Supplementary information of "Exploring controls on perfluorocarboxylic acid (PFCA) gas-particle partitioning using a model with observational constraints"

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This part includes: comparison of the different Log Korganic/water values modeled by different models and proxies (Figure S1), chemical structure of water-insoluble organic matter TermB (Figure S2), the modeled temperature dependence and salt effect of phase partitioning equilibrium constants (Figure S3), modeled particle phase fraction of C10-C16 as a function of organic matter mass loadings (Figure S4), comparison between the modeled particle phase fraction ranges and several observation results that sampled particles prior to gas phase removal (Figure S5), a summary of the modeling results and literature values for the thermodynamic parameters (Table S1), a summary of the sampling information of the studies used for detailed phase partitioning analysis (Table S2), and a description of the reference chemical composition and acidity of PM from the five representative studies (Section 1).

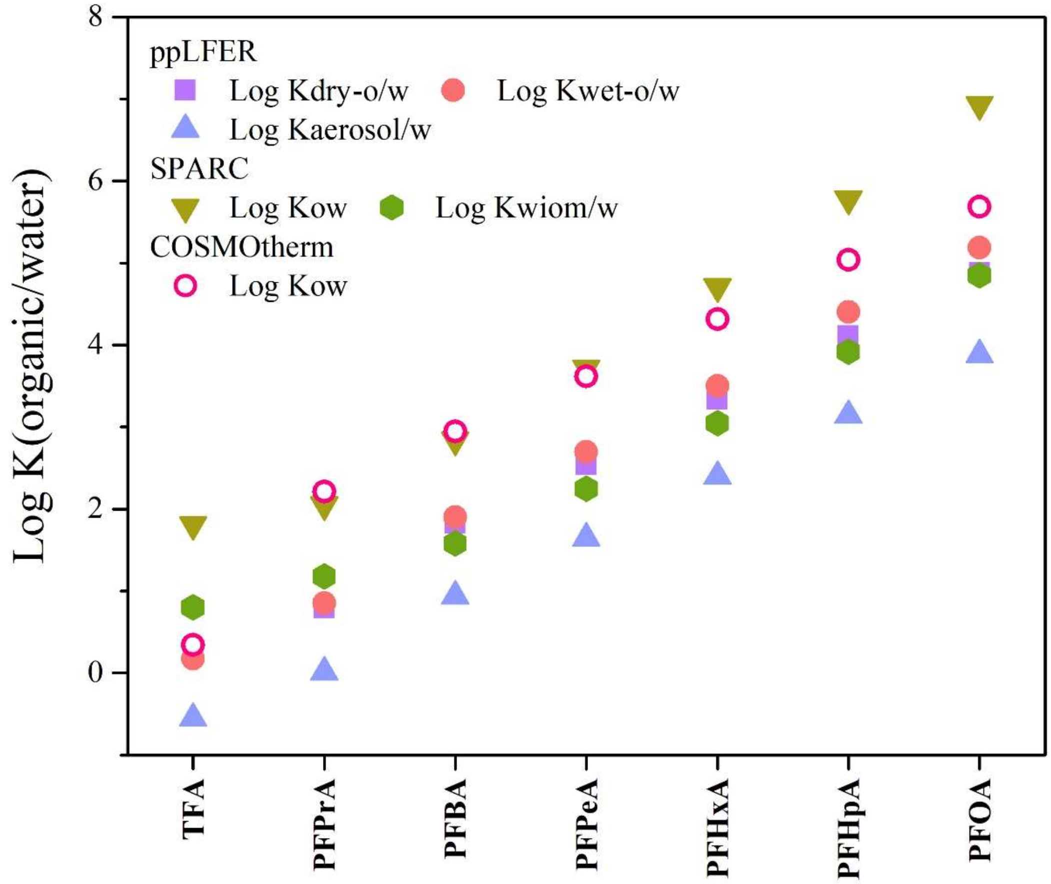
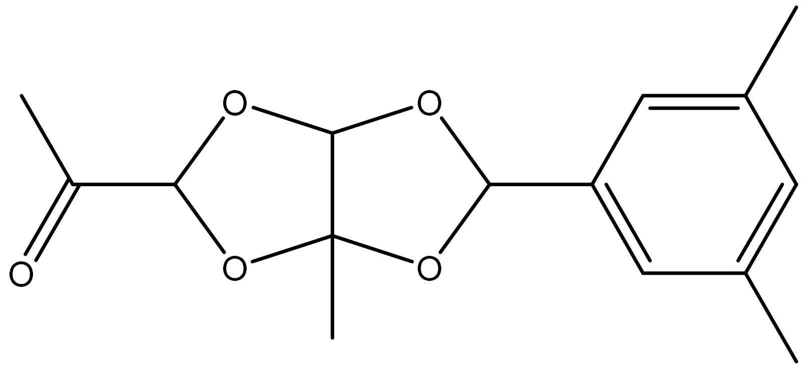


Figure S1. Comparison of the different logK$_{organic/water}$ values using different models and proxies.



