



# *In situ* measurement-based partitioning behavior of perfluoroalkyl acids in the atmosphere

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## ABSTRACT

Environmental fate of ionizable organic pollutants such as perfluoroalkyl acids (PFAAs) are of increasing interest but has not been well understood because of uncertain values for parameters related with atmospheric interphase partitioning behavior. In the present study, not only the values for air-water partition coefficient ( $K_{AW}$ ) and dissociation constant ( $pK_a$ ) of PFAAs were induced by adjusting to *in situ* measurements of air-water distribution coefficient between vapor phase and rainwater but also gas-particle partition coefficients were also estimated using three-phase partitioning model of ionizable organic pollutants, *in situ* measurements of PFAAs in aerosol and air vapor phase, and obtained parameter values. The  $pK_a$  values of PFAAs we obtained were close to the minimum values suggested in literature except for perfluorooctane sulfonic acids, and COSMOtherm-modeled  $K_{AW}$  values were assessed to more appropriate among suggested values. When applying parameter values we obtained, it was predicted that air particle-associated fate and transport of PFAAs could be negligible and PFAAs could distribute ubiquitously along the transection from urban to rural region by pH-dependent phase transfer in air. Our study is expected to have some implications in prediction of the environmental redistribution of other ionizable organic compounds.

**Keywords:** Acidity, Fog, Inter-phase distribution, Ionizable organic pollutants, PFAAs,  $pK_a$

## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are global pollutants, which were listed as persistent organic pollutants (POPs) by the Stockholm Convention [1]. Once released into the environment, organic pollutants experience various phase-partitioning between solid phases (e.g., soil, sediment, air particle, and biota, etc.), water phase, and air vapor phase. Particularly, atmospheric fate and transport plays an important role to their redistribution among environmental compartments and long-range transport, as frequently mentioned as 'grasshopper effect' [2].

In atmosphere, the partitioning behavior of neutral PFASs such as fluorotelomer alcohols and perfluorooctane sulfonamidoethanols have been predicted comparatively easily using their two-phase partitioning coefficient (e.g., gas-particle partition) because of their

less soluble property [3, 4]. Acid PFAS group (perfluoroalkyl acids (PFAAs)) exist as the free acid form (i.e., neutral species) and their conjugate base form (i.e., ionic species) as shown in perfluoroalkyl carboxylic acids/carboxylates (PFCAs) or perfluoroalkane sulfonic acids/sulfonates (PFASAs) [5]. Differently from neutral PFASs, the environmental fate of PFAAs has been less known and is still in debate, which is related with the presence of both neutral and ionic species and the significant uncertainties in their physicochemical properties such as dissociation constant (i.e.,  $pK_a$ ) and air-water partition coefficient ( $K_{AW}$ ) [6-8].

PFAAs are dissociated into their ionic species when they meet the aqueous phase and in the typical aquatic pH conditions are known to exist as mostly ionic species, which is difficult to be volatilized [8]. Therefore, their airborne transport mechanism has been ignored for long time because PFAAs were considered to



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be rarely present in the atmosphere. Their presence observed in rain water, had not been well explained, was later attributed to the transformation of volatile and less soluble precursors (i.e., neutral PFASs) to soluble PFCAs and PFSAs [6, 7]. In our previous study [8], however these ionizable organic pollutants (i.e., PFCAs and PFSAs) were measured in rain samples as well as air samples such as gas- and particle-phases. Furthermore, gradually decreasing distribution pattern from source (urban) area to non-source (rural) area could not be explained by previous precursor-based transport mechanism [6, 7, 9]. Furthermore, elevated occurrence of PFAAs in surface runoff samples implicated that their redistribution among environmental compartments through air-water (or surface) partition might occur significantly [8, 10]. Since then, several studies also confirmed the presence of PFAAs in atmospheric compartments including aerosol and air vapor phases [11-13]. As a possible mechanism to account for the occurrence of PFAAs in atmosphere, McMurdo *et al.* [14] proposed "PFAAs enrichment in aerosol by the splashing of surface water and occurrence of gaseous PFAAs by gradual volatilization of water molecules". Thus, the redistribution of PFAAs through atmospheric transport can be more significant in coastal region or urban area with large human and/or industrial activities and large water body, considering that 1) surface water can be easily splashed into air by strong wind and wave, 2) their ionic species can exist abundantly in seawater (particularly, they can highly accumulate in the surface microlayer) [15], and additionally 3) fog can frequently be formed owing to difference of air-water temperature [16]. By redistribution process in the environment, human being may be exposed to these toxic substances through multiple pathways via drinking, food intake, dermal contact and inhalation [17, 18].

Differently from insoluble and neutral POPs, ionizable organic pollutants such as PFAAs distribute among three phases in atmosphere, including particle phase, vapor phase, and aqueous phase [11, 12, 14]. The redistribution of PFAAs among environmental compartments thus may be significantly influenced by the atmospheric three-phase distribution (or partitioning) behavior which strongly depends on the extent of their dissociation [19]. It is thus indispensable to use accurate values for the parameters related with their dissociation such as  $pK_a$ , solution pH, and water volume (e.g., relative humidity) in predicting their atmospheric inter-phase-partitioning behavior. Until recently, wide ranges of  $pK_a$  and  $K_{AW}$  (~10,000 times difference between minimum and maximum values) have been suggested (see references described in section 3.2). Uncertain parameter values could be significant factors amplifying the uncertainty in the prediction of atmospheric fate and transport, including air-water distribution coefficient ( $D_{AW}$ ), gas-particle partition coefficient ( $K_p$ ) dry/wet deposition, and long-range transport potential [12, 20-22].

