

Annual Cycle of PCBs Concentration in the Atmosphere

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Abstract

PCBs의 대기 중 농도는 고용량 PUF sampler를 이용하여 2000년부터 2002년까지 주 1회 수도권 인근지역인 경기도 안성에서 측정하였다. 본 논문은 비선형 회귀모델을 이용하여 대기 중 가스상 PCBs의 연간, 월간 사이클을 평가 하고자 한다. Clausius-Clepeyron 식을 이용한 가스상 PCBs의 기울기는 고분자로 갈수록 증가하는 경향이였다. 이는 고분자 PCBs는 저분자 PCBs에 비해 온도 의존성이 크다는 것을 의미한다. 다시 말해, 고분자 PCBs는 다른 지역에서 장거리 이송되어 오는 오염물질의 영향보다는 지역적인 오염원(예, 토양, 수계 등)에 의해 영향을 크게 받고 있다는 것을 시사한다. Lorentzian 모델을 이용한 총 PCBs의 일별, 월별 회귀식의 결정계수(R^2)는 각각 0.62($p < 0.0001$), 0.88($p < 0.0001$)로 나타나 유의한 결과를 보였다. 또한, 비선형 회귀식 모델을 활용하여 구한 가스상 PCBs의 일별, 월별 사이클을 모사한 방정식도 매우 유의한 결과($p < 0.0001$)를 나타내었다.

Key words : nonlinear regression model, PCB homologs, Determination coefficient, Monthly variations

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1. Introduction

In recent years persistent organic pollutants (POPs) have gained a lot of attention from the scientific as well as governmental, environmental policy community and non-governmental organizations like Greenpeace.^{1,2)} One of the international for a where the POPs discussions started is the United Nations Economic Commission for Europe (UN-ECE), comparing eastern and western Europe, Canada and the United States of America. The UN-ECE initiatives on POPs begin in 1992 with the establishment of a Task Force on POPs under the framework of the Convention on Long-Range Transboundary Air Pollution (CLRTAP). In 1996, a Preparatory Working Group was formed by the Executive Body (EB) to start negotiations on a POP Protocol. Two year later, in June 1998 at the Fourth Pan-European Environmental Ministerial Conference in Aarhus, Denmark the UN-ECE POP Protocol was signed by 33 member states and the European Union (EU).³⁾ The POP Protocol will enter into force when 16 countries have ratified it.

Semi-volatile organic compounds (SOCs) such as polychlorinated biphenyls (PCBs) have a propensity to (re) volatilize from secondary source compartments such as soil, vegetation, water and atmospheric particles. Outgassing from these compartments is believed to account for the contemporary atmospheric burden of gaseous phase PCBs, now that primary sources have been largely reduced (i.e. manufacture

and specific use/handling of PCBs). For these secondary sources, temperature is invoked as the primary controller for the condensation/volatilization process, effectively accounting for the cycling nature of SOCs between air and surfaces. Evidence of seasonality in air concentrations has been reported for many SOCs in year-round monitoring studies.^{4,5,6)} This exchange between air and surfaces (soil, water, vegetation, snow etc.) can be described using a thermodynamic approach, assuming equilibrium phase partitioning between the surface in question and the overlying atmosphere. Several notable studies have investigated this phenomenon utilizing the Calusius-Clayperon equation, whereby air concentrations expressed as partial pressure are plotted against inverse temperature.^{5,7)} Atmospheric transport is primarily responsible for the bulk transfer of PCBs around the globe. Air masses can travel hundreds of kilometers in hours and can cause levels of PCBs in the air at any place to fluctuate relatively quickly due to changes in the place of 'origin' of currently residing air mass.^{8,9,10)} However, partitioning of PCBs between the terrestrial surface and air is expected to occur relatively quickly,^{5,11)} so levels in air do not necessarily remain the same as an air mass moves from one region to another. Seasonal (i.e. temperature dependent) variability in PCB levels in the atmosphere has been reported in temperate regions¹²⁾. The importance of atmospheric transport in the budget of PCBs in remote regions has been clearly

demonstrated. For example, studies indicate that 85–90% of the gross PCB flux into Lake Superior results from atmospheric deposition, and PCBs detected in remote regions are the apparent result of atmospheric transport and deposition.¹³⁾

The partitioning of SOCs in the atmosphere is an important factor in their fate, transport and transformation in urban and adjacent coastal atmosphere. Also, the partitioning of SOCs to aerosols distinguishes chemicals that are scavenged from chemicals that remain in the gas phase and are therefore able to transport great distance.¹⁴⁾ It has been proposed that dry gas deposition is the major uptake pathway of PCBs and other SOCs for grass,¹⁵⁾ but there has been little research on this, and the importance of wet deposition in particle may be underestimated. The cleansing of vegetation by precipitation, by removing surface adhering particles, may also be important, particularly for compounds which are found mainly in particulate phase in ambient air. The objectives of the research presented in this paper were to investigate the seasonal variation and relations between levels of PCBs in the atmosphere and to estimate the cycle of gaseous PCBs concentration in the atmosphere using nonlinear regression model.

2. Experiment

2.1 Sampling program

Atmospheric samples were taken

from September, 2001 to July, 2002 with GPS-1 PUF sampler (General Metal Workes Inc., Ohio). The sampling program was conducted in a rural area of Kyonggi-do in South Korea. The sampling site is located at the National Hankyong university campus, which is about 1 km northeast of downtown Ansong, and 10 km west of Kyongbu express-way. The population of Ansong is about 130,000, population density is 882 (people/km²), and agricultural fields make up 33% of the total area in the sampling site. There is a complex mix between agricultural and industrial regions on the south side of Seoul (Fig. 1). Samples (N=28) were collected using a high-volume sampler. The air was drawn through a glass fiber filter (GFF, diameter 10cm) to collect particles and then through a polyurethane form (PUF) plug (length 8.0 cm, diameter 7.5 cm) to collect compounds present in the gas phase. The duration of sampling was 48 hr, average flowrate was 0.23 m³/min and the sample volume was approximately 600–800 m³. Meteorological data such as temperature, wind speed, wind direction and relative humidity were obtained from the Korea Meteorological Administration located in Seoul and a meteorological tower (AWS) located on top of a building located in the Hankyong University campus.

2.2 Chemical analysis

The GFFs (glass fiber filters) were precombusted at 450 °C for 24 hours in loosely wrapped aluminum foil envelopes then they were sealed and stored at 4 °C until sampling. The

PUFs were precleaned by soxhlet with hexane : dichloromethane (9:1 V/V) and then placed in a vacuum dry oven to dry and stored in sealed glassware at 4 °C until sampling. After sampling, the GFFs and PUFs were all wrapped in glassware and stored at -26 °C until analysis. PUFs were spiked with PCBs surrogate standards prior to sampling to determine analytical recovery. The surrogate standards were made up of PCB 28, 52, 101, 138, 153, 180, 209, and 4,4'-dibromooctafluorobiphenyls (Supelco, USA) were used as the internal standard. The GFF and PUF samples were extracted and analyzed separately in order to study the gas/particle partitioning of PCBs. The samples were extracted in soxhlet apparatus with hexane: dichloromethane (9:1 V/V) for 48 hours. Extracts were concentrated to approximately 2 ml in a rotary evaporator (BUCHI, R-124). The

first clean-up of PCBs was eluted with hexane 15 ml, hexane: dichloromethane (1:1 V/V) 12 ml and dichloromethane 25 ml on a silica column (activated silica 3 g at 350 °C overnight, sodium sulfate at 450 °C overnight) to remove any polar organics that might interfere with the analysis. The second clean-up and fraction was eluted with hexane: dichloromethane (1:1 V/V) on a GPC (gel permeation chromatography, BUCHI, B-688) column. The samples were then concentrated under a gentle stream of purified nitrogen concentrator to 50 µL by using dodecane (SIGMA, D-4259) which was added to the extracts to prevent losses during the volume reduction to 50 µL using N₂ concentrator and analyzed on a Hewlett Packard 6890 equipped with MS detector (HP 5973). Table 1 summarizes the operation parameters and conditions of the GC/MSD used in this study.

Table 1. GC/MSD operating parameters for PCBs analysis.

<i>Instruments</i>	<i>Parameters</i>
Detector	MSD (mass selective detector) HP-5MS capillary column
Column	(5% diphenyl & 95% dimethylpolysiloxane) length 30 m × 0.25 mm, film thickness 0.25 µm
Inlet	Splitless
Aux temp.	300 °C
Injection volume	1 µL 150 °C for 2 min.
Temp. program	300 °C/min. to 170 °C 4 °C/min. to 200 °C for 13 min. 4 °C/min. to 268 °C 70 °C/min. to 320 °C for 4.09 min.
Carrier gas	He (99.9999 %)
Total run time	45 min.

2.3 Quality assurance/Quality control (QA/QC)

The analytical quality of the data was determined using LOD (limit of detection), recovery, reproducibility, linearity and by checking sampling artifacts, etc. The detection limit was obtained by spiking a blank sample with the calibration standard at a concentration of 1~5 times the expected LOD. LOD is defined as three times the average mass plus 3 standard deviations (3σ). The detection limit of the PCB standards ranged from 0.005 (PCB 18) to 0.04 pg/m^3 (PCB 52) with normalizing average sampling volume (800 m^3), respectively. The materials used in the present study were assessed for possible analytical contaminants. The purpose of blank test is to check whether and how much contamination of PCBs can be found in experiment materials. Due to the many experimental materials used in this study, it was necessary to check the background concentration level of PCBs in a considerable number of individual matrices. The solvent-cleaned and pre-combusted sampling materials, glass fiber filters, filters for PUF samplers, and PUF plug, were Soxhlet extracted by HEX: DCM (9:1). The results of the blank tests did not show any interference peaks that would inhibit quantifying the PCB congeners in PUFs and GFFs. The recoveries ($n=5$) of PCBs surrogate standards were $77.2\pm 5.5\%$ for PCB 28, $62.9\pm 7.3\%$ for PCB 52, $78.0\pm 9.2\%$ for PCB 101, $100.8\pm 9.7\%$ for PCB 153, $106.1\pm 8.2\%$ for PCB 138, $116.6\pm 10.2\%$, and $116.0\pm 13.4\%$ for PCB 209. The linearity of calibration standards were calculated by regression analysis with values ranging from 0.9917–1.0000 (R^2) for PCBs. Sampling artifacts associated with the GFF and PUF can affect the apparent

gas-particle distributions of PCBs. The GFF may exhibit two such artifacts with counteracting effects on the distribution. First, gas phase PCBs may adsorb to the filter surface and particles collected on the filter.^{16,17,18} Second, the more volatile compounds may be stripped from the filter by continuing gas flow if the gas phase concentration decreases, the temperature increases during the sampling periods, or due to gas phase reactions on the filter.^{19,20} The extent of gas adsorption is often estimated using a second filter. A backup filter was used on 5 samples collected in Ansong city. The percent mass on the second filter for individual PCBs was either below 5% or not detected at all. Therefore, the mass from the backup filter was neither subtracted from the particle phase concentration nor added to the gas phase concentration. Also, volatilization from the filter has the opposite effect. This was not determined, but Zhang and McMurry²⁰ have suggested that this impact is usually less than or equal to 10%.

Spilt PUFs were collected to assess gas phase breakthrough. The bottom half of the spilt PUFs contained an average of 12% ($N=3$) of the total mass, indicating minimal breakthrough. Therefore, the gas phase concentrations in this study were adjusted accordingly. Sincik et al.²¹ examined gas phase breakthrough in the same manner with this study in Chicago and over Lake Michigan during July when the ambient temperature was highest. Individual PCBs on the bottom half of the spilt PUFs were all less than 15% of their total PUF masses. We concluded that the GFF- and PUF-associated concentrations of PCBs are a good estimate of the true gas and particle concentrations in this study.

Table 2. PCB congeners routinely quantified using GC/MSD (SIM) analysis

<i>PCB congeners</i>	Monitoring ions (m/z)
PCB 18/27/28/33/38	256 [#] , 258, 186
PCB 44/47/49/52/60/61/74/77/79	292 [#] , 290, 220
PCB 87/101/105/110/118/114/123/126	326 [#] , 324, 256
PCB 138/141/149/151/153/155/156/157/167/169	360 [#] , 362, 290
PCB 170/180/183/187/189	394 [#] , 396, 324
PCB 194	430 [#] , 428, 360
<i>PCB isotopes</i>	Monitoring ions (m/z)
PCB 28	268 [#] , 270, 198
PCB 52	304 [#] , 302, 232
PCB 101	338 [#] , 340, 266
PCB 138/153	372 [#] , 374, 302
PCB 180	406 [#] , 408, 336
PCB 209	510 [#] , 512, 440

Target Ion

PCBs were identified by the mass to charge (m/z) ratios from a full scan, then compared to the m/z of standards or matched to the computer database (NIST library). Once the compounds were identified, Selected Ion Monitoring (SIM) was used for routine analysis, because, 1) SIM is more sensitive than full scan for ions and 2) full scan data always occupy large amounts of disk space. Table 2 gives the monitored m/z ratios and the retention time of the compounds.

3. Results and Discussion

3.1. Nonlinear regression application of total PCBs

For a full understanding of surface-air exchange processes and, hence, model development, it is pertinent to consider what is driving PCB air concentrations above the terrestrial surface-release/exchange from soil, the overlying vegetation or both. These exchange processes operate at different rate and time scales, i.e., hourly, daily, seasonally, and over many years. In this study, two

days cycle, there was a rapid response of the air concentrations to temperature-driven change in the surface-air partition coefficients.

An accurate model of daily variations in air concentration of SOCs would require extensive meteorological information, including the dependence of eddy diffusivity, velocity, and temperature as a function of height and time. The height of the atmosphere impacted by exchange of SOCs across the air-surface interface is critical when attempting to derive estimates of changing air concentration. In the absence of detailed data, here, we develop a simple one-dimensional model to assist data interpretation. Hoff et al.⁵⁾ found that the Lorentzian model gave the best fit to their annual seasonal cycles of PCB and organochlorine air concentrations.

Attempts were made to fit the daily and monthly variation date of total PCBs in this study to the Lorentzian model. The parameters of Lorentzian model for total PCBs were shown in Table 3.

Table 3. Model parameters of nonlinear regression equations for total PCBs

Total PCBs	a	b	x ₀	y ₀	R ²
Daily	344.05 (p<0.0001)	7.66 (p<0.0001)	46.35 (p<0.0001)	--	0.62 (p<0.0001)
Monthly	320.65 (p<0.0001)	1.30 (p<0.0001)	14.40 (p<0.0001)	64.90 (p<0.0001)	0.88 (p<0.0001)

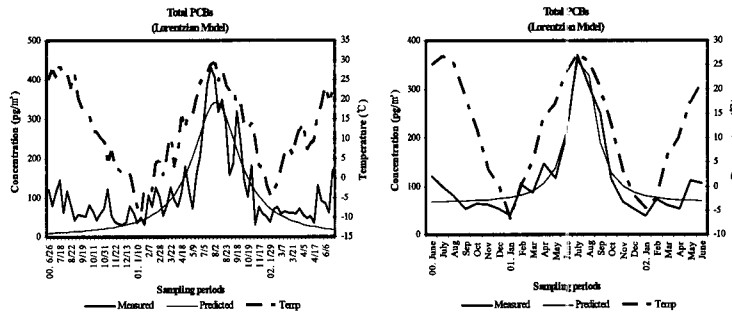


Fig.1. Daily and monthly variations of total PCBs using nonlinear regression model

As a result of the daily and monthly variation for PCBs, the Lorentzian model equation as follows :

1) Daily variations :

Lorentzian model (3 parameters) :

$$y = \frac{a}{1 + \left(\frac{x - x_0}{b}\right)^2}$$

2) Monthly variations :

Lorentzian model (4 parameters) :

$$y = y_0 + \frac{a}{1 + \left(\frac{x - x_0}{b}\right)^2}$$

As to the above result, the Lorentzian model of 2-day total

PCBs was characterized 3 parameters. However, the Lorentzian model of monthly total PCBs was characterized 4 parameters. The determination coefficient (R²) of the Lorentzian model for 2-day and monthly total PCBs were 0.62(p<0.0001), 0.88(p<0.0001), respectively. The parameters of Lorentzian model for 2-day and monthly variations were also very significant (p<0.0001). That is, nonlinear regression model of Lorentzian accounted for 62, 88 % of the variations of total PCBs during the sampling periods, especially from January 2001 to January 2002. Figure 1 shows the comparison of measured and predicted total PCBs using nonlinear regression Lorentzian model.

3.2. Nonlinear regression application of PCB homologs

Determinate parameters of nonlinear regression model (sinusoidal and Lorentzian) for PCB homologs shown in Table 4.

We have examined three distributions, which can be easily parameterized in models: sinusoidal, Gaussian, and Lorentzian. The best fit for the majority of the PCB homologs in this study was sinusoidal and Lorentzian:

3) Sinusoidal model (4 parameters) :

$$y = y_0 + a \sin\left(\frac{2\pi x}{b} + c\right)$$

4) Lorentzian model (3 parameters) :

$$y = \frac{a}{1 + \left(\frac{x - x_0}{b}\right)^2}$$

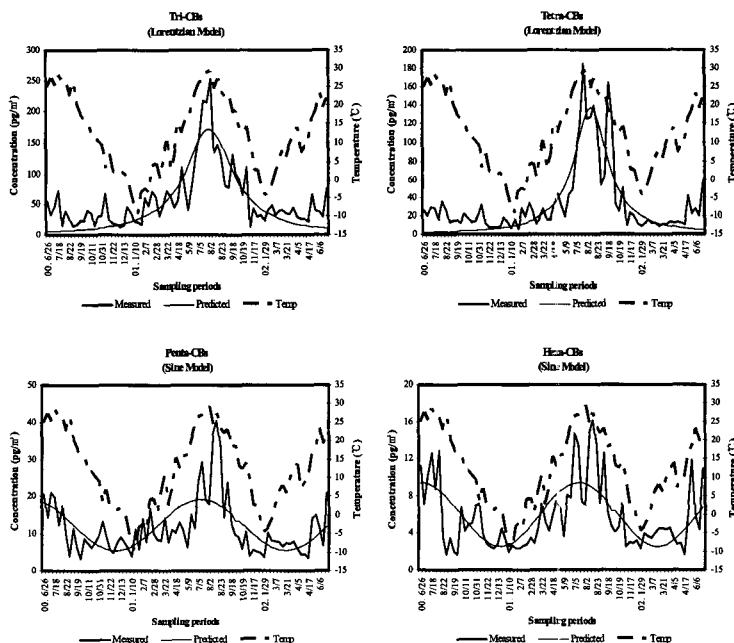
5) Lorentzian model (4 parameters) :

$$y = y_0 + \frac{a}{1 + \left(\frac{x - x_0}{b}\right)^2}$$

The equations of the two nonlinear regression models for 2-day and monthly homologs variations were very significant ($p < 0.0001$, Figure 2, 3). However, the best fit model among PCB homologs had a difference: the concentrations of tri-, tetra-, and hepta- in the atmosphere were predicted by Lorentzian model and the concentrations of penta-, hexa-, octa- and deca-CBs were characterized sinusoidal model. That is, concentration of penta-, hexa-, and deca-CBs in the atmosphere are peaked in every summer and weakly peaked in other seasons (especially winter) from June 2000 to June 2002. Otherwise, the concentration of tri- and tetra-CBs in the atmosphere are only strongly peaked in summer 2001 and hepta-CBs are also only strongly peaked in summer 2000. The intercepts of sinusoidal model in tri-, tetra-, and hepta-CBs were not significant values which imply that these homologs were not rather affected by local sources during the sampling periods. However, the intercepts of Lorentzian model in penta-, hexa-, octa- and deca-CBs were very significant values ($p < 0.0001$) which imply that these homologs were strongly dependent on temperature variations during the sampling periods (Table 4). These patterns showed similarly in 2-day and monthly variation of PCB homologs.

Table 4. Model parameters of nonlinear regression equations for PCBs homologs

Homologs	Periods	a	B	c	xo	yo	R2
Tri-CBs	Daily (Lorentzian)	171.28 (p<0.001)	8.14 (p<0.001)	-	45.68 (p<0.001)	-	0.64 (p<0.001)
	Monthly (Lorentzian)	165.40 (p<0.001)	1.42 (p<0.001)	-	14.14 (p<0.001)	30.78 (p<0.001)	0.92 (p<0.001)
Tetra-CBs	Daily (Lorentzian)	137.79 (p<0.001)	5.72 (p<0.001)	-	47.10 (p<0.001)	-	0.68 (p<0.001)
	Monthly (Lorentzian)	131.26 (p<0.001)	1.84 (p<0.001)	-	14.76 (p<0.001)	-	0.76 (p<0.001)
Penta-CBs	Daily (Sine)	6.88 (p<0.001)	46.25 (p<0.001)	1.90 (p<0.001)	-	12.34 (p<0.001)	0.40 (p<0.001)
	Monthly (Sine)	6.63 (p<0.001)	13.70 (p<0.001)	1.55 (p<0.001)	-	11.82 (p<0.001)	0.57 (p<0.001)
Hexa-CBs	Daily (Sine)	3.40 (p<0.001)	42.90 (p<0.001)	1.38 (p<0.001)	-	6.97 (p<0.001)	0.44 (p<0.001)
	Monthly (Sine)	3.09 (p<0.001)	11.32 (p<0.001)	6.28 (p<0.001)	-	5.57 (p<0.001)	0.54 (p<0.001)
Hepta-CBs	Daily (Lorentzian)	10.02 (p<0.001)	7.82 (p<0.001)	-	6.48 (p<0.001)	-	0.44 (p<0.001)
	Monthly (Lorentzian)	29.61 (p<0.001)	6.28 (p<0.001)	-	-8.59 (p<0.001)	-	0.54 (p<0.001)
Octa-CBs	Daily (Sine)	0.15 (p<0.001)	50.41 (p<0.001)	2.49 (p<0.001)	-	0.35 (p<0.001)	0.35 (p<0.001)
	Monthly (Lorentzian)	0.61 (p<0.001)	1.30 (p<0.001)	-	13.08 (p<0.001)	0.25 (p<0.001)	0.81 (p<0.001)
Deca-CBs	Daily (Sine)	0.11 (p<0.001)	45.50 (p<0.001)	1.71 (p<0.001)	-	0.19 (p<0.001)	0.41 (p<0.001)
	Monthly (Sine)	0.11 (p<0.001)	0.11 (p<0.001)	2.32 (p<0.001)	-	0.20 (p<0.001)	0.55 (p<0.001)



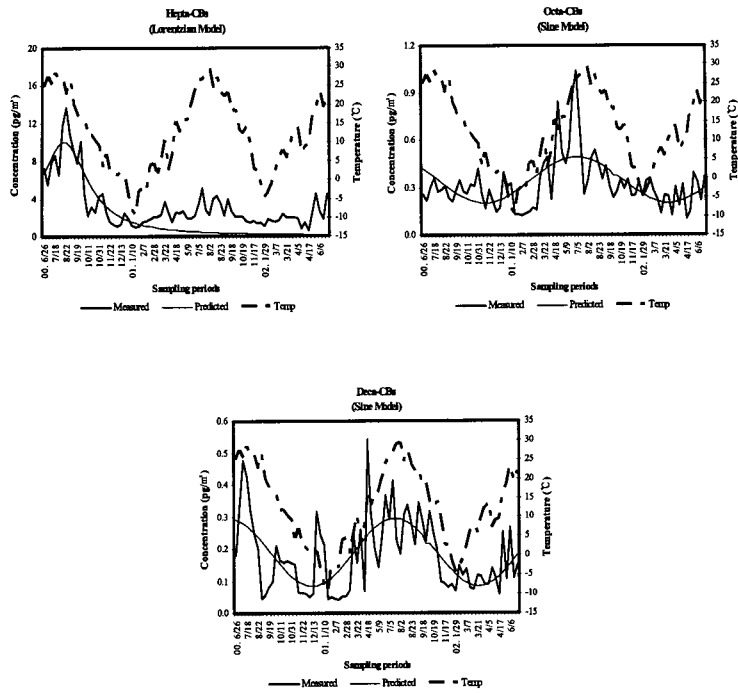
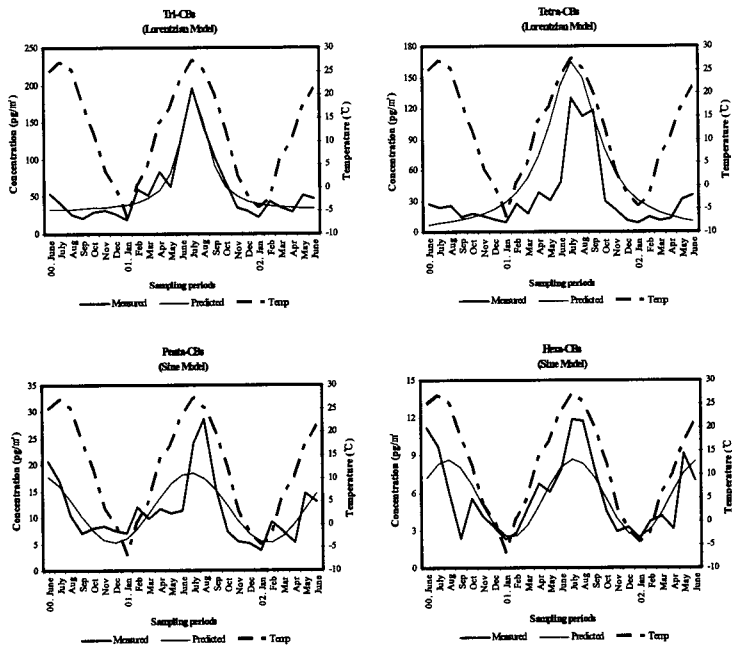


Fig. 2. Daily variations of PCB homologs using nonlinear regression model



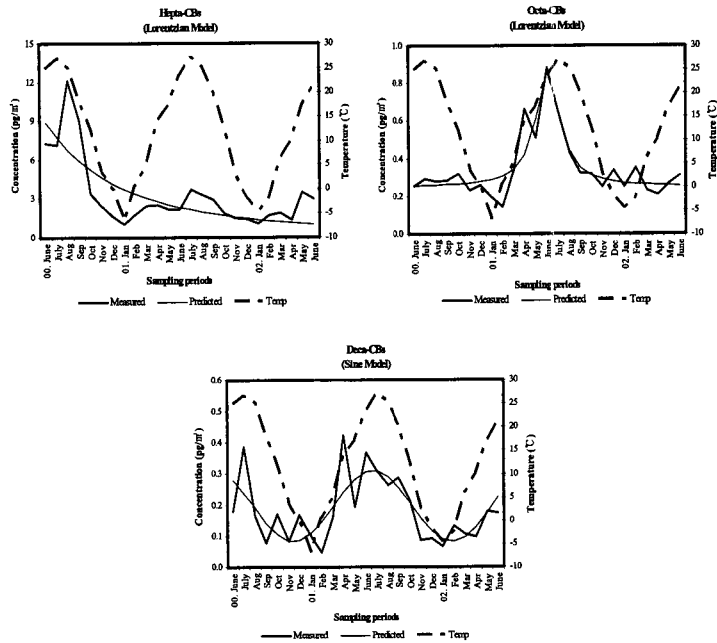


Fig. 3. Monthly variations of PCB homologs using nonlinear regression model

4. Conclusion

This study might be intended to estimate the cycle of gaseous PCBs concentration in the atmosphere using nonlinear regression model in rural of Kyong-gi province in 2000-2002 for every one week with short-term sampling period (2 days) with high volume air sampler.

The determination coefficient (R^2) of the Lorentzian model for 2-day and monthly total PCBs were 0.62($p < 0.0001$), 0.88($p < 0.0001$), respectively. The parameters of Lorentzian model for 2-day and monthly variations were also very significant ($p < 0.0001$).

The equations of the two

nonlinear regression models using Lorentzian and Sine model for 2-day and monthly homologs variations were very significant ($p < 0.0001$).

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