Water-insoluble organic matter TermB

Figure S2. Chemical structure of the water-insoluble organic matter TermB as a proxy for particulate organic matter used in the phase partitioning thermodynamic modeling.

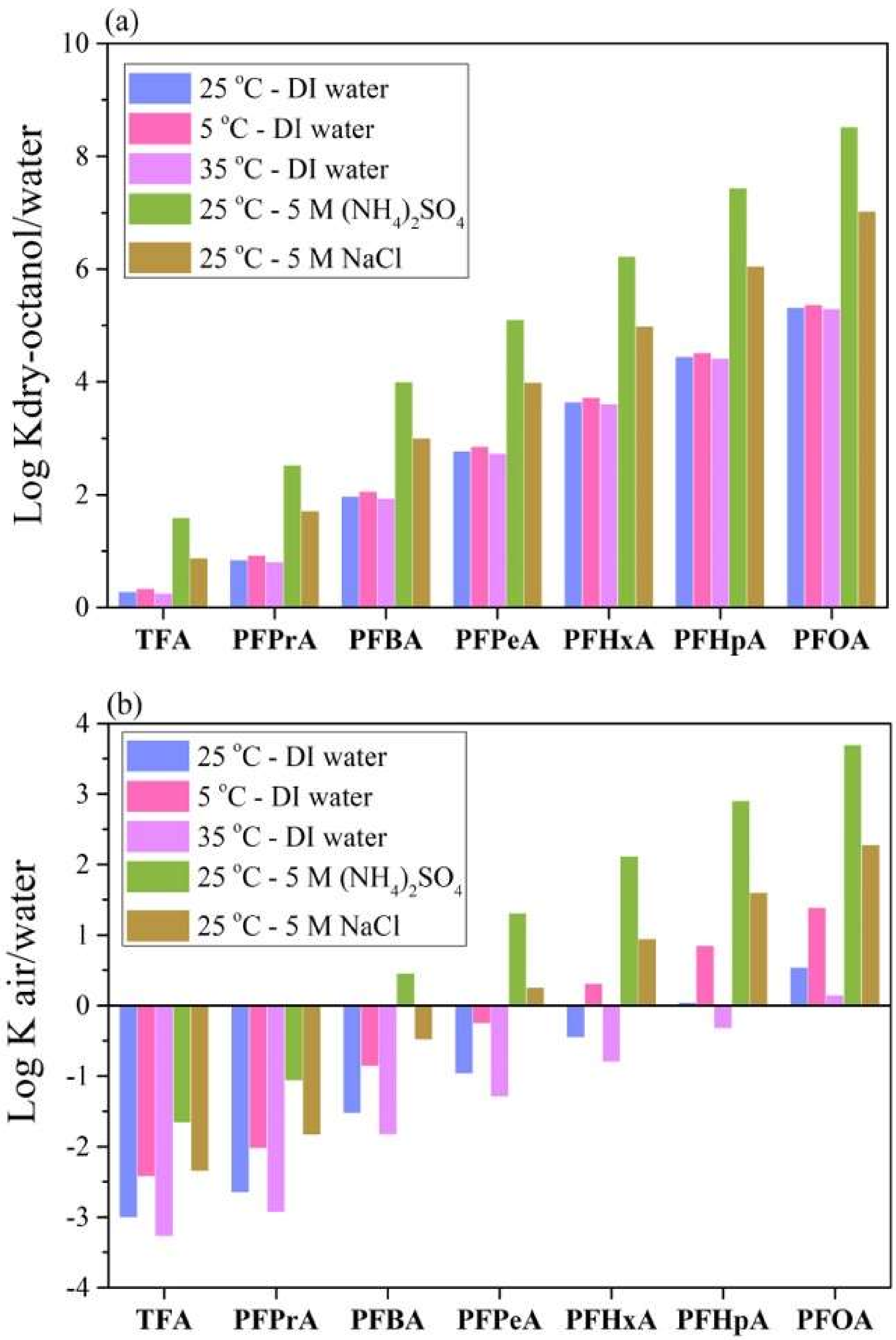


Figure S3. The ppLFER modeled temperature dependence and salt effect of the (a) Log $K_{dry\text{-}octanol/water}$ and (b) Log $K_{air/water}$ values of C2-C8 PFCAs.