The present work aimed 1) to estimate the reliable  $pK_a$  and  $K_{AW}$  values by adjusting  $t$  to *in situ*  $D_{AW}$  measured between air vapor phase and rainwater, 2) to induce  $K_p$  using *in situ* measured gas-aerosol partition coefficient ( $K_p$ ) and adjusted values for  $K_{AW}$  and  $pK_a$ , and finally 3) to predict their occurrence in each phase of atmosphere with variation of meteorological condition.

## 2. Materials and Methods

### 2.1. Sampling and Chemical Analysis

The present study focuses on the interpretation of the partition behavior of ionizable organic compounds such as PFAAs, based on our previous measurements [8]. Thus, only brief information on sampling of atmospheric phases was described here and the more details of sampling and chemical analysis were presented elsewhere [8].

In brief, three atmospheric phases (air gaseous and particulate phases, and rainwater) were collected at the Washington Park in downtown Albany, New York with a population of 96,000. The Washington Park (ca., total area of 360,000 m<sup>2</sup>) lake has a water surface area of  $2 \times 10^5$  m<sup>2</sup> and an average depth of 3 m (so, lake water volume = ~70,000 m<sup>3</sup>). All of the atmospheric samples were collected on the roof of a lake house building about ten meters above the surface of lake, located at the Washington Park. Gaseous and particulate phase of air ( $n = 8$ ) were collected from May to July, 2007 using a high-volume air sampler. PUF/XAD-2/PUF sandwich (Supelco, Bellefonte, PA) and quartz fiber filter (QMA, Whatman) were used to collect gaseous and particulate phases, respectively. The collected air samples were kept at 4°C with prior to analysis and were extracted with no desiccation in a few days after sampling. Desiccation of QMA can cause a removal of water phase on the filter and sequential volatilization of neutral species in water phase. Thus, no desiccation of QMA sample can prevent the potential loss of neutral species. Rainwater samples ( $n = 3$ ) of ~200 mL were collected in methanol-rinsed polypropylene bottles equipped with a funnel next to air sampler.

### 2.2. Partition Behavior of PFAAs Among Atmospheric Compartments

Once organic acids such as PFCAs and PFSAs are dissociated in aqueous phase, the acids (hereafter, neutral species) are in equilibrium with their conjugate base (hereafter, ionic species) as shown in an example of perfluorooctanoic acids (PFOA) Eq. (1-1) and (1-2). Such a dissolution yields the presence of both neutral species ( $C_7F_{15}COOH$ ) and ionic species ( $C_7F_{15}COO^-$ ) that strongly depends on their dissociation constants ( $pK_a$ ) and pH of aqueous phase as shown in Eq. (1)-(2).



$$\frac{[C_7F_{15}COO^-]}{[C_7F_{15}COOH]} = 10^{(pH - pK_a)} \quad (1-2)$$

Typically atmosphere consists of aerosol phase (air particle phase and water droplet phase) and air vapor phase. As POPs, well known as representative neutral organic compounds, are rarely water soluble, their  $K_p$  can be well modeled using a two-phase (i.e., air vapor-particle) sorption equation where a water droplet phase of aerosol can be ignored [23]. However, PFAAs can be present in all of three phases and then their speciation in vapor and water phases should be quantified in advance, being expressed by  $D_{AW}$

(dimensionless) incorporating both neutral and ionic species as shown in Eq. (2).

$$D_{AW} = \frac{K_{AW}}{1 + 10^{(pH - pKa)}} \quad (2)$$

where  $D_{AW}$  indicates the ratio of the concentration of neutral species in air vapor to the total concentration of neutral and ionic species in aqueous phase at the given solution pH. The  $K_{AW}$  is the air-water partition coefficient of neutral species ( $\text{m}^3_{\text{water}}/\text{m}^3_{\text{airvapor}}$ ).

Gas-particle partitioning can be quantified on basis of the measured concentrations as expressed in Eq. (3), in which the term of  $C_p'$  (unit;  $\text{mol}/\text{m}^3$ ) indicates the measured concentrations of all PFAA species present on aerosol that is a sum of neutral species adsorbed on particle, neutral species in water phase, and ionic species in water phase, and the denominator ( $C_A$ ;  $\text{mol}/\text{m}^3$ ) indicates the measured concentration of neutral PFAA species present in vapor phase.

$$K_p' = \frac{(C_p' / TSP)}{C_A} \quad (3)$$

where  $TSP$  is the mass concentration of total suspended particulate matter in air ( $\mu\text{g}/\text{m}^3_{\text{air}}$ ). Although  $K_p'$  based on the measured  $C_p'$  and  $C_A$  indicates TSP-normalized partition coefficient, PFAAs on aerosol ( $C_p'$ ) include both neutral and ionic species in aerosol (i.e., particle-phase and water-phase) and then can vary with the volume of water phase (i.e., relative humidity). Therefore, it is necessary to convert  $K_p'$  to the gas-particle partition coefficient

independent on the volume of water-phase ( $K_p$ ), which is known to be a conventional gas-particle partition coefficient for insoluble organic pollutants.

