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Contamination of Perfluorooctane Sulfonated (PFOS) and Perfluorooctanoic Acid (PFOA) in Air

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Abstract**—** PFOS and PFOA are widely used in industrial and commercial products. There are consisting of (C-F bonds) with a sulfonated group and carboxylic group, which make its persistent, bioaccumulative and toxic. PFOS and PFOA are introduced into environment by several processes such as wastewater, leaching from consumer products or dust during production process. The analytical procedure for determination in ambient air which collected monthly during 2010-2012 in 4 provinces, Thailand, were performed using ASE, SPE and HPLC-MS/MS. The results show that concentration of PFOS was higher than PFOA ranging between 0.44-6.75 ng/g and 0.23-0.46 ng/g, respectively. Trends of distribution were founded dominantly in TSP particles of PFOS 0.74-6.75 ng/g and PFOA 0.20-0.35 ng/g, while PM_{10} was found lower in ranges 0.41-0.51 ng/g and 0.06-0.34 ng/g, respectively. Contamination of PFOS and PFOA in ambient air could be a potential source of human exposure which may cause human health risk for who lives nearby the source.

Keywords**—** PFOS, PFOA, dust, airborne

I. INTRODUCTION

RECENTLY, environmental problem issue have been increasing considered due to the adaptation of technologies, rapidly increasing of population or higher requirement of products (various products from manufacturing process were served these requirements). Many industries are used perfluorooctane sulfonated (PFOS) and perfluorooctanoic acid (PFOA) in production processes such as soil, stain, grease resistance to carpets, textiles or leather and chemical resistant for tubing, coating on cookware including food containers. It is also a surfactant for cleaning the products and performance chemical (example, semiconductor manufacture, photolithography, hydrolic fluid additives, acid mist suppressants for metal plating) [1], [2].

PFOS and PFOA are very strong carbon-fluorine bond that makes them resist to breakdown when it was released into environment. Thus, there are many reported about PFOS and PFOA contamination in environments such as, water, drinking water, soil, sediments, and dust (indoor and outdoor) and it may cause several effect for environment and human as well. The toxicity of PFOS and PFOA has been found immunotoxicity, genotoxicity and epigenetic effects, reproductive and developmental toxicities, neurotoxicity, effects on the endocrine system, and carcinogens [3]. PFOS and PFOA contamination in ambient air are also very important for human health risk because there is a possibility that PFOS and PFOA can absorp on dust then exposure into human body via dust ingestion. Although, these compounds have been detected frequently, but there is still no standard and control of use, thus it is quite interesting to study.

This research aims to study the concentrations of PFOS and PFOA in airborne dust as total suspended particulate matter (TSP) and particulates smaller than 10 microns (PM_{10}) and its distribution in the atmosphere in terms of particle sizes and seasonal variation and calculated human health risk assessment.

II. MATERIALS AND METHODS

A. Samples and sampling sites

The 290 samples of total suspended particulate matter (TSP) and particulates smaller than 10 microns (PM_{10}) which collected from 9 stations located in 4 provinces were shown in Fig. 1 including Saraburi (2 Stations), Nontaburi (1 Stations), Bangkok (3 Stations), and Samutprakarn (3 Stations) were received from Pollution Control Department (PCD) and Ministry of Natural Resources and Environment of Thailand (envi 7). The samples were conducted monthly during 2010-2012. Each sample, approximately 1,600 m^3 of air, were collected over a period 24 hours with High volume air sample. Air dust samples as TSP particles were collected on a glass fiber filter (PALLFLEX 2500QAT-UP, pattern as 8x10 in., Pallflex Products Corporation, USA) and PM_{10} particles were collected on a quartz membrane filter (Whatman, pattern as 8x10 in., Whatman International Ltd., England). All filter samples were kept in Ziploc and stored at room temperature until analyzed.