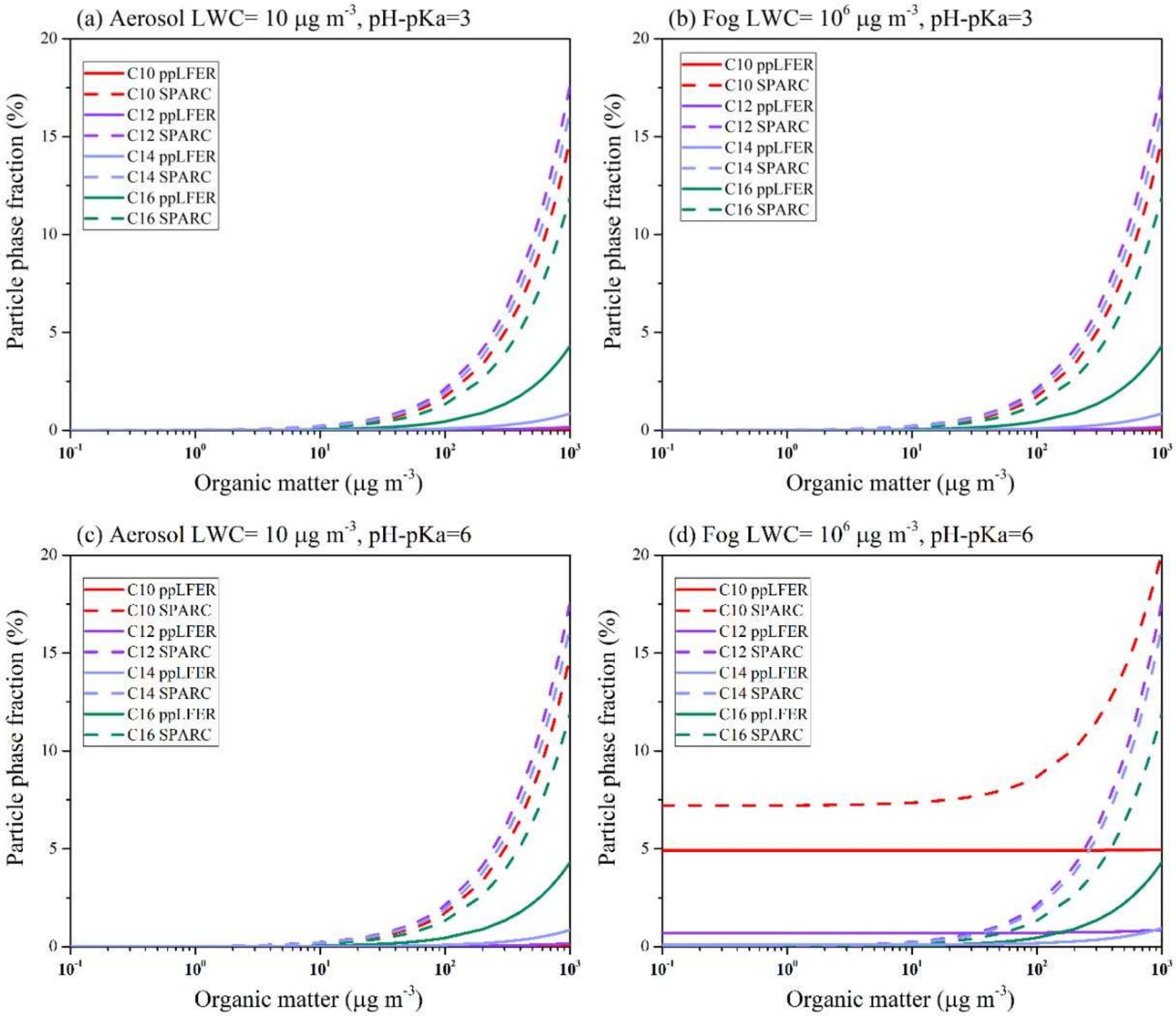


Figure S4. Modeled particle phase fraction of the selected PFCAs (C10: PFDA, C12: PFDoA, C14: PFTeDA, and C16: PFHxDA) with thermodynamic parameters calculated by ppLFER and SPARC (values listed in Table S4) under set scenarios (a) aerosol, strongly acidic, (b) fog, strongly acidic, (c) aerosol, weakly acidic, and (d) fog, weakly acidic.