Contrary to  $K_p'$ , the  $K_p$  is defined as the partitioning coefficient between air vapor and particle for the neutral species alone. Meanwhile, it is difficult to isolate and measure solely neutral species adsorbed on particle-phase because both neutral and ionic species exist together in aerosol consisting of particle and water-phase. Furthermore neutral species can be lost via evaporation when filter paper is desiccated. Alternatively, the  $K_p'$  can be converted to  $K_p$  by multiplied by the fraction of particle-adsorbed neutral species to total species in aerosol ( $\alpha_{\text{neutral on particle}}$ ) as given by the following expression:

$$K_p \left( = \frac{C_p / TSP}{C_A} \right) = K_p' \alpha_{\text{neutral on particle}} \quad (4-1)$$

$$\begin{aligned} \alpha_{\text{neutral on particle}} &= \frac{C_{\text{neutral on particle}} (= C_p)}{C_{\text{total aerosol}} (= C_p')} \\ &= \frac{C_{\text{neutral on particle}}}{C_{\text{neutral on particle}} + C_{\text{neutral in water}} + C_{\text{ionic in water}}} \end{aligned} \quad (4-2)$$

Likewise, the fractions of neutral species adsorbed on the air particle ( $\alpha_{\text{neutral on particle}}$ ), neutral species dissolved in water phase ( $\alpha_{\text{neutral in water}}$ ), ionic species in water phase ( $\alpha_{\text{ionic in water}}$ ), and neutral species in air vapor ( $\alpha_{\text{neutral in air vapor}}$ ) in total air which consist of gaseous, particulate, and water phases can be calculated as follows:

$$\alpha_{\text{neutral on particle}} = \frac{C_{\text{neutral on particle}} TSP}{(C_{\text{neutral on particle}} TSP + C_{\text{neutral in water}} V_{W\_rH} + C_{\text{ionic in water}} V_{W\_rH}) + C_{\text{neutral in air vapor}} V_{\text{air vapor}}} \quad (5-1)$$

$$\alpha_{\text{free acid in water droplet}} = \frac{C_{\text{neutral in water}} V_{W\_rH}}{(C_{\text{neutral on particle}} TSP + C_{\text{neutral in water}} V_{W\_rH} + C_{\text{ionic in water}} V_{W\_rH}) + C_{\text{neutral in air vapor}} V_{\text{air vapor}}} \quad (5-2)$$

$$\alpha_{\text{anion in water droplet}} = \frac{C_{\text{ionic in water}} V_{W\_rH}}{(C_{\text{neutral on particle}} TSP + C_{\text{neutral in water}} V_{W\_rH} + C_{\text{ionic in water}} V_{W\_rH}) + C_{\text{neutral in air vapor}} V_{\text{air vapor}}} \quad (5-3)$$

$$\alpha_{\text{free acid in air vapor}} = \frac{C_{\text{neutral in air vapor}} V_{\text{air vapor}}}{(C_{\text{neutral on particle}} TSP + C_{\text{neutral in water}} V_{W\_rH} + C_{\text{ionic in water}} V_{W\_rH}) + C_{\text{neutral in air vapor}} V_{\text{air vapor}}} \quad (5-4)$$

where  $C_{\text{neutral on particle}}$ ,  $C_{\text{neutral in water}}$ ,  $C_{\text{ionic in water}}$ , and  $C_{\text{neutral in air vapor}}$  are the concentrations of neutral species adsorbed on air particle ( $\text{mol}/\mu\text{g}_{\text{air particle}}$ ), neutral species dissolved in water phase of air ( $\text{mol}/\text{m}^3_{\text{water phase of air}}$ ), ionic species dissolved in water phase of air ( $\text{mol}/\text{m}^3_{\text{water phase of air}}$ ), and neutral species in air vapor phase ( $\text{mol}/\text{m}^3_{\text{air vapor}}$ ), respectively. The  $V_{W\_rH}$  and  $V_{\text{air vapor}}$  indicate

the volume of water phase ( $\text{m}^3_{\text{water droplet}}/\text{m}^3_{\text{air}}$ ) at a given relative humidity (rH) and the volume of air vapor phase ( $\text{m}^3_{\text{air vapor}}/\text{m}^3_{\text{air}}$ ) in an unit air volume ( $V_{\text{air}}$ ;  $1 \text{ m}^3_{\text{air}}$ ), respectively. Strictly speaking total air volume is the sum of the volumes of air vapor ( $V_{\text{air vapor}}$ ), air water ( $V_{W\_rH}$ ), and air particle ( $V_{\text{air particle}}$ ), but practically  $V_{\text{air}} (= 1 \text{ m}^3) \cong v_{\text{air vapor}}$  because the fraction of  $V_{W\_rH}$  and  $V_{\text{air particle}}$

account for just  $10^{-5}$  (at relative humidity = 50%) and  $10^{-11}$  (at a typical TSP =  $60 \mu\text{g}/\text{m}^3$ ), respectively. Dividing Eq. (5-1) to (5-4) by  $C_{\text{neutral in water}} V_{W_{rH}}$  yields

$$\alpha_{\text{neutral on particle}} = \frac{K_{PW} \left( \frac{TSP}{V_{W_{rH}}} \right)}{K_{PW} \left( \frac{TSP}{V_{W_{rH}}} \right) + 1 + 10^{(pH-pKa)} + K_{AW} \left( \frac{V_{air}}{V_{W_{rH}}} \right)} \quad (6-1)$$

$$\alpha_{\text{neutral in water droplet}} = \frac{1}{K_{PW} \left( \frac{TSP}{V_{W_{rH}}} \right) + 1 + 10^{(pH-pKa)} + K_{AW} \left( \frac{V_{air}}{V_{W_{rH}}} \right)} \quad (6-2)$$

$$\alpha_{\text{ionic in water droplet}} = \frac{10^{(pH-pKa)}}{K_{PW} \left( \frac{TSP}{V_{W_{rH}}} \right) + 1 + 10^{(pH-pKa)} + K_{AW} \left( \frac{V_{air}}{V_{W_{rH}}} \right)} \quad (6-3)$$

$$\alpha_{\text{neutral in air vaopr}} = \frac{K_{AW} \left( \frac{V_{air}}{V_{W_{rH}}} \right)}{K_{PW} \left( \frac{TSP}{V_{W_{rH}}} \right) + 1 + 10^{(pH-pKa)} + K_{AW} \left( \frac{V_{air}}{V_{W_{rH}}} \right)} \quad (6-4)$$

where  $K_{PW}$  is the particle-water partition coefficient (unit;  $\text{m}^3/\mu\text{g}$ ) which is frequently used to explain partitioning between sediment and water in aquatic system. The  $K_{PW}$  is associated with organic carbon-water partition coefficient ( $K_{OC}$ ) or octanol-water partition coefficient ( $K_{OW}$ ) as shown in Eq. (7).

$$K_{PW} = \beta f_{OC} K_{OC} = \beta f_{OC} (0.41 K_{OW}) \quad (7)$$

where  $\beta$  is a correction factor ( $= 10^{12}$ ) to match the units of  $K_{PW}$  ( $\text{m}^3/\mu\text{g}$ ) and  $K_{OC}$  (L/kg). The  $f_{OC}$  is the fraction of organic carbon in particle (dimensionless) and 0.2 was used for  $f_{OC}$  of air particle [24, 25].

Again, the fractions of individual-phase of neutral and ionic species in aerosol are induced from Eq. (6-1) to (6-4) and can be obtained as follows:

$$\alpha_{\text{neutral on particle}}' = \frac{\beta f_{OC} K_{OC} \left( \frac{TSP}{V_{W_{rH}}} \right)}{\beta f_{OC} K_{OC} \left( \frac{TSP}{V_{W_{rH}}} \right) + 1 + 10^{(pH-pKa)}} \quad (8-1)$$

$$\alpha_{\text{neutral on water droplet}}' = \frac{1}{\beta f_{OC} K_{OC} \left( \frac{TSP}{V_{W_{rH}}} \right) + 1 + 10^{(pH-pKa)}} \quad (8-2)$$

$$\alpha_{\text{neutral on water droplet}}' = \frac{10^{(pH-pKa)}}{\beta f_{OC} K_{OC} \left( \frac{TSP}{V_{W_{rH}}} \right) + 1 + 10^{(pH-pKa)}} \quad (8-3)$$

where we used the relationship of  $K_{OC} = 0.41 K_{OW}$  [26].

### 3. Results and Discussion

#### 3.1. PFAAs Measured in Atmospheric Compartments

Mean concentrations of PFAAs used for atmospheric partitioning of this study were listed in Table 1. Of six PFCAs, PFOA was the most prevalent compound which was detected in all samples of air vapor (n = 8), air particle (n = 8), and rainwater (n = 3). Perfluoroheptanoic acids (PFHpA), perfluorononanoic acids (PFNA), perfluorodecanoic acids (PFDA) were detected above LOQ in all samples except for only one air particle sample, two air particle samples, and one rainwater sample, respectively. More highly fluorinated PFCAs, perfluoroundecanoic acid (PFUnDA) and perfluorododecanoic acid (PFDoDA), were less frequently detected. Particularly, air particle samples did not contain any detectable

**Table 1.** Concentrations of PFAAs Measured in Atmospheric Compartments

	Air vapor (mol/m <sup>3</sup> )	Air particle (mol/μg)	Rain water (mol/m <sup>3</sup> )
PFHpA	7.2E-16 ± 3.1E-16	1.5E-17 ± 8.6E-18	1.5E-09 ± 9.1E-11
PFOA	7.6E-15 ± 3.8E-15	6.6E-17 ± 2.7E-17	6.7E-09 ± 3.9E-10
PFNA	4.6E-16 ± 1.0E-16	5.0E-18 ± 2.7E-18	3.0E-09 ± 4.8E-10
PFDA	1.2E-15 ± 8.7E-16	8.2E-18 ± 6.5E-18	2.2E-09 ± 3.4E-12
PFUnDA	–	–	1.0E-09 ± 1.7E-10
PFDoDA	4.4E-16 ± 1.4E-16	1.0E-17 ± 7.0E-18	9.3E-10 ± 0.0E+00
PFHS	7.7E-16 ± 2.5E-16	–	–
PFOS	3.4E-15 ± 1.4E-15	1.9E-17 ± 9.8E-18	1.9E-09 ± 6.6E-10
PFDS	–	3.1E-18 ± 1.0E-18	5.6E-10 ± 0.0E+00
PFOSA	1.3E-15 ± 1.4E-15	1.0E-17 ± 6.2E-18	–

PFAS concentration include neutral and ionic species. Values < LOQ was treated to 'zero'.