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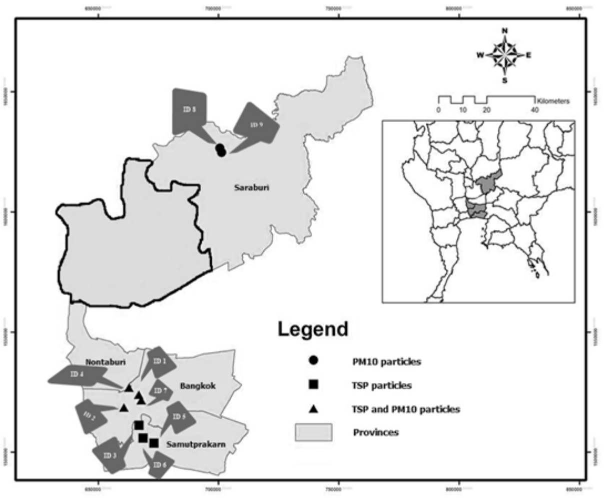


Fig. 1 Locations

B. Analytical Processes

The concentrations of PFOS and PFOA in samples were extracted using Accelerated Solvent Extractor (ASE, Dionex 200). Filter samples were cut in small pieces, divided into three layers and inserted directly into a 33 mL stainless steel extraction cells. The extraction process was run for 20 minute (1 cycle) by using methanol (LC/MS grade) as a solvent at temperature 100 °C, preheating 1 minute, heating 5 minute, pressure 1500 psi, and 100% flush volume. Final extracted solution was about 60 mL.

The extracted solution were dried in water bath to remove any methanol. MilliQ-water 400 mL were added into dried samples then were loaded into cartridge (Precep C-Agri C_{18}, Wako, Japan) by Solid – phase extraction (SPE) technique by using Sep-Pak concentrator at flow rate 10 mL/min. Each cartridge was dried using vacuum manifold for 2 hours. PFOS and PFOA were eluted by using 4 mL of methanol (LC/MS grade) and 2 mL of acetronitrile. The eluent were dried with nitrogen gas and reconstituted by 0.5 mL of 40% acetronitrile. Quantification of PFOS and PFOA were performed using HPLC – MS/MS which was done under conditions, guard column Agilent Eclipse XDB - C_{18}, 4.6 x 50 mm, 1.8 µm and analytical column Agilent Eclipse Plus C_{18}, 2.1 x 100 mm, 1.8 µm, temperature of column set at 40°C. Sample injection volume was 10 µL. Mobile phase were used (A): 10 mM CH_3COONH_4 / Ultrapure water and (B): CH_3CN (HPLC grade). Column was used gradient it started flushing with A= 45%; B = 55%, and finally A = 90; B = 10 at 15 min at flow rate 0.25 mL/min. Mass spectrometer was detected sample in Electrospray ionization (ESI- negative mode). Ion monitored of PFOS was 80 m/z and PFOA was 369 m/z. The retention time(RT) were 10.9 min for PFOS and 4.8 min for PFOA.

C. Human Health Risk Assessment

Human health risk assessment could be using The Pharmacokinetic (PK) model. This model used widely for assessment potential health risk from PFOS and PFOA exposure as a function of dose, volume of distribution and elimination rate [4] – [7]. Assuming at adult humans inhale 15 m^3 or 15,000 L of air per day.

$$\text{Health risk assessment via inhalation} = \frac{\text{Exposure of PFOS and PFOA concentration in air (ng/L)}}{\text{Guideline values of human exposure}}$$

Assuming steady state conditions exist, one can solve for blood serum concentration as:

$$CP = DP/\ (kP \times Vd)$$

While

CP = The serum concentration (ng/mL) of PFOA or PFOS

kP = The first-order elimination rate (day^{-1}), kP values of 0.0008 day^{-1} for PFOA and 0.0003 day^{-1} for PFOS