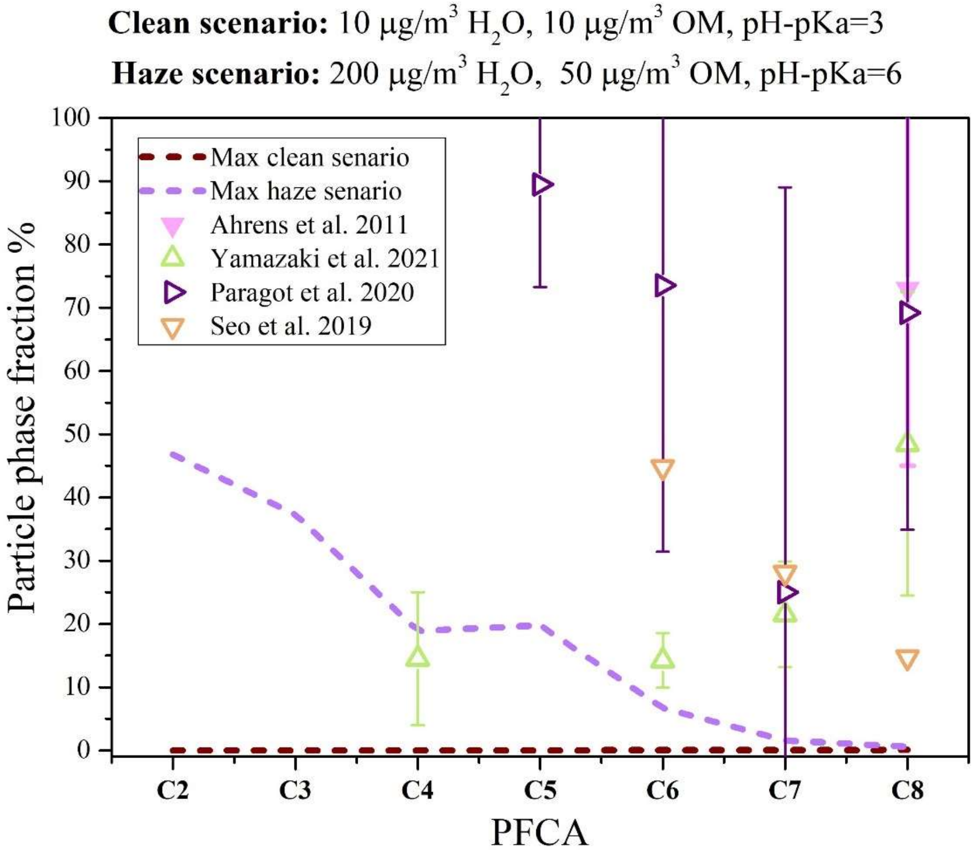


Figure S5. Comparison between the modeled possible ranges of particle phase fraction of C2-C8 PFCAs and several observational results that sampled particles prior to gas phase removal [1-4].

Table S1. The summary of modeling results and selected literature values of the thermodynamic parameters (Log K_{OW}, Log K_{OA}, and pKa) of C2-C8 PFCAs.

	TFA C2	PFPrA C3	PFBA C4	PFPeA C5	PFHxA C6	PFHpA C7	PFOA C8	Source
				Log K_{OW}				
Model	0.286	0.794	1.822	2.543	3.333	4.108	4.884	ppLFER
Model	1.81	2.05	2.84	3.72	4.71	5.78	6.93	SPARC
Model	0.344	2.214	2.944	3.618	4.318	5.038	5.684	COSMOTherm
Model			3.93	5.29	5.97	6.86	7.75	Yu, et al. [5]
Model			2.82	3.43	4.06	4.67	5.30	Wang, et al. [6]
Experiment			1.05	3.19	3.99	4.40	4.67	Xiang, et al. [7]
				Log K_{OA}				
Model	3.367	3.519	3.429	3.591	3.862	4.137	4.414	ppLFER
Model	4.40	4.84	6.01	6.81	7.26	7.62	7.91	SPARC
Model	5.453	5.687	5.950	6.240	6.624	6.883	7.196	COSMOTherm
Model			6.04	6.33	6.63	6.92	7.23	Wang, et al. [6]
				Log K_{AW}				
Model	-3.01	-2.65	-1.53	-0.97	-0.45	0.04	0.54	ppLFER
Model	-2.59	-2.79	-3.17	-3.09	-2.55	-1.84	-0.98	SPARC
Model	-5.38	-3.53	-3.02	-2.61	-2.27	-1.77	-1.41	COSMOtherm
Model			0.30	0.86	1.43	2.00	2.57	QSAR [8]
				pKa				
Model	1.14	0.1	0.05	-0.1	-0.17	-0.20	-0.21	SPARC
Model	0.05	0.38	0.37	0.40	0.42	0.47	0.50	COSMOTherm
Model			0.85	0.81	0.84	0.82	0.90	Wang, et al. [6]
Experiment	0.57	0.48	0.39	0.57	0.84			Moroi, et al. [9]

Table S2. The summary of the sampling information of the studies cited in Figure 2.

Study source	Sampling location	Sampling date	Sampling method	Particle size
Hu et al. 2013 [10]	Beijing, China	2012.04 ~2012.10	Annular denuder + quartz filter	$PM_{2.5}$
Wu et al. 2019 [11]	Beijing, China	2013.06~2013.11	Annular denuder + quartz filter	$PM_{2.5}$
Ahrens et al. 2011 [12]	Toronto. Canada	2010.11~20110.12	Annular denuder + glass fiber filter + sorbent impregnated filters	$PM_{2.5}$
Martin et al. 2003 [13]	Guelph and Toronto, Canada	2020.01~2020.12	Annular denuder + quartz filter	PM_{10}
Wu et al. 2014 [14]	Beijing, China	2012.05~2013.04	Annular denuder + quartz filter	$PM_{2.5}$
Zhang et al. 2018 [15]	Beijing, China	2013.04~2016.04	Annular denuder + quartz filter	$PM_{2.5}$
Tian et al. 2018 [16]	Tianjin, China	2016.05~2016.06	Passive sampler + dry deposition sampler	TSP

Section 1: Reference of the chemical composition and acidity of the PM from the five listed studies in Figure 3.

The reference chemical composition and acidity for the PM sampled along with PFCAs in the five studies shown in Figure 3 are obtained from reported literature values and include contributions from secondary inorganic ions (NH_4^+, NO_3^-, SO_4^{2-}), non-volatile cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), and organic carbon to the measured PM mass loadings for a given size range of sampled aerosol. In detail, the chemical composition from Zhao, et al. [17], Park, et al. [18], Zhang, et al. [19] are chosen to be reasonable representations of the aerosol chemical composition for the PFCA measurements of Wu, et al. [11]. Similarly, Xiang, et al. [20] and Zhang, et al. [19] are considered representative descriptions of the chemical composition and pH values for Hu, et al. [10]. Finally, Ni, et al. [21], and Meng, et al. [22] are used to infer the PM chemical composition for the PFCA measurements reported in Tian, et al. [16]. The chemical composition used for Martin, et al. [13] (sampled in Guelph, Ontario) and Ahrens, et al. [12] (sampled in Toronto, Ontario) were obtained from the PM_{10} and $PM_{2.5}$ components measured in Etobicoke (60 km east side of Guelph) and downtown regions of Toronto provided by Canadian Government supported NAPS database (https://data-donnees.ec.gc.ca/data/?lang=en), respectively. The pH values for the aerosol water are calculated by E-AIM IV with the input of water-soluble inorganic ions and the average meteorological parameters. The details used here for the pH calculations are consistent with that described in Tao and Murphy [23]. A summary of the used parameters is listed in Table S3.

Table S3. The summary of the parameters used to calculate reference modeled Log 1/Kp ranges shown in Figure 3.

Cited study	PM (μg m^{-3})	T (°C)	RH (%)	SII (%) [a]	OM (%) [b]	pH [c]
Martin et al.	24.6	18	71	33	33	5
Wu et al.	62.4	22.4	55	37	25	4.3
Hu et al.	63.4	21.3	57	35	51	4.3
Tian et al.	200	22.5	68	27	20	6.5
Ahrens et al.	9.5	1.6	78	51	25	3

a. Percentage of mass loadings of secondary inorganic ions (SII) to the total PM mass loadings.
b. Percentage of mass loadings of organic matter (OM) to the total PM mass loadings.
c. The pH values are calculated with either E-AIM III [24] or E-AIM IV [25] thermodynamic model (http://www.aim.env.uea.ac.uk/aim/aim.php).