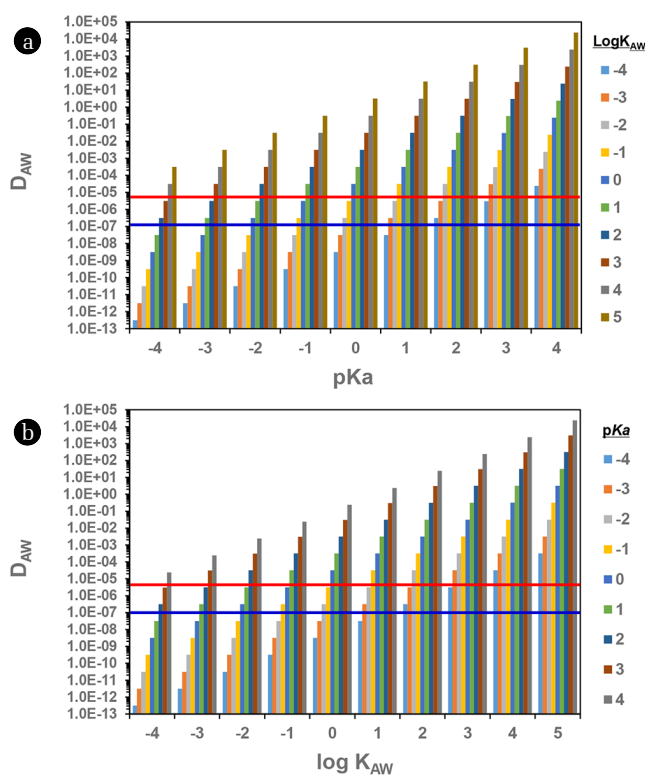
level of PFUnDA and contained PFDoDA above LOQ in only two samples. This may be attributable to rare occurrence of the highly fluorinated compounds in atmosphere. Otherwise, a relatively high particle-phase concentration would have been observed considering their relatively high octanol-air partition coefficients ( $K_{OA}$ ) compared with C7-C10 PFCAs.

Of four PFSA, perfluorooctanesulfonic acid (PFOS) was also predominantly found in three atmospheric phases. The other PFSA were not at all detected at least one of three phases; that is, perfluorohexanesulfonic acid (PFHS) in air particles and rainwater, perfluorodecanesulfonic acid (PFDS) in air vapors, and perfluorooctane sulfonamide (PFOSA) in rainwaters were not detected. Thus, it was not allowed to calculate their  $D_{AW}$  values and to predict their  $pK_a$  for the three PFSA.

### 3.2. Estimation of $pK_a$ from Observed $D_{AW}$

As mentioned earlier, the partitioning of PFAAs among atmospheric compartments strongly depends on their  $pK_a$  and  $K_{AW}$  and solution pH (Eq. (1)-(8)). A pH of 4.5 was used for a typical rainwater and air water phase on the basis of the meteorological data measured at urban area including northeastern states of US and Canada [11, 27]. For  $pK_a$ , a number of values for PFAAs have been suggested so far, which were estimated theoretically [28, 29], calculated from computational approach using software COSMO-RS [30, 31] and SPARC [32], or measured from laboratory experiment [33-35]. The suggested  $pK_a$  values ranged from -0.21 to 3.8 for PFOA and from -3.3 to 0.14 for PFOS (Table 2). Various two-phase partition coefficients including  $K_{AW}$ ,  $K_{OW}$ , and  $K_{OA}$  have been also estimated from molecular structure (i.e., quantitative structure-activity relationships) using a variety of tools such as U.S. EPA's EPI Suite, ClogP, SPARC, and COSMOtherm [36]. According to previous results (see the literature in Table 2), those QSAR-based models produced the partition coefficients that differed more than three orders of magnitude: for instance,  $\log K_{AW} = -2.37$  (COSMOtherm) to 0.57 (EPI Suite) for PFOA and -2.40 (COSMOtherm) to -0.35 (EPI Suite) for PFOS. Recently, Kim *et al.* [37] who used molar volume as a molecular descriptor suggested  $K_{AW}$  values greater than 10 times than the maximum values suggested by previous QSAR-based models (Table 2).

Such wide ranges of  $pK_a$  and  $K_{AW}$  (~10,000 times difference between minimum and maximum values) could be significant fac



**Fig. 1.** Dependency of  $D_{AW}$  on  $pK_a$  and  $K_{AW}$ . The red and blue solid lines indicate the maximum and minimum value of observed  $D_{AW}$  (see Table 3).

tors enlarging the uncertainty in the prediction of atmosphere-associated fate and transport including  $D_{AW}$ ,  $K_p$ , dry/wet deposition, and long-range transport potential [12, 20-22]. To cover all PFAAs, we tested the sensitivity of  $D_{AW}$  with varying  $pK_a$  (-4 to 4) and  $K_{AW}$  ( $10^{-4}$  to  $10^5$ ) suggested (Fig. 1). At a given  $pK_a$ , the  $D_{AW}$  value increases proportionally to 1:1 as  $K_{AW}$  value increase. The suggested  $K_{AW}$  range ( $\log K_{AW} = -2.37$  to 2.57 for PFOA and -2.4 to 3.29 for PFOS) produced the differences of  $10^4$  and  $10^5$  for  $D_{AW}$ , respectively. Similarly,  $D_{AW}$  value at a given  $K_{AW}$  increased in proportion to the increment of  $pK_a$ ; that is, the  $pK_a$  ranging from -4 to 4 yielded the variation of

**Table 2.** Physicochemical Properties for Fate of PFAAs Recommended in Literature

PFASs	pKa		Log KAW				Log KOW			Log KOC		
	value	refs.	COSMO-therm	Ref.	QSAR	Ref.	COSMO-therm	Ref.	QSAR	refs.	Sorption test	refs.
PFHpA	-0.2 – 3.8	[11, 28, 29, 43-45]	-2.66	[36]	2	[37]	3.82	[36]	1.19	[37]	2.1	[47]
PFOA	-0.21 – 3.8	[11, 28, 29, 43-45]	-2.37	[36]	2.57	[37]	4.3	[36]	1.79	[37]	2.11	[48]
PFNA	-0.21 – 2.575	[11, 28, 29, 43]	-2.03	[36]	3.14	[37]	4.84	[36]	2.4	[37]	2.5	[48]
PFDA	-0.42 – 2.606	[11, 28, 29, 43]	-1.79	[36]	3.7	[37]	5.3	[36]	3	[37]	2.92	[48]
PFUnDA	-0.39 – 3.128	[11, 28, 29, 43]	-1.52	[36]	4.18	[37]	5.76	[36]	3.51	[37]	3.47	[48]
PFDoDA	-0.87 – 3.2	[11, 28, 29]	-0.58	[46]	4.84	[37]	6.41	[36]	4.21	[37]	4.7	[47]
PFOS	-3.3 – 0.14	[11, 45]	-2.4	[36]	3.29	[37]	5.25	[36]	2.56	[37]	2.68	[48]

**Table 3.** Estimated pKa from Observed  $D_{AW}$  of PFAAs between Air Vapor and Rainwater

	Measured $D_{AW}$				Estimated pKa	
	Median	Average	Min	Max	This study	SPARC <sup>a</sup>
PFHpA	4.2E-07	3.8E-07	1.3E-07	8.4E-07	0.75	-0.20
PFOA	1.1E-06	1.2E-06	6.3E-07	3.0E-06	0.96	-0.21
PFNA	1.1E-07	1.4E-07	7.9E-08	5.0E-07	-0.31	-0.21
PFDA	4.9E-07	5.6E-07	2.1E-07	1.4E-06	0.04	-0.22
PFUnDA	2.7E-07	2.6E-07	1.9E-07	3.9E-07	-0.55	-0.22
PFDoDA	4.7E-07	4.8E-07	2.5E-07	7.5E-07	-1.24	-0.22
PFOS	1.5E-06	1.8E-06	6.3E-07	8.4E-06	1.16	0.14

<sup>a</sup> pKa estimated using SPARC (requoted from [11]).

eight orders of magnitude in  $D_{AW}$  value. This implied again that the use of the more accurate values for pK<sub>a</sub>, pH and K<sub>AW</sub> could be very important.

In the present study, we induced more reasonable values for K<sub>AW</sub> and pK<sub>a</sub> from  $D_{AW}$  values which were calculated from PFAA concentrations measured in air vapor and rainwater. In calculating  $D_{AW}$  ( $= C_{air\ vapor} / C_{rainwater}$ ), it was assumed that the solely neutral species in air vapor phase and both neutral and ionic species in rainwater were present because the ionic species are nonvolatile: for example, log K<sub>AW</sub> of PFOA is -2.37 for neutral species (at suggested minimum value) versus -6.5 for ionic species [38]. The measured  $D_{AW}$  values in this study ranged from  $7.9 \times 10^{-6}$  to  $8.4 \times 10^{-6}$  as for all investigated PFAAs (Table 3). When based on measured  $D_{AW}$ , thus log K<sub>AW</sub> values should be within -4.0 to 0 for PFOA and -2 to 2 for PFOS as for their suggested pK<sub>a</sub> ranges. This indicated that at least the maximum values of K<sub>AW</sub> which were suggested by Kim *et al.* [37] would be not supported by our measurement. Two laboratory studies reported the K<sub>AW</sub> values of 0.001 [39] and 0.004-0.007 [40], which were a good agreement with COSMOtherm-modeled data within less than an order of magnitude. So, the COSMOtherm-modeled values [36] were used for K<sub>AW</sub> values of individual PFAAs in this study in order to maintain systematic consistency among the estimates of K<sub>AW</sub>. As the next step, we adjusted pK<sub>a</sub> values (at COSMOtherm-based K<sub>AW</sub> and pH = 4.5) to produce the best fitting (within  $\pm 1\%$ ) to the measured  $D_{AW}$  (Table 3). The estimated pK<sub>a</sub> values in this study were close to the minimum values of previously suggested values except for PFOS which was greater than the suggested maximum value but were slightly higher than the estimates of SPARC.

Under the typical atmospheric condition (relative humidity = 50% and TSP = 60  $\mu\text{g}/\text{m}^3$ ), the combination of the adjusted pK<sub>a</sub> values and the minimum K<sub>AW</sub> values suggested in literature predicted the 25% and 75% of PFOA and 33% and 67% of PFOS in air vapor and water phase, respectively. On the other hand, the use of the maximum value of suggested K<sub>AW</sub>s yielded the presence of almost 100% of PFOA and PFOS in air vapor phase. Similarly, the major phase of PFAA might significantly change within the suggested pK<sub>a</sub> range of -0.21 to 3.8 for PFOA and -3.3 to -0.14 for PFOS. For instance, it was predicted under the same typical condition with their adjusted K<sub>AW</sub>s that the majority of atmospheric

PFOA and PFOS might exist in water phase when their minimum pK<sub>a</sub> values were applied while 99% of PFOA and 4.5% of PFOS in atmosphere might exist in air vapor phase when their maximum pK<sub>a</sub> values were used. Again, this indicated that use of inappropriate values for pK<sub>a</sub> and K<sub>AW</sub> would cause significant errors in prediction of partitioning among three phases and related fate and transport.

### 3.3. Estimation of $K_p$ from Measured $K_p'$

The  $K_p'$  was calculated using Eq. (3) from TSP-normalized total concentrations (a sum of neutral and ionic species) measured from aerosol and the concentration measured from air vapor phase (i.e., gaseous concentration of neutral species). The log  $K_p'$  values measured in this study, ranging from  $-2.27 \pm 0.26$  for PFOS to  $-1.65 \pm 0.47$  for PFDoDA, were in very good agreement with log  $K_p'$  values measured at a semi-urban location in Toronto, Canada [11] and at Lake Chaohu, China [13] (Table 4). It is particularly noticeable that the log  $K_p'$  values we obtained most closely matched the values measured by annular diffusion denuder sampler used to avoid the sampling artifacts [11].