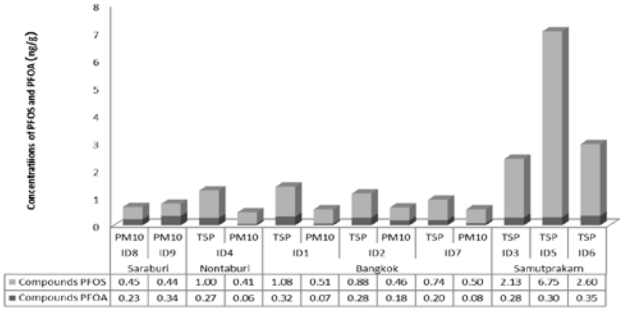
Vd = The volume of distribution (mL/kg bw), Vd value of 170 mL/kg bw for PFOA and 230 mL/kg bw for PFOS [7]

DP = The daily absorbed dose (ng/kg bw/day)

III. RESULTS & DISCUSSION

A. PFOS and PFOA distribution in ambient air

Concentrations of PFOS and PFOA contaminated in dust collected in study area were founded that PFOS concentration were higher than PFOA as in the range 0.44 – 6.75 ng/g and 0.23 – 0.46 ng/g, respectively. Fig. 2 PFOS concentration in dust was normally found higher than PFOA which may due to its emission from source and its chemical and physical properties.



	PM10 ID8	PM10 ID9	TSP ID4	PM10 ID4	TSP ID1	PM10 ID1	TSP ID2	PM10 ID2	TSP ID7	PM10 ID7	TSP ID3	TSP ID5	TSP ID6
	Saraburi		Nontaburi		Bangkok						Samutprakarn		
▨ Compounds PFOS	0.45	0.44	1.00	0.41	1.08	0.51	0.88	0.46	0.74	0.50	2.13	6.75	2.60
■ Compounds PFOA	0.23	0.34	0.27	0.06	0.32	0.07	0.28	0.18	0.20	0.08	0.28	0.30	0.35

Fig. 2 Concentrations of PFOS and PFOA in dust of each sampling site

Fig. 2 shown the concentrations of PFOS and PFOA in dust samples with significant different in both individual and regional samples. Production processes and using related product of PFOS and PFOA could be a possible source of releasing PFOS and PFOA to atmosphere. In this study, high concentrations of PFOS were detected from all of stations at Samutprakarn province where many PFOS and PFOA related industries were located there. Similar to previous study [8] which were detected high concentration of PFOS and PFOA of water sample in industrial estate located in Samutprakarn province and founded concentration of PFOS and PFOA in effluent of central wastewater treatment plant (WWTP) as shown in Table I. From results, PFOS and PFOA were dominant concentrations in Samutprakarn province and can be indicated industrial effluent might be the source of PFOS and PFOA contamination in water environment. So, it might be concluded activities in industrial estate can disperse those compounds to the atmosphere too.

TABLE I
PFOS AND PFOA CONCENTRATION IN EFFLUENT SAMPLES FROM CENTRAL WWTP OF INDUSTRIAL ESTATE IN SAMUTPRAKARN PROVINCE

Location	Sample	Conc. PFOS (ng/L)	Conc. PFOA (ng/L)
Samutprakarn province	Effluent	18.6 - 37.4	21.8 - 316.3

Variation of PFOS and PFOA concentration in the air may also related to its chemical and physical properties. PFOA has higher solubility than PFOS therefore PFOA will be wash out by wet deposition. Then, PFOS was founded concentration higher in the air than PFOA. Furthermore, PFOS has high potential to long-range transport [9] and persistence in the atmosphere for a long time. Similar pattern were also reported several researches as shown in Table II.

The magnitude of PFOS and PFOA in the air were also vary depending on space. Table 2 shows a different range of PFOS and PFOA contamination such as the dust which direct emit from manufacturing in China [10] was very high up to 160 µg/g and 4,692 µg/g for PFOA and PFOS, respectively. Lower contamination of PFOS and PFOA were founded in the house dust where PFOS and PFOA were emit from consumer product under uncirculated atmosphere while very low amount of PFOS and PFOA in the ambient air due to the transportation and dilution.