Table S4. The summary of modeling results of the thermodynamic parameters (Log K_{OW}, Log K_{OA}, and Log K_{AW}) of C9-C18 PFCAs.

	PFNA C9	PFDA C10	PFUnA C11	PFDoA C12	PFTeDA C14	PFHxDA C16	PFOcDA C18	Source
				Log K_{OW}				
Model	5.66	6.45	7.22	8.00	9.56	11.12	12.68	ppLFER
Model	8.14	9.35	10.65	12.03	14.91	17.61	20.51	SPARC
				Log K_{OA}				
Model	4.69	4.96	5.23	5.51	6.05	6.60	7.16	ppLFER
Model	8.14	8.24	8.31	8.33	8.29	8.13	7.85	SPARC
				Log K_{AW}				
Model	1.03	1.55	2.04	3.06	3.55	4.56	5.55	ppLFER
Model	-0.002	1.11	2.34	3.70	6.62	9.48	12.66	SPARC

References

1. Ahrens, L.; Harner, T.; Shoeib, M.; Lane, D. A.; Murphy, J. G., Improved Characterization of Gas–Particle Partitioning for Per- and Polyfluoroalkyl Substances in the Atmosphere Using Annular Diffusion Denuder Samplers. *Environmental Science & Technology* **2012,** *46*, (13), 7199-7206.

2. Yamazaki, E.; Taniyasu, S.; Wang, X.; Yamashita, N., Per- and polyfluoroalkyl substances in surface water, gas and particle in open ocean and coastal environment. *Chemosphere* **2021,** *272*, 129869.

3. Paragot, N.; Becanova, J.; Karaskova, P.; Prokes, R.; Klanova, J.; Lammel, G.; Degrendele, C., Multi-year atmospheric concentrations of per- and polyfluoroalkyl substances (PFASs) at a background site in central Europe. *Environ Pollut* **2020,** *265*, (Pt B), 114851.

4. Seo, S. H.; Son, M. H.; Shin, E. S.; Choi, S. D.; Chang, Y. S., Matrix-specific distribution and compositional profiles of perfluoroalkyl substances (PFASs) in multimedia environments. *J Hazard Mater* **2019,** *364*, 19-27.

5. Yu, S.; Liu, W.; Xu, Y.; Zhao, Y.; Wang, P.; Wang, X.; Li, X.; Cai, C.; Liu, Y.; Xiong, G.; Tao, S.; Liu, W., Characteristics of perfluoroalkyl acids in atmospheric PM10 from the coastal cities of the Bohai and Yellow Seas, Northern China. *Environ Pollut* **2018,** *243*, (Pt B), 1894-1903.

6. Wang, Z.; MacLeod, M.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K., Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). *Environmental Chemistry* **2011,** *8*, (4).

7. Xiang, Q.; Shan, G.; Wu, W.; Jin, H.; Zhu, L., Measuring log Kow coefficients of neutral species of perfluoroalkyl carboxylic acids using reversed-phase high-performance liquid chromatography. *Environ Pollut* **2018,** *242*, (Pt B), 1283-1290.

8. Kim, M.; Li, L. Y.; Grace, J. R.; Yue, C., Selecting reliable physicochemical properties of perfluoroalkyl and polyfluoroalkyl substances (PFASs) based on molecular descriptors. *Environ Pollut* **2015,** *196*, 462-472.

9. Moroi, Y.; Yano, H.; Shibata, O.; Yonemitsu, T., Determination of Acidity Constants of Perfluoroalkanoic Acids. *Bulletin of the Chemical Society of Japan* **2001,** *74*, (4), 667-672.

10. Hu, X.; Wu, J.; Zhai, Z.-H.; Zhang, B.-Y.; Zhang, J.-B., Determination of Gaseous and Particulate Trifluoroacetic Acid in Atmosphere Environmental Samples by Gas Chromatography-Mass Spectrometry. *Chinese Journal of Analytical Chemistry* **2013,** *41*, (8), 1140-1145.

11. Wu, J.; Jin, H.; Li, L.; Zhai, Z.; Martin, J. W.; Hu, J.; Peng, L.; Wu, P., Atmospheric perfluoroalkyl acid occurrence and isomer profiles in Beijing, China. *Environ Pollut* **2019,** *255*, (Pt 1), 113129.

12. Ahrens, L.; Shoeib, M.; Harner, T.; Lane, D. A.; Guo, R.; Reiner, E. J., Comparison of annular diffusion denuder and high volume air samplers for measuring per- and polyfluoroalkyl substances in the atmosphere. *Anal Chem* **2011,** *83*, (24), 9622-9628.

13. Martin, J. W.; Mabury, S. A.; Wong, C. S.; Noventa, F.; Solomon, K. R.; Alaee, M.; Muir, D. C., Airborne haloacetic acids. *Environ Sci Technol* **2003,** *37*, (13), 2889-2897.

14. Wu, J.; Martin, J. W.; Zhai, Z.; Lu, K.; Li, L.; Fang, X.; Jin, H.; Hu, J.; Zhang, J., Airborne trifluoroacetic acid and its fraction from the degradation of HFC-134a in Beijing, China. *Environ Sci Technol* **2014,** *48*, (7), 3675-3681.

15. Zhang, B.; Zhai, Z.; Zhang, J., Distribution of trifluoroacetic acid in gas and particulate phases in Beijing from 2013 to 2016. *Sci Total Environ* **2018,** *634*, 471-477.

16. Tian, Y.; Yao, Y.; Chang, S.; Zhao, Z.; Zhao, Y.; Yuan, X.; Wu, F.; Sun, H., Occurrence and Phase Distribution of Neutral and Ionizable Per- and Polyfluoroalkyl Substances (PFASs) in the Atmosphere and Plant Leaves around Landfills: A Case Study in Tianjin, China. *Environ Sci Technol* **2018,** *52*, (3), 1301-1310.

17. Zhao, P. S.; Dong, F.; He, D.; Zhao, X. J.; Zhang, X. L.; Zhang, W. Z.; Yao, Q.; Liu, H. Y., Characteristics of concentrations

and chemical compositions for PM2.5 in the region of Beijing, Tianjin, and Hebei, China. *Atmospheric Chemistry and Physics* **2013,** *13*, (9), 4631-4644.

18. Park, E. H.; Heo, J.; Hirakura, S.; Hashizume, M.; Deng, F.; Kim, H.; Yi, S.-M., Characteristics of PM2.5 and its chemical constituents in Beijing, Seoul, and Nagasaki. *Air Quality, Atmosphere & Health* **2018,** *11*, (10), 1167-1178.

19. Zhang, B.; Shen, H.; Liu, P.; Guo, H.; Hu, Y.; Chen, Y.; Xie, S.; Xi, Z.; Skipper, T. N.; Russell, A. G., Significant contrasts in aerosol acidity between China and the United States. *Atmospheric Chemistry and Physics* **2021,** *21*, (10), 8341-8356.

20. Xiang, P.; Zhou, X.; Duan, J.; Tan, J.; He, K.; Yuan, C.; Ma, Y.; Zhang, Y., Chemical characteristics of water-soluble organic compounds (WSOC) in PM2.5 in Beijing, China: 2011–2012. *Atmospheric Research* **2017,** *183*, 104-112.

21. Ni, T.; Li, P.; Han, B.; Bai, Z.; Ding, X.; Wang, Q.; Huo, J.; Lu, B., Spatial and Temporal Variation of Chemical Composition and Mass Closure of Ambient PM10 in Tianjin, China. *Aerosol and Air Quality Research* **2013,** *13*, (6), 1832-1846.

22. Meng, Z.; Seinfeld, J. H.; Saxena, P.; Kim, Y. P., Atmospheric gas-aerosol equilibrium: IV. Thermodynamics of carbonates. *Aerosol Science and Technology* **1995,** *23*, (2), 131-154.

23. Tao, Y.; Murphy, J. G., The sensitivity of PM2.5 acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites. *Atmospheric Chemistry and Physics* **2019,** *19*, (14), 9309-9320.

24. Clegg, S. L.; Brimblecombe, P.; Wexler, A. S., Thermodynamic Model of the System H+-NH4+-Na+-SO42--NO3--Cl--H2O at 298.15 K. *The Journal of Physical Chemistry A* **1998,** *102*, (12), 2155-2171.

25. Friese, E.; Ebel, A., Temperature dependent thermodynamic model of the system H+-NH4+-Na+-SO42--NO3--Cl--H2O. *The journal of physical chemistry. A* **2010,** *114*, (43), 11595-11631.