According to Eq. (4) and (8-1), the  $K_p$  can be induced by multiplying  $K_p'$  and the fraction of neutral species on air particle to all species in aerosol ( $\alpha_{neutral\ on\ particle}$ ). Our log  $K_p$  values ranged from  $-8.28 \pm 0.27$  (for PFNA) to  $-6.66 \pm 0.23$  (for PFOS). Contrary to  $K_p'$ , the  $K_p$  values showed the differences by an order of magnitude between different studies (Table 4). Unfortunately, Ahrens *et al.* [11] used the fraction of neutral species in water phase to all species in water phase instead of  $\alpha_{neutral\ on\ particle}$ . So, the difference between measured  $K_p$  values may originate from the equation error. Use of different pK<sub>a</sub> values, for which SPARC-modeled value was used in in Ahrens *et al.* [11], can be another possible cause of  $K_p$  difference.

### 3.4. Dependency of Atmospheric Fate on pH and Relative Humidity

A pH of 4.5, a typical value measured at urban area, was used in this study. Acid rain monitoring showed the variation of pH of 3.2-5.4 in the study area [27, 41]. Rain pH can be changed by acid-causing gases (ACGs) like SO<sub>2</sub>, NO<sub>x</sub>, and CO<sub>2</sub> as well as

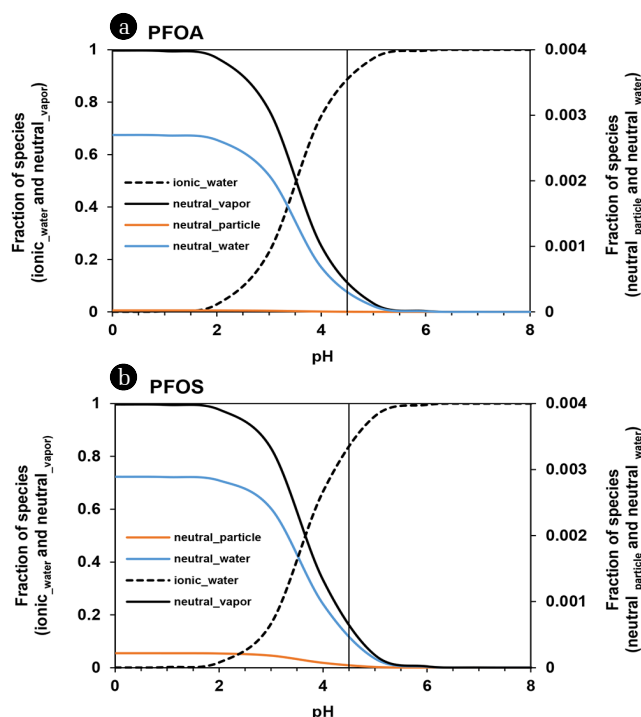
**Table 4.** Measured Gas-particle Partition Coefficients (Log  $K_p'$  versus Log  $K_p$ )

	Log $K_p'$ ( $m^3/g$ )				Log $K_p$ ( $m^3/g$ )			
	This study		[11] <sup>a</sup>	[13] <sup>a</sup>	This study		[11] <sup>a</sup>	
PFHpA	-1.66	± 0.33	–	-1.67	-7.88	± 0.36 (0.75) <sup>b</sup>	–	–
PFOA	-2.05	± 0.26	-2.43	-1.34	-7.59	± 0.26 (0.96)	-7.14	± 0.3 (-0.21)
PFNA	-2.00	± 0.28	-2.31	-1.89	-8.28	± 0.27 (-0.31)	-7.02	± 0.5 (-0.21)
PFDA	-2.17	± 0.40	-2.26	-1.58	-7.63	± 0.32 (0.04)	-7.08	± 0.6 (-0.22)
PFUnDA	–	–	-1.59	-1.64	–	–	-6.31	± 0.3 (-0.22)
PFDODA	-1.65	± 0.47	-1.75	-1.49	-7.40	± 0.29 (-0.55)	-6.53	± 0.6 (-0.22)
PFBS	–	–	-2.30	-2.52	–	–	-1.90	± 0.4 (0.14)
PFHS	–	–	–	-1.59	–	–	–	–
PFOS	-2.27	± 0.26	-1.42	-1.91	-6.66	± 0.23 (1.16)	-5.78	± 0.3 (0.14)

<sup>a</sup> cited literature; <sup>b</sup> values in parentheses indicate  $pK_a$  used.

by particulate matter (PM), causing large variation as shown evidently in observed pH values (from < 4.5 to 7.5) [42].