B. Distribution of PFOS and PFOA between TSP and PM_{10}

PFOS and PFOA concentration in dust were also show significant in the different portion of the dust. Both of PFOS and PFOA concentration in TSP were higher than PM_{10}, it might be that PM_{10} particles is a portion of TSP particles. PFOA concentrations in TSP samples were founded in ranges 0.20-0.32 ng/g and PM_{10} 0.06-0.18 ng/g, while PFOS concentrations in TSP and PM_{10} samples were founded 0.74-1.08 ng/g and 0.41-0.51 ng/g, respectively. Fig. 3 and Fig. 4 shows the proportion of PFOS and PFOA in PM_{10} is about 41 % – 67.57 % and 21.88 % – 64.29 %, respectively of TSP.

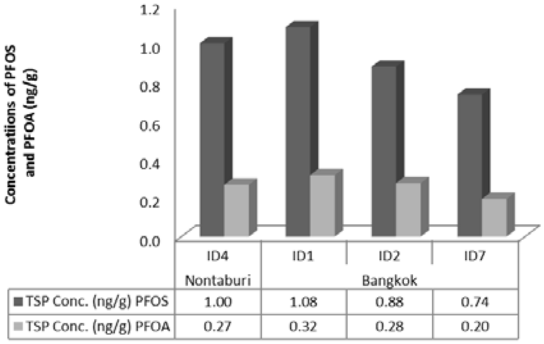


Fig. 3 TSP particles distribution of PFOS and PFOA

TABLE II
PFOS AND PFOA CONCENTRATIONS IN DUST IN THIS STUDY AND OTHER REPORTED

Author	Sampling site	Conc. PFOS	Conc. PFOA
Wang et al., (2010)	Dust in manufacturing facility (China)	4,692 µg/g dust (max.)	160 µg/g dust (max.)
Xu et al., (2013)	House dust (Bavaria, Germany)	3.3 - 1046 ng/g dust	1 - 676 ng/g dust
Strynar et al., (2008)	House dust (Ohio and North Carolina, USA)	12.1 µg/g dust (max.)	1.96 µg/g dust (max.)
This study	airborne dust	0.44 - 6.75 ng/g dust	0.23 - 0.46 ng/g dust

TABLE III
RESULTS OF PFOS AND PFOA CONCENTRATIONS BETWEEN TSP AND PM_{10} PARTICLES

Stations		Particles	PFOS			PFOA		
			pg/g	$\mu g/m^3$	portion of PM_{10} in TSP	pg/g	$\mu g/m^3$	portion of PM_{10} in TSP
Nontaburi	ID4	TSP	399.20 - 2051.50	9.41 - 65.96	41.00%	15.60 - 765.20	0.32 - 14.06	22.22%
		PM_{10}	167.30 - 1193.30	7.32 - 53.44		3.60 - 219.20	0.13 - 6.40	
Bangkok	ID1	TSP	236.70 - 2102.70	6.12 - 49.56	47.22%	48.80- 669.40	0.95 - 18.09	21.88%
		PM_{10}	159.30 – 1023.00	7.99 - 44.68		8.10 - 194.10	0.24 - 6.15	
	ID2	TSP	334.50 - 3646.30	12.60 - 112.66	52.27%	43.90 - 759.60	0.83 - 18.06	64.29%
		PM_{10}	222.90 - 1644.20	9.91 - 75.57		4.20 - 709.20	0.13 - 25.09	
	ID7	TSP	0.60 - 1806.90	0.02 - 44.73	67.57%	6.80 - 624.20	0.13 - 11.52	40.00%
		PM_{10}	165.50 - 1194.20	7.13 -51.26		2.70 - 245.70	0.08 - 7.30	

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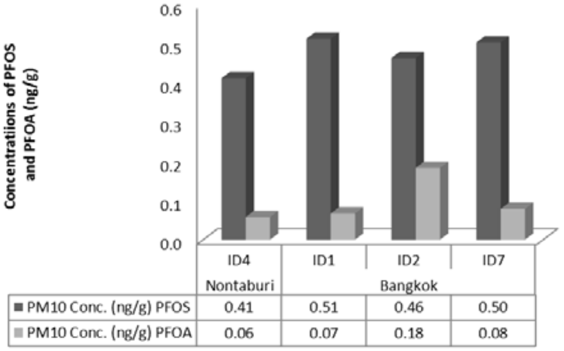


Fig. 4 PM_{10} particles distribution of PFOS and PFOA

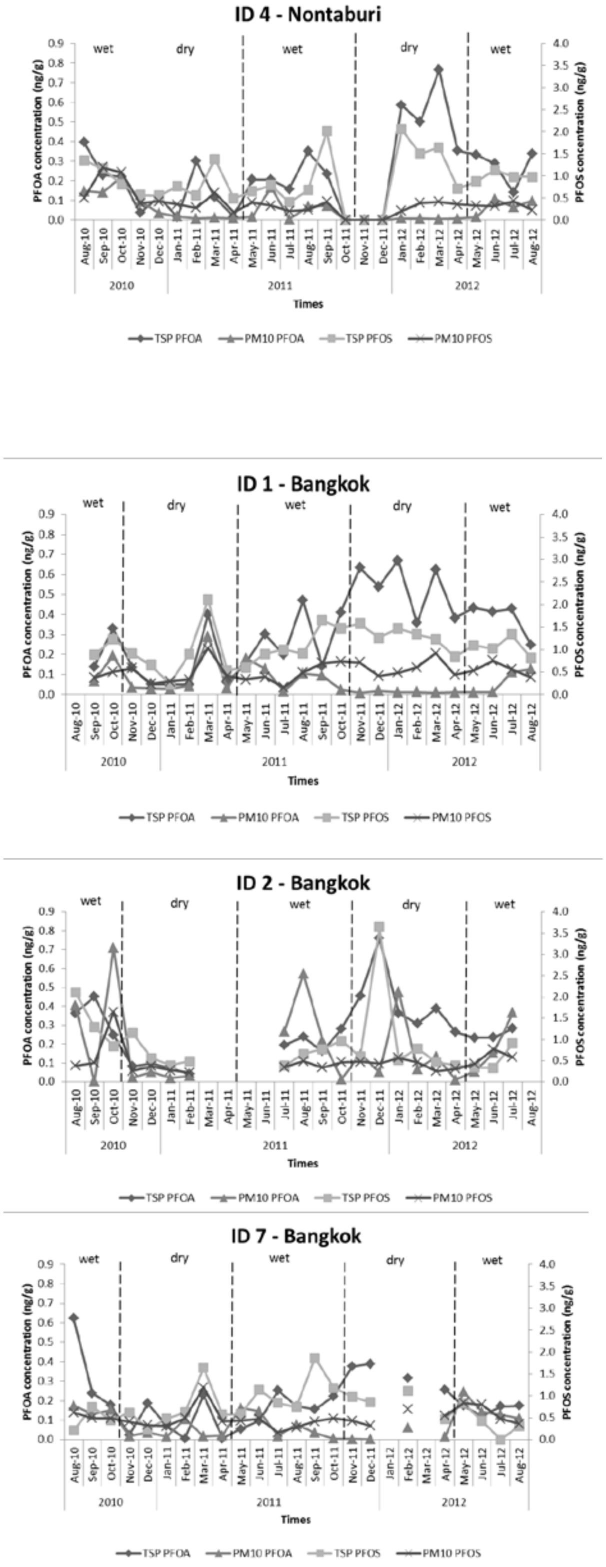
This high variation could be related to the amount of emission from source and the distribution in the air as well. Harada et al. [11] were also founded that proportion of PFOS and PFOA in respirable particle in ranges 58.3 – 89.8 % which similar pattern to this study.

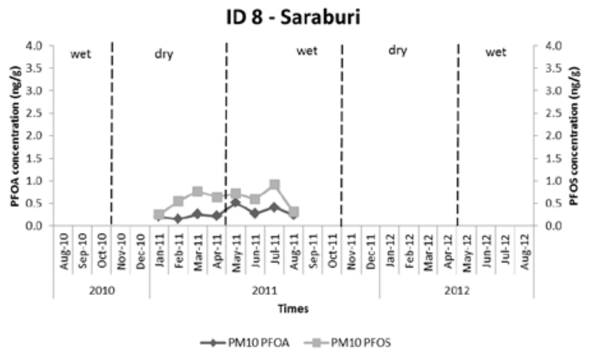
PFOS and PFOA contamination in dust could be a potential source for human exposure of these compounds. Although PM_{10} samples were founded concentrations lower TSP samples, but PM_{10} dust can penetrate deep into the thoracic part of the airway such as, the lungs, its may caused health problems. TSP dust may deposit in the upper airways (nose and throat) but were detected highest compounds in particles, may cause harm as well.

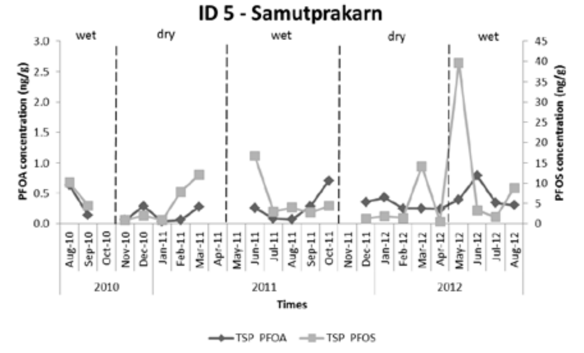
C. Seasonal variation of PFOS and PFOA

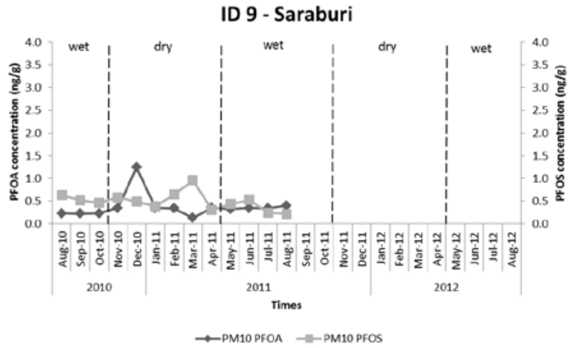
The seasonal change are also the other important factor which related to chemical effect on dust in the ambient air. However, the results of this study were shown the seasonal variation affect to PFOS and PFOA in the air. Fig. 5 shows the sampling sites were not located near industrial areas (Nontaburi, Bangkok, and Saraburi provinces) were founded concentrations in wet seasons has lower than dry season may also related to chemical and physical properties of these compounds. Seasonal variation were affected to PFOS and PFOA contamination due to wet deposition in wet seasons because properties of PFOA has higher solubility than PFOS therefore PFOA will be wash out by the air and wind dilution of PFOS because its has long-range transport and persistence in the atmosphere for a long time.

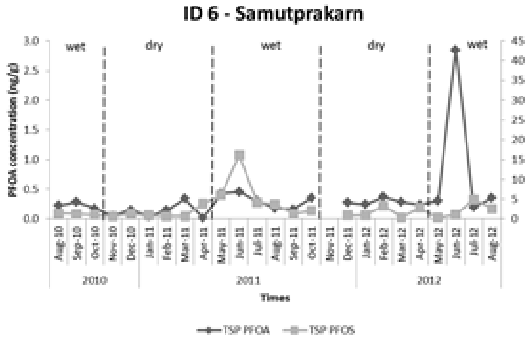
Some areas were located near the source (Samutprakarn provinces), seasonal variation are not affect to PFOS and PFOA concentration due to emission of these compounds during the production process were occur continuously and using of various products is available at all times might causing emissions continuous as well.











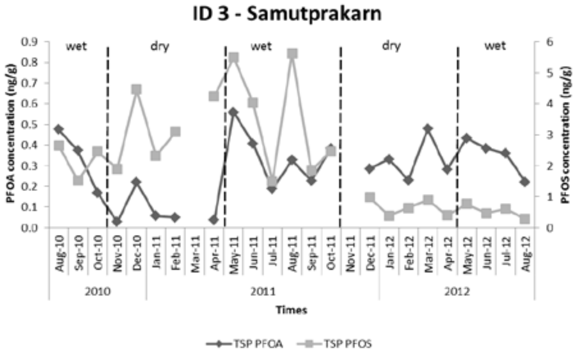


Fig. 5 Seasonal variation PFOS and PFOA of each sampling sites

D. Human Health Risk Assessment

PFOS and PFOA contamination in ambient air could be effect to human health due to its toxicity by inhalation. Results of health risk assessment and the Pharmacokinetic (PK) model were shown in Table 4 and 5. Calculated assessment health risk of PFOS and PFOA from dust ingestion by using the highest concentrations of PFOS and PFOA in dust samples compare with guideline of human exposure. All of dust samples the values of sudden to human health risk assessment were less than 1, its might be indicated that still safe for ingestion or low risk for human health.

TABLE IV
CALCULATED HEALTH RISK ASSESSMENT OF PFOS AND PFOA FROM DUST INGESTION

Stations		Samples	Maximum concentration (ng/day)		Calculated health risk assessment	
			PFOS	PFOA	PFOS	PFOA
Guideline values of human exposure (ng/day)			600	120		
Saraburi	ID8	PM_{10}	0.23	0.08	0.0004	0.0007
	ID9	PM_{10}	0.25	0.25	0.0004	0.0021
Nontaburi	ID4	TSP	0.62	0.13	0.0010	0.0011
		PM_{10}	0.50	0.06	0.0008	0.0005
Bangkok	ID1	TSP	0.46	0.17	0.0008	0.0014
		PM_{10}	0.42	0.06	0.0007	0.0005
	ID2	TSP	1.06	0.17	0.0018	0.0014
		PM_{10}	0.71	0.24	0.0012	0.0020
	ID7	TSP	0.42	0.11	0.0007	0.0009
		PM_{10}	0.48	0.07	0.0008	0.0006
Samutprakarn	ID3	TSP	1.17	0.10	0.0020	0.0008
	ID5	TSP	11.89	0.19	0.0198	0.0016
	ID6	TSP	3.72	0.69	0.0062	0.0058

TABLE V
PREDICTED CONTRIBUTIONS OF PFOS AND PFOA FROM DUST INGESTION TO DAILY SERUM CONCENTRATIONS AND LONG-TERM DUE TO CAUSED HEALTH PROBLEM (DAYS)

	Calculated serum concentrations (ng/mL)		Long-term due to caused health problem (days)	
	PFOS	PFOA	PFOS	PFOA
Threshold level of human exposure (ng/mL)	130.4348	13.2353		
Minimum	0.0490	0.0064	2661.93	2068.02
Maximum	2.5839	0.0273	50.48	484.81
Average	0.3666	0.0145	355.80	912.30

The Pharmacokinetic (PK) model was used to predict daily concentrations of PFOS and PFOA in serum after contaminated by PFOS and PFOA by guideline values of human exposure were shown in Table 5. From results, long - term due to accumulation in human body til threshold level of PFOS in serum approximately 355.80 day at the average serum concentration (calculated from maximum concentrations of all stations) of PFOS 0.3666 ng/mL/day and PFOA about 912.30 day at the average serum concentration (calculated from maximum concentrations of all stations) 0.0145 ng/mL/day. If the concentrations and times to expose of those compounds were exceed than the above its might be caused accelerate human health problem from dust ingestion around there.

IV. CONCLUSION

This study was determined concentrations of PFOS and PFOA in ambient air. All of samples were contaminated of both compounds. We can conclude followings;

1. All sampling sites, PFOS was detected at higher concentration than PFOA due to its properties.
2. High concentration of PFOS and PFOA were dominantly found in TSP than PM_{10} particles.
3. Activities in industries were related amount of PFOS and PFOA because of results can detected highest concentrations at Samutprakarn province.

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