dimensionless, temperature-specific Henry law constant. K_{OL} comprises resistances to mass transfer across the air layer and the water layer (Schwarzenbach et al., 2003):

$$1/K_{\text{OL}} = 1/K_{\text{W}} + 1/K_{\text{A}}H' \quad (2)$$

where K_{A} and K_{W} (m/d) are the mass transfer coefficients across the air layer and water layer, respectively. K_{A} can be estimated with $K_{\text{A}} = k_{i,\text{H}_2\text{O}}(D_{i,\text{air}}/D_{\text{H}_2\text{O},\text{air}})^{0.67}$, where $k_{i,\text{H}_2\text{O}}$ (m/d) is related to compound i through H_2O , $D_{i,\text{air}}$ and $D_{\text{H}_2\text{O},\text{air}}$ are the diffusivities of

Table 1

Full name, CAS number, abbreviation, Henry constants (H) ($\text{Pa m}^3/\text{mol}$) at 25 °C of the 12 PFASs, and their fluxes of gas diffusive deposition, particle dry deposition and total (gas + particle) deposition ($\text{pg}/(\text{m}^2 \text{d})$) at Büsum in northern German coast.

Full name	CAS number	Abbr.	H	Gas deposition fluxes ^a			Particle deposition fluxes			Gas + particle fluxes			%Particle to Σ PFASs
				Mean	Std	%	Mean	Std	%	Mean	Std	%	
6:2 Fluorotelomer alcohol	647-42-7	6:2 FTOH	146	51	70	4.7	16	12	8.2	66	71	5.2	23.5
8:2 Fluorotelomer alcohol	678-39-7	8:2 FTOH	505	74	49	6.8	49	29	26.0	123	67	9.7	39.9
10:2 Fluorotelomer alcohol	865-86-1	10:2 FTOH	1598	4.1	2.6	0.4	25	12	13.4	29	13	2.3	86.0
12:2 Fluorotelomer alcohol	39239-77-5	12:2 FTOH	4728	0.4	0.3	0	23	14	11.9	23	14	1.8	98.2
6:2 Fluorotelomer acrylate	17527-29-6	6:2 FTA	16,685	0.02	0	0	6.4	6.2	3.4	6.4	6.2	0.5	99.6
8:2 Fluorotelomer acrylate	27905-45-9	8:2 FTA	121,985	0.01	0	0	5.4	5.0	2.9	5.4	5.0	0.4	99.8
N-methyl perfluorobutane sulfonamide	68298-12-4	MeFBSA	3.7	477	394	43.9	8.2	5.4	4.4	485	394	38.0	1.7
N-methyl perfluorooctane sulfonamide	31506-32-8	MeFOSA	50	14	9.8	1.3	5.6	3.1	3.0	20	11	1.6	28.5
N-ethyl perfluorooctane sulfonamide	4151-50-2	EtFOSA	38	12	7.8	1.1	4.3	2.5	2.2	17	8.5	1.3	25.4
N-methyl perfluorobutane sulfonamidoethanol	34454-97-2	MeFBSE	0.032	300	167	27.6	19	15	10.2	319	171	25.0	6.0
N-methyl perfluorooctane sulfonamidoethanol	24448-09-7	MeFOSE	0.44	118	61	10.8	16	6.4	8.7	134	62	10.5	12.3
N-ethyl perfluorooctane sulfonamidoethanol	1691-99-2	EtFOSE	0.47	37	35	3.4	11	8.7	5.7	48	37	3.8	22.6
		Σ PFAS _{flux}		1088	611		189	75		1277	627	14.8	

^a Std: standard deviation; %: percentage of the compound to Σ PFAS_{flux}.

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