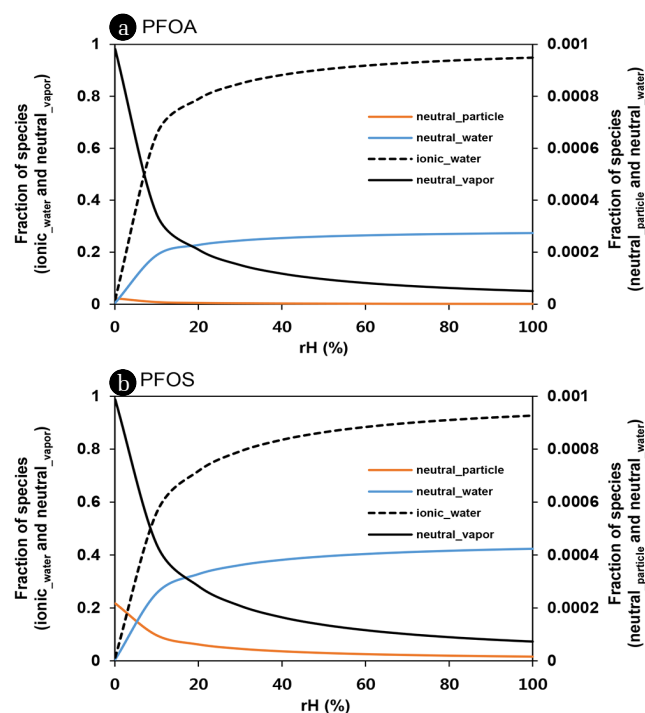
Fig. 2 shows the pH-dependence of the occurrence of PFAAs in each of three phases. Under the meteorological condition of  $rH = 50\%$  and  $TSP = 60 \mu g/m^3$ , the  $pH = 4.5$  yielded that > 90% of individual PFCAs (90% of PFOA) and 86% of PFOS might exist in water phase, 0.2-10% of PFCAs (10% of PFOA) and 14% of PFOS in vapor phase, and < 1% of PFCAs and PFOS in particle phase. The water phase fraction of PFAAs, mostly ionic species, can increase with increment of pH and then reach more than 99%



**Fig. 2.** Fraction of neutral and ionic species of PFOA (a) and PFOS (b) adsorbed on air particle, in air vapor, and in water phase with pH values. A vertical solid line indicates  $pH = 4.5$ .

above  $pH = 6.0$ . It was predicted that drastic change in the fraction of PFAAs could occur in the lower pH condition. At  $pH = \sim 3.5$  and  $\sim 3.7$ , a half of PFOA and PFOS may exist in vapor phase and another half in water phase. More acidified condition (i.e., more severe atmospheric pollution by ACGs) can cause the prevalent vapor phase (> 99%) of PFOA at  $pH = 1.3$  and of PFOS at  $pH = 1.5$ . Consequently, PFAAs in ACG-polluted air of urban/industrial area, i.e., at low pH air condition, can be moved via gaseous diffusion and wind-driven gaseous transport to other region and then can reside more shortly in the environmental system of the emitted region. On the other hand, PFAAs in rural area, of which air may be less polluted by ACGs and then be at relatively high pH (mostly, >  $\sim 5.4$ ), can reside much longer in the environment of the domain system because the majority of individual PFAAs may exist in water phase (e.g., clouds and fogs) and can fall down via deposition of atmospheric water (e.g., rainfall and snow). Moreover it is difficult for deposited PFAAs to be evaporated considering the higher pH condition of freshwater ( $pH = \sim 7.5$ ) where non-volatile ionic species may exist exclusively. In short, PFAAs can distribute ubiquitously and relatively uniformly from urban to rural regions by their pH-dependent atmospheric fate.

The volume of atmospheric water is extremely variable in time and space with the meteorological condition. Dependency of phase fractions of each species on relative humidity was presented in Fig. 3. Increase of relative humidity is inevitably associated with increasing occurrence of PFAA in water phase. In > 40% of  $rH$ , the most of PFOA and PFOS (i.e., > 80%) may exist in atmospheric water phase. However, the more than 1% of PFAAs (e.g., 5% of PFOA and 7% of PFOS) can be still present as a neutral species in vapor phase even in water-saturated condition such as fog. Vapor phase fraction of PFOA and PFOS may be more abundant below 5% and 8% of  $rH$ , respectively. More fluorinated PFCAs (> C10 PFCAs) were predicted to exist mostly in a vapor phase (> 50%) under the perfectly dried condition (< 2% of  $rH$ ). Air particle-phase of PFAA accounted for < 0.1% in any cases with  $rH$  variation and exceeded 1% only for an extreme condition such as  $TSP = 5,000 \mu g/m^3$  and  $rH = 0\%$ . This indicates that dry deposition and rain scavenging of particle-adsorbed PFAAs are likely negligible.



**Fig. 3.** Fraction of neutral and ionic species of PFOA (a) and PFOS (b) adsorbed on air particle, in air vapor, and in water phase with relative humidity.

## 4. Conclusions

Environmental fate of ionizable organic pollutants such as PFAAs strongly depends on their water-phase associated physicochemical properties such as  $pK_a$ , pH, and  $K_{AW}$ . So far a wide range of values for the parameters ( $\sim 10,000$  times difference between minimum and maximum values of  $pK_a$  and  $K_{AW}$ ) have been suggested, could be significant factors enlarging the uncertainty in the prediction of atmosphere-associated fate and transport including  $D_{AW}$ ,  $K_p$ , dry/wet deposition, and long-range transport potential. The result of our sensitivity analysis showed that the major phase of PFAAs present in atmosphere could significantly change within the range of suggested values for the parameters, indicating that the accurate values for the parameters are essential in assessing atmospheric and sequential fate. So, we induced the  $pK_a$  and  $K_{AW}$  values by adjusting to *in situ* measurements of  $D_{AW}$  between air vapor phase and rainwater, and estimated  $K_p$  of PFAAs using *in situ* measured gas-aerosol partition coefficient and obtained parameter values.

Our study is expected to have some implications in prediction of the environmental redistribution of other ionizable organic compounds since the atmospheric three-phase partitioning of ionizable organic pollutant is strongly associated with their redistribution among environmental compartments via volatilization, dry/wet deposition, rainfall scavenging, advection, and sorption to terrestrial surface. The redistribution of ionizable organic pollutants through atmospheric fate can be of particular importance in the coastal region where those pollutant can move backward, i.e., from the

sea to the land. Our study will be helpful to understand such a fate of ionizable organic pollutants.

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