



Seasonal Variation and Gas/Particle Partitioning of PCBs in Air from Central Urban Area of an Industrial Base and Coastal City –Tianjin, China

Zhi-Yong Li*, Yu-Ling Zhang, Lan Chen

School of Environmental Science and Engineering, North China Electric Power University, No.689 Huadian Road, Baoding 071000, China

ABSTRACT

The 26 air samples were collected from Tianjin urban areas from July 2010 to May 2011 for the analysis of 86 PCB congeners to investigate the gas/particle partitioning of PCBs. The total PCBs concentration (in pg/m^3) ranged from 31.28 to 650.33 (mean: 273.77) and showed a significantly seasonal variation as summer > autumn > spring > winter. Gas PCBs accounted for 80.79% of total PCBs. The fraction of each gas PCB homolog increased with the decreasing chlorine atoms. The contribution of gas PCBs to total PCBs showed a strong seasonal variation with summer (94.07%) > autumn (78.91%) > spring (78.19%) > winter (56.02%). Tri-, tetra- and penta-PCBs were the predominantly homologs in Tianjin atmosphere. The natural logarithm of partial pressure of PCBs were well correlated with the inverse absolute environmental temperature ($R = 0.79$). The steep slope of -4933.64 obtained from Clausius–Clapeyron (C.C) plot indicated the influence of local PCBs sources. In generally, the C.C slopes and the surface-air exchange enthalpy (ΔH_{SA}) for different PCB homologs increased with the increasing chlorine atoms. The fraction of particle bound PCBs were underestimated for PCBs with $P_L^0 > 10^{-3.85}$ Pa and overestimated for PCB congeners with $P_L^0 < 10^{-3.85}$ Pa by Junge-Pankow model. The logarithm of particle/gas partitioning coefficients ($\log K_p$) of PCBs were well correlated with the logarithm of respective sub-cooled vapor pressures ($\log P_L^0$) ($R = 0.72$) and the octanol-air partition coefficient ($\log K_{OA}$) ($R = 0.77$). The slopes for $\log K_p$ against $\log P_L^0$ and $\log K_{OA}$ plots were -0.44 and 0.48 , deviated significantly from the expected -1 and $+1$ for the equilibrium state of gas/particle partitioning, possibly explained by the emission of PCBs and particles from the local industries and other sources. The TEQ concentrations (fg/m^3) for 12 dioxin-like PCB congeners ranged from 35.628 to 612.796 with the mean value as 144.878.

Keywords: PCBs; Gas/particle partitioning; Clausius-Clapeyron plot; Sub-cooled vapor pressure; Octanol-air partition coefficient.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a well-known class of ubiquitous pollutants characterized by high lipophilicity, extreme toxicity and high resistance to environmental degradation process (Breivik *et al.*, 2002; Guo *et al.*, 2014; Liu *et al.*, 2014). These physiochemical properties are representative of persistent organic pollutants (POPs) and PCBs can act as their ideal marker compounds for global redistribution of POPs (Hornbuckle *et al.*, 1993; Ockenden *et al.*, 2003). Decades after restrictions, atmospheric PCBs have reached a steady level, and in several areas the PCBs levels were found to decrease only slowly or not at all (Panshin and Hites, 1994; Hillery *et al.*, 1997; Haugen *et al.*,

1999; Hung *et al.*, 2005). The atmosphere is the main transport pathway, major source of PCBs to many aquatic ecosystems and an important media to under the behavior of PCBs (Hoff *et al.*, 1996; Tseng *et al.*, 2014a). PCBs are semi-volatile compounds (Tseng *et al.*, 2014b) and redistribute between the gas and particle after they enter the atmosphere, are subjected to removal mechanisms and reach a partitioning equilibrium depended on temperature and vapor pressure of chemicals (Wania *et al.*, 1998; Yeo *et al.*, 2003). The fate of atmospheric POPs is primarily determined by their gas-particle partitioning (Pankow and Bidleman, 1992; Cotham and Bidleman, 1995; Cincinelli *et al.*, 2014). The removal mechanisms including wet and dry deposition, photolysis, and reaction with OH radicals act differently on gas and particle bound POPs, thereby determine the efficiency and scope of their long-range transport (Bidleman, 1988).

In China, about 10,000 tons of PCBs were produced from 1965 to 1974 and the PCBs containing transformers were used until the late 1990s (Xing *et al.*, 2005). In addition, unknown amounts of electric equipments were imported

* Corresponding author.

Tel.: +86 312 7525505; Fax: +86 312 7525505
E-mail address: lzy6566@126.com

from America, France, Japan and Holland (Mai *et al.*, 2005). In addition to the emission of conventional PCBs products, some industrial activities such as oil refinery, petrochemical, metal reclamation, coal and refuse incineration for power generation, and paint production would be the new PCBs sources (Li *et al.*, 2011b; Park *et al.*, 2013). Previous studies reported higher atmospheric PCBs levels in industrialized and highly populated cities (Breivik *et al.*, 2002; Gouin *et al.*, 2005; Kim and Masunaga, 2005; Manodori *et al.*, 2006). Lots of models focused on gas/particle partitioning of PCBs have been studied extensively (Yamasaki *et al.*, 1982; Pankow, 1987; Finizio *et al.*, 1997; Harner and Bidleman, 1998; Lohmann *et al.*, 2000). However, the research on gas/particle partitioning of PCBs is still at a relatively early stage in China.

As the economic center, Tianjin holds the largest harbor of northern China. In this region, lots of industrial activities such as shipbuilding, oil exploiting and refinery, petrochemical and coal and refuse incineration for power generation may be potential sources of PCBs. Li *et al.* (2011b) reported the “primary sources fractionation effect” of soil PCBs in Tianjin. So the detailed and thorough analysis of atmospheric PCBs for Tianjin under the influence of commercial PCBs application and new industrial activities will provide the baseline for future in China. The main aims of this study are to investigate: 1) the seasonal variation of atmospheric PCBs levels; 2) the gas/particle partitioning of atmospheric PCBs; 3) individual congener and homologs distribution in gas and particle phase; 4) the state of PCBs gas/particle partitioning using different models.

METHODS

Sampling Programs

Tianjin located at the east of the Bohai Sea (E 116.72°–118.07° and N 38.57°–40.25°), is the biggest coastal industrial base in north China. In this study, air samples (N = 26) were collected on a platform located on the roof of a six-story building (19 m height) at Nankai University (E 117.16°, N 39.10°) using a modified TH-1000 air sampler (Tianhong instrument Co., Ltd, Wuhan, China) operating at a flow of 1050 L/min during the period of July 2010–May 2011. The air was drawn through a glass fiber filter (GFF) to collect particles and then through polyurethane foam (PUF) (length 12 cm, diameter 6.35 cm) plug to collect compounds present in the gas. The sampling period was 24h (from first day 8:00 a.m. to second day 8:00 a.m.). The average sample volume (under the standard state) ranged from 1486.47 to 1690.55 m³ with the mean value as 1557.99 m³. Meteorological parameters such as temperature, wind speed, wind direction and relative humidity were obtained from the China Tianjin Meteorological Administration.

Chemical Analysis

The GFFs were pre-combusted at 450°C for 12 h in loosely wrapped aluminum foil envelopes, then sealed and stored at 4°C until sampling. The PUFs were washed by boiled water, methanol and Soxhlet extraction with acetone:n-hexane (1:1 v/v) for 24 h before sampling. After sampling,

GFFs and PUFs were all sealed in glass jars and stored at –20°C until analysis. Three groups of PCB standards with the catalog numbers as C-IADN-01, 02 and 03 (containing 84 congeners) and PCB-157 and -189 (Accustandard, Inc. (New Haven, CT)) were used in this study. PCB-14, 65, 166 were spiked to samples before extraction as surrogate standards, 2,4,5,6-tetrachloro-m-xylene and PCB-209 (Accustandard, Inc. (New Haven, CT)) were used for internal standards. Other solvents including n-hexane and acetone (pesticide grade, Fisher Scientific, Inc. Fair Lawn, New Jersey) were also used to the analysis of PCBs. The GFFs and PUFs were extracted and analyzed separately to study the PCBs gas/particle partitioning. The samples were Soxhlet extracted with n-hexane:acetone (1:1 v/v) for 24 h. The extracts were concentrated to 2 mL by rotary vacuum evaporation and solvent-exchanged to hexane. The concentrated extracts were cleaned up using a silica gel column, which was made up using a 1 g silica gel column (CNW Technologies GmbH, Germany) filled with 1 cm anhydrous sodium sulfate and 1 g of acid silica gel (50% concentrated sulfuric acid, wt/wt). When the extracts passed through this column, PCBs fractions were eluted with 30 mL n-hexane. The collected eluent was concentrated by a rotary evaporator and then reduced to 0.5 mL under a gentle N₂ stream for analysis. The extracts were analyzed using a HP 6890GC/5973i MS system equipped with a DB-5 fused silica capillary column (60 m × 0.25 mm i.d.). The GC column was maintained at 100°C for 2 min and ramped at 1 °C/min to 240°C, then ramped at 10 °C/min to 280°C and maintained for 20 min and the total run time was 165 min.

GC/MS system was processed using selected ion monitoring mode with m/z as 222, 224 for di-PCBs, 256, 258 for tri-PCBs, 290, 292 for tetra-PCBs, 326, 328 for penta-PCBs, 360, 362 for hexa-PCBs, 394, 396 for hepta-PCBs, 428, 430 for octa-PCBs, 462, 464 for nona-PCBs and 498 for deca-PCBs, respectively. The ions as 222, 256, 292, 326, 360, 394, 428, 464 498 were selected to quantify the homologs as di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and deca-PCBs, respectively.

Quality Control and Assurance

A procedural blank, a matrix-spiked sample, a sample duplicate and a solvent blank were processed every 8 samples. No any target compounds were detected in the procedural and solvent blank. The detection limits were defined as detectable concentration when a signal-to-noise ratio greater than three times of the average baseline variation. The estimated method detection limits (in pg/m³, assuming a 1500 m³ of sampling volume) ranged from 0.07 for PCB-156 to 1.10 for PCB-12/13 with the mean value as 0.25. The recoveries for surrogate standard PCB-14, 65, and 166 were 92 ± 17%, 89 ± 12 and 86 ± 14% for PUFs. For GFFs, they were 90 ± 19%, 87 ± 11% and 84 ± 15%, respectively. The recoveries for 86 PCB congeners in 5 matrix-spiked samples were all within 72–121% and the standard deviation was lower than 12%. The standard deviations for 6 pairs of repeated samples were all lower than 11%. The sampling artifacts associated with GFFs and PUFs would significantly affect the gas/particle partitioning.

The GFFs have two contrary effects on the gas/particle partitioning: 1) the gas PCBs may be absorbed to GFFs surface and particles on this surface; 2) the more volatile PCBs may be stripped from the GFFs by gas flow when the gas PCBs decreases, temperature increases or due to gas PCBs reactions on GFFs. The rear second filter was used to access the adsorption extent of PCBs on GFFs. The mass of PCBs in the backup filter ($N = 6$) accounted for less than 4.5% of total amount or not detected at all. Therefore, these values were neither subtracted from particles nor added to gas. The volatilization from GFFs has not been accessed in this study. The PUFs were cut into two halves before sampling to assess the potential for gas PCBs breakthrough. The bottom half of the PUFs ($N = 5$) accounted for average of 9.88% of the total PCBs mass and dominated by tri- and tetra-PCBs. In this study, the gas PCBs concentrations were adjusted accordingly.

RESULT AND DISCUSSION

Atmospheric PCBs Concentrations

The atmospheric PCBs during the sampling period ranged from 39.18 to 659.62 pg/m^3 with the mean value as $273.77 \pm 164.94 \text{ pg}/\text{m}^3$ (Fig. 1). The maximum occurred on 22 July (summer) and the minimum occurred on 20 October (a raining day). The particle phase PCBs could be effectively washed out by rain was reported by Offenberg and Baker (1997). The PCBs concentrations were well correlated with the temperature ($R = 0.78$, $P < 0.005$) and relative humidity ($R = 0.63$, $P < 0.005$). The samples collected in winter reduced the correlation coefficient between the

$\Sigma 86\text{PCBs}$ and temperature. When the temperature was lower than 0°C , the atmospheric PCBs concentrations were not correlated with the temperature (Carlson and Hites, 2005). The high relative humid can promote the volatilization process was reported in Hippelein and McLachlan (2000). The PCBs concentrations showed strong seasonal variation corresponding to seasonal temperature changes with summer ($430.99 \pm 103.17 \text{ pg}/\text{m}^3$) > autumn ($193.87 \pm 121.86 \text{ pg}/\text{m}^3$) > spring ($185.34 \pm 42.94 \text{ pg}/\text{m}^3$) > winter ($96.16 \pm 39.63 \text{ pg}/\text{m}^3$) (Fig. 1(b)). The increasing volatilization rate with the increasing temperature may be the explanation for this variation. Similar seasonal trends were also reported (Manodori *et al.*, 2006; Castro-Jiménez *et al.*, 2009).

For individual PCB congener, the higher molecular weight (HMW) congeners with 6–9 chlorines accounted the higher fraction of particle PCBs, while the lighter molecular weight (LMW) congeners with 2–5 chlorines accounted for the higher fraction of gas PCBs (Table S1).

Further, all the top 20 congeners in gas were LMW PCBs, while the HMW PCBs accounted for 46.06% of the top 20 particle congeners (Fig. 2).

The annual average gas and particle PCBs concentrations were 242.43 ± 170.15 and $31.34 \pm 16.94 \text{ pg}/\text{m}^3$, both of them exhibited seasonal variation. For gas PCBs, they were summer (406.90 ± 104.71) > autumn (162.23 ± 111.04) > spring (147.06 ± 51.64) > winter (56.15 ± 37.01). For particle PCBs, they were winter (40.02 ± 17.42) > spring (38.29 ± 24.87) > autumn (31.64 ± 19.07) > summer (24.09 ± 9.14). The similar trends for gas PCBs were reported in Great Lakes and Niigata (Hillery *et al.*, 1997; Murayama *et al.*, 2003). The contribution of particle PCBs to total PCBs decreased

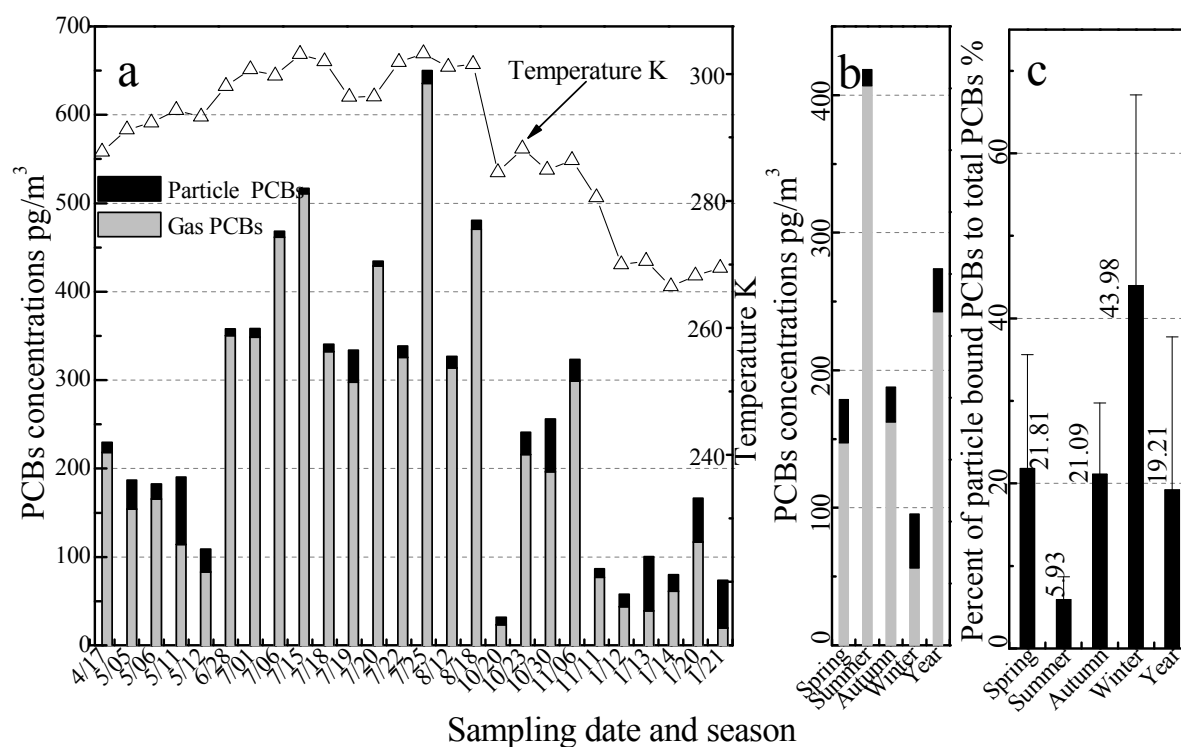


Fig. 1. Concentrations of gas and particle PCBs for the different a) sampling date and b) seasons as well as c) the percent of particle bound PCBs to total PCBs.

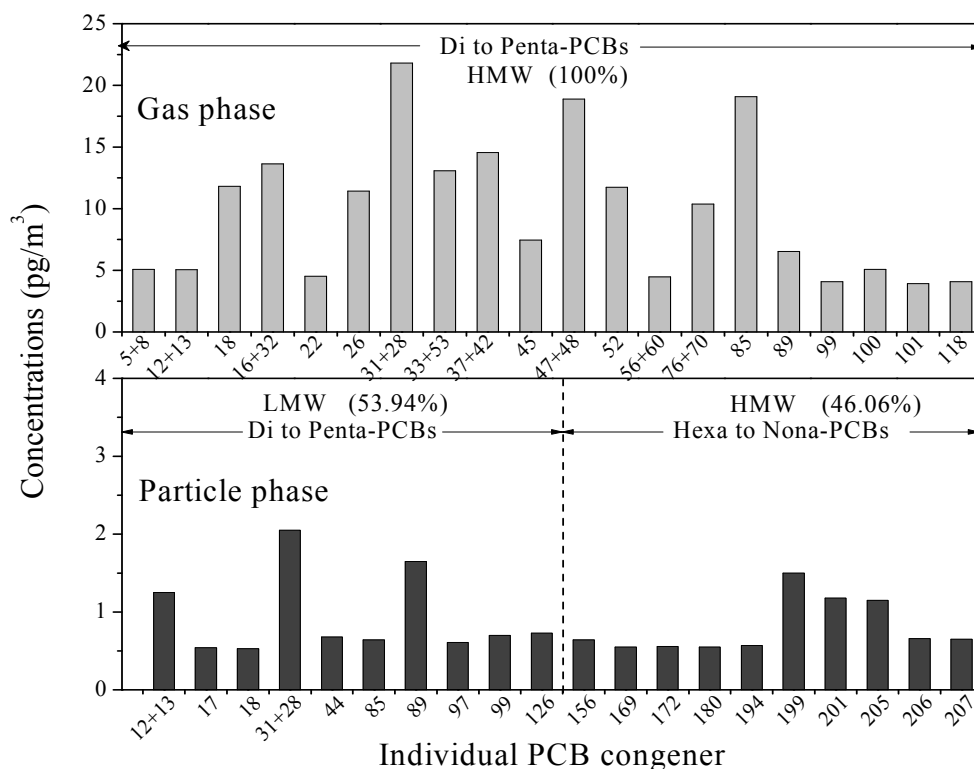


Fig. 2. Concentrations of the top 20 PCB congeners in gas and particle phase.

with the increasing temperature ($R = -0.72$, $P < 0.05$) and showed the strong seasonal variation with winter (43.98%) > spring (21.81%) > autumn (21.09%) > summer (5.93%) (Fig. 1(c)). The gas PCBs accounted for 80.79% of total PCBs for Tianjin, was slightly lower than those of other studies. They were 98.94% for Athens (Mandalakis *et al.*, 2002), 95% for Milwaukee (Wethington and Hornbuckle, 2005), 87% for Izmir (Cetin *et al.*, 2007) and 84.31% for Bursa (Cindoruk *et al.*, 2007). The higher atmospheric particles ($325.82 \pm 43.28 \mu\text{g}/\text{m}^3$) concentration in Tianjin would be responsible for the lower gas PCBs fraction ($80.79\% \pm 18.53\%$).

The annual average percentage of gas and particle fraction to each PCB homolog was shown in Fig. 3. In generally, the percentage of gas fraction increased with the decreasing chlorines except di-PCBs. The similar contribution patterns were also reported in Ansong (Yeo *et al.*, 2003) and Yokohama (Kim and Masunaga, 2005).

The predominant PCB homologs in Tianjin urban atmosphere were tri- (30.91%), tetra- (26.42%), penta- (22.50%) and di-PCBs (9.04%) (Fig. S1). The lighter homologs with 2–4 chlorines have higher vapor pressure, so have the higher levels in atmosphere. Similar homolog distribution patterns were reported in urban and rural areas in Korea (Yeo *et al.*, 2004) and urban area of Bursa (Cindoruk *et al.*, 2007). While different results were found in some other regions, they were tetra-, penta- and hexa-PCBs for Yokohama (Kim and Masunaga, 2005) and di-, tri- and tetra-PCBs for King George Island (Li *et al.*, 2012b). The homolog distribution patterns varied according to sampling locations, the difference of selected PCB congeners among different studies, local historical application, historical

production of PCBs and the emission intensity would be explained these difference of homolog distribution.

Comparison with Other Regions in the World

Seven indicator PCB congeners (IPCs) including PCB-28, 52, 101, 118, 138, 153, and 180 were commonly measured and often compared in PCBs analysis. The sum of IPCs showed a strong seasonal trends (in pg/m^3) with summer (73.04) > spring (43.72) > autumn (32.21) > winter (17.93). To better understand the atmospheric PCBs levels in Tianjin, comