CONCENTRATION AND PATITIONING OF PCDDs/Fs AND PCBs IN AMBIENT AIR, KOREA

Heo JW[1]*, Lee GW[2]

[1]Gyeonggi-do Institute of Health and Environment ,95,Pajangcheon-ro, Jangan-gu, Suwon-si,Korea; [2]Hankuk University of Foreign Studies, 81, Oedae-ro, Mohyeon-myeon, Cheoin-gu,Yongin-si, Korea

Introduction

Polychlorinated Biphenyls(PCBs)were synthesized first by Schmidt and Shultzhave used in wide industrial application since 1920s due to their chemical stability having high heat resistance properties and non-flammability. They have been used in electrical equipment as dielectric fluids in capacitors and transformers over the past 50year.Polychlorinateddibezo-*p*-dioxins and furans (PCDDs/Fs)were first detected in incineration ash and are highly toxic and persistent and unintentionally were released into environment from combustion processes and production of chlorinated chemicals. Because PCBs and PCDDs/Fsarepersistent organic pollutants (POPs) with significant bioaccumulation in environmental systems and long range transport, many countries have great concern for them. The Stockholm convention aims to ban the productionand use of POPs worldwide and enforced environmental monitoring for them to protect human health and environment.

Despite of this prohibition and concern, PCBs and PCDDs/Fsstill continue to be detected in the ambient and the concentration of PCBs and PCDDs/Fsin the environment is not negligible.PCBsare being released into the atmospheric environment via volatilization from uncontrolled landfills and illegal dumping of wastes or parts containing the PCBs, emission form stored and incomplete incineration of certain wastes.

Atmospheric transport is an important pathway for delivery of POPs to water and terrestrial surfaces.Gas-particle partitioning process for individual congeners is very important factor in determining the POPs fate in the atmosphere. To understand of POPs gas-particle partition, many researchers suggested the adsorption-absorption modeldepending on particle surface property and octanol-air partitioning coefficient (K_{OA}) as an alternative sub-cooled liquid vapor pressure (P_L^o).However, there are a few data for the atmospheric gas-particle concentration of individual PCBs and PCDDs/Fs simultaneously and temporal PCBs distribution in Korea.

In the present study, we investigated the individual PCBs180and PCDDs/Fs 17congenerslevel and gas/particle concentration to estimate partition of gas-particle at urban and industrial area in Gyeonggi-do, Korea.

Material and methods

Active high volume air samplers were deployed at Suwon (SW) and Ansan (AS) of air pollutants observatory in Gyeonggi-do. Suwon is central of Gyeonggi-do and is defined as a urban-residential area having a about one million populations. Ansanis largest industrial sector development in Gyeonggi-do.

Air sampling of PCDDs/Fs and PCBs were collected with high volume air sampler (HV-700F, Sibata, Japan). The high volume air sampler equipped with quartz fiber filter (QFFs ;Adventec, 20 cm×25 cm) and polyurethane form (PUF, length 5cm, diameter 9.0cm) was operated with flow rate 100L/min during a week period and we collected the samples per week. The volume of air aspirated per sample per week was in the range 940~1423 m^3. Samples in Suwon and Ansan were collected for 370days and 173 days respectively starting February, 2010.

PCDDs/Fs and PCBs were conducted according to US EPA 1613 and 1668B respectively using an HRGC/HRMS (Agilent 6890 and Autospec NT, Micromass, UK) with sp2331 (60 m×0.32 mm× 0.2 um, Supelco) column for PCDDs/Fs and DB-5MS (60 m×0.2 mm×0.25um , J&W Scientific) for PCBs.Laboratory blank was analyzed for every pretreatment event, and only high chlorinated congeners were detected. The limit of detection (LOD) was defined as the three times the standard deviation of the lowest calibration points, which was 0.04 ~ 0.46pg/sample (average:0.15)for PCDDs and 0.00 ~ 0.29pg/sample (average : 0.14) for PCB, respectively.The average recoveries of the surrogate PCDDs/Fs and PCBs were in the range 80.3± 11.0 ~117.4 ± 25.0% and 76.8 ± 20.6 ~119.1 ± 12.6 % respectively.

Results

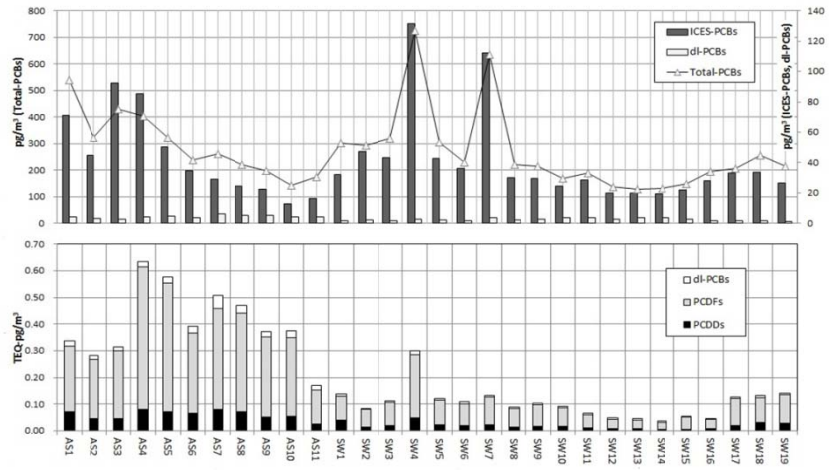
Concentration of PCDDs/Fs and PCBs and in the ambient

The notation ΣPCDDs/Fs and ΣPCBs refers to the sum of the 2,3,7,8 substituted PCDDs/Fs17 species and 180

congeners of PCBs. And International Council for the Exploration of the Seas designated the 7 congeners PCB groupdefined as ICES-PCBs(28, 52, 101, 118, 138, 153, 180) commonly finding in the environment as markers the degree of contamination.

The concentration of ΣPCDDs/Fs based on the TEQ in ambient of SW and AS ranged from 0.033 to 0.284pg-TEQm^{-3}(mean value of 0.098pg-TEQm^{-3}), from 0.153 to 0.613pg-TEQ/m^{3} (mean value of 0.379pg-TEQm^{-3}), respectively. AS values are higher than SW sites, confirming the existence of sources PCDDs/Fs in industrial area. These concentrations of PCDDs/Fs in Ansan ambient are similar to in other Asia industrialized country[1, 2] and was higher thanthoseofJapan[3].

The concentration of ΣPCBs in ambient of SW and AW ranged from 127.6 to 725.9pgm^{-3}(mean value of 263.9pgm^{-3}), from 142.5 to 540.7pgm^{-3}(mean value of 295.7 pgm^{-3}), respectively.



Site	Σ_{17} PCDD/Fs (pg/m^3)	Σ_{17} PCDD/Fs (pg-TEQ/m^3)	Σ_{180} PCBs (pg/m^3)	Σ_{7} ICES-PCBs (pg/m^3)	Σ_{12} dl-PCBs (pg/m^3)	Σ_{12} dl-PCBs (pg-TEQ/m^3)
Suwon	1.690 ± 0.701	0.098 ± 0.056	263.9 ± 159.1	40.02 ± 30.02	2.409 ± 0.821	0.006 ± 0.003
(Range)	0.700 ~ 3.530	0.033 ~ 0.284	127.6 ~ 725.9	19.37 ~ 131.25	1.160 ~ 3.739	0.003 ~ 0.016
Ansan	10.298 ± 4.282	0.379 ± 0.131	295.7 ± 121.8	44.03 ± 27.72	4.340 ± 0.970	0.024 ± 0.009

Fig. 1 PCDDs/F and PCBs concentration at Suwon and Ansan sampling sites

Regardlessoftheurbanandindustrial areas, average of ΣPCBsand ICES-PCBs concentration was showed the similar levels in the both areas and this result was thought due to emission into the atmosphere primarily asgases volatilized from areas where they have been used,stored, spilled, or atmospherically deposited and the relative importance of secondary re-emissions is expected to increase. It is known that the Asia region is hotspots as the lack of reliable data of the POPs. In East Asia area, average air PCB concentration in Japan (184 pg m^{-3}) and Korea (156 pg m^{-3}) was comparable, while that of China (1100 pg m^{-3}) was much higher[4], these data was contributed by improper management of decommissioned capacitors and electronic wastes.

Profile congeners of PCDDs/Fs and PCBs and in the ambient

PCDDs/Fs : The main contributors to the Σ2,3,7,8-PCDDs/Fs were OCDDs(SW:19.6, AS:14.8%), OCDFs(SW:15.7, AS: 32.2 %)and 1,2,3,4,6,7,8-HpCDF(SW: 22.5, AS: 23.2%). SW presents typical pattern for urban areas with OCDD being the most prevalent congener[5, 6], while OCDF for ASindustrial area was shown the largest contributor. In previous studies[7], OCDF was found mainly in incinerator neighborhood and industrial complex areas.

PCBs :Owing to the large number of analyzed PCBs, the only dl-PCBs, ICES-PCBs, and major PCBs which are contributed over 1% of ΣPCBs are reported in this study.The dl-PCBs were similar to previous studies[8, 9] with higher contribution of congeners PCBs-118, PCB-105 and PCBs-77. The ICES-PCBs level decrease with increase chlorine- number for all samples and all site. The percentage of ICES-PCBs to ΣPCBs was about 15% and the coefficient of determination (R^2) between ΣPCBs and ICES-PCBs was 0.92 ($p<0.001$), which indicate that total PCBs concentration can be deduced from ICES-PCBs. In both two areas, PCB11, 28/31, 47/45, 5/8, 20/33, 18, 52, 22 in order from high to low level, accounting for about 50% of the ΣPCBs. Relatively high concentration of PCB-11 is found in atmosphere, accounting for 15.1 % in AS and 24.6% in SW of the ΣPCBs, respectively. This notables PCB-11 existed high concentration, unique in the atmosphere and recently reported in ambient of the various regions[10, 11]. The origin of PCB11may be inferred from yellow dye used to in printing and painting application, from the degradation of higher chlorinated PCBs congeners[11], although real emission sources of PCB-11 unknown. The 2-CBs, 3-CBs and 4-CBs were great homologue group and these homologue account for 10.4 ~ 49.7 %, 10.56 ~ 42.24 % and 13.3~31.6% for ΣPCBs, respectively.

Gas / particle partition of PCDDs/Fs in the atmosphere

PCDDs/Fs were associated with particle phase while most of PCBs were gas phase chemicals with high vapor pressure relatively. Commonly, the higher molecular weight of chemical with increasing number of chlorine, the higher Octanol- Partitioning coefficient (K_{OW}) and the more much easily related to particle phase.

Log Kp – log P_L^o plot

Partitioning of semi-volatile organic compounds(SOCs) between the gas and particle phases affect their rate of wet and dry deposition and their long-range transport. To evaluate these two phases partition, usually particle-gas partition coefficient, K_p (m^3 ug^{-1}) and the regression of K_p versus the corresponding sub-cooled liquid vapor pressure (P_L^o) were used in previous studies:

Log K_p = log [(F/TSP)/A] = m log P_L^o + b(1)

where, F is particle-phase concentration (pg m^{-3}), A is gas-phase concentrations(pgm^{-3}), and TSP is concentration of total suspended particle matter (ug m^{-3}). The slope (m) and intercept (b) calculated from log K_p vs. log logP_L^o plots are useful regression parameters which can describe the equilibrium state of adsorption / absorption.To avoid the temperature effects and dependence, we compared the data during same sampling date in both sites. Plot log K_p vs. log $P_L^o$for PCDDs/Fs and dl-PCBs yield slope of -0.53 and -0.76 for SW(urban-residential area) and -0.94 and -0.80 for AS(industrial area), respectively. When PCDDs/Fs and dl-PCBs adsorbed onto particles from 1st combustion emission sources emitted to atmosphere, slopes of the AS with the predominance of emission sources is steeper than those of SW (Fig.2).

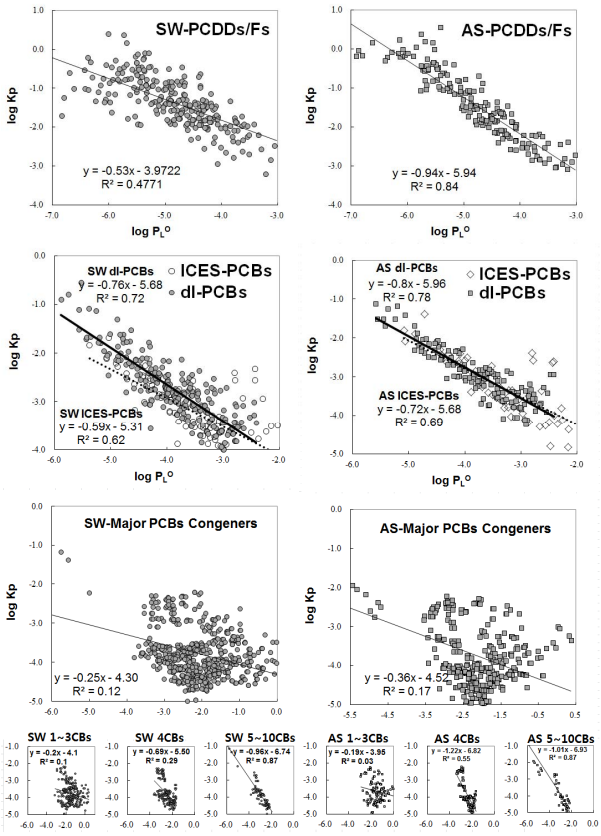


Fig. 2Plot of log Kp vs. log P_L^o for PCDDs/Fs and PCBs congeners in each sites

Mono-, di, tri-PCBs compounds will be able to quickly reach the gas-particle equilibrium comparing with high chlorinated compounds. Slow re-equilibrium of LMW PCBs with higher diffusivities-vapor pressure may be responsible for shallow slopes obtained from both sites. This result is agreement with previous studies[12].

Comparison of gas-particle portioning models

To evaluate the gas-particle partitioning of the semi-volatile organic compounds, many researchers used representative the Jung-Pankow adsorption model Eq(2) based on the linear Langmuir isotherm and K_{OA} absorption model used only the K_{OA} and organic fraction of the aerosol (f_{om}).These two models can predict the particle bounced fraction (φ) and particle-gas partition coefficient (K_p), respectively. Jung-Pankow(J-P) model is defined as follows :$\varphi = c\theta/(P^o_L + c\theta) = F/(F + A)$ (2) where, θ (m^2 of aerosol $m^{-3}$of air) is the total suspended particulate surface area concentration, and c depend on the heat of desorption from the particle surface, the heat of vaporization of chemicals and surface properties.

The K_{OA} absorption model is based on the assumption that all of the aerosol organic matters are available to absorb gaseous compounds and can be given as Eq.(3) :Log K_p = log K_{OA} + log f_{OM}– 11.91(3)

The K_{OA} values for PCDDs/Fs were calculated from equation of temperature functionsandthose for PCBs were obtain from Eq.(4) using K_{OW} data and dimensionless Henry's law constant ($K_{H'}$) .

K_{OA}= K_{OW} RT/K_H=Kow/$K_{H'}$ (4)where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature(K) and K_H is the Henry's law constant.Fig. 3 shows the particle bounded fraction (%) predicted by J-P model with each sampling event measured value for PCDDs/Fs and PCBs.

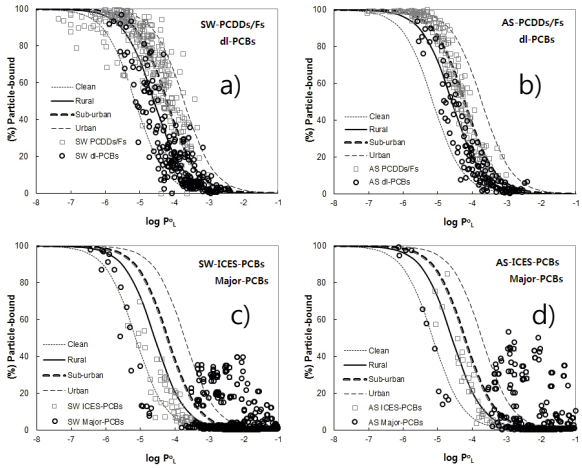


Fig. 3The Junge-Pankowadsorption model-plot of measured and predicted particle bound percentage (%) for PCDDs/Fs and PCBs

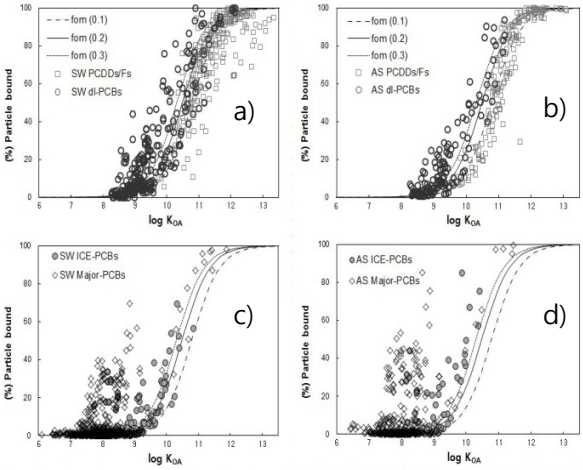


Fig. 4K_{OA}absorption model-plot of measured and predicted particle bound percentage (%) for PCDDs/Fs and PCBs

Fig. 3 shows the particle bounded fraction(%) predicted by J-P model with each sampling event measured value for PCDDs/Fs and PCBs. Almost of plots for PCDDs/Fs represented between urban and rural line of J-P model. Plots of P_L^o vs. particle percentage in Ansan are more denser in predicted line than those in Suwon. But plots for dl-PCB and ICES-PCBs were close to clean and background predicted line, it was far from real area characteristics. Compared to dl-PCBs, the gas-particle partitioning of particle associated compound like PAHsand PCDDs/Fs agreed well the J-P adsorption model.

Fig. 4 describes the K_{OA} absorption model with measured values for PCDDs/Fs and PCBs. In general, the organic matter fraction (f_{OM}) range for urban ambient is 10 % between 20%, some study reported average f_{OM} value is above 50%[13]. From Fig. 4 a) and b), dl-PCBs and ICES-PCBs data fit in K_{OA}absorption model in f_{OM} range from 10 to 30%rather than PCDDs/Fs data. Plots for PCDDs/Fs below f_{OM} 10 % in K_{OA} model, it shows that the K_{OA} model tends to underestimate PCDDs/Fsdistribution.

LMWPCBswithhigh vapor pressure $>10^{-3}$ Pa or low $K_{OA}< 10^8$ under predicted by both models, while high molecular weight(HMW) PCBs are slightly closer approach the predicted line (between clean and rural) <Fig. 4 c), d)>.But, major LMW PCBs(mono-, di-, tri-) have high the potential for gas phase breakthroughin reality, gas phase concentrationis low comparing with particle phase concentration. It is cause to overestimate K_p and particle phase concentration. So, owing to the effect of sampling artifact, we could not be adequately evaluated for LMW gas-particle partition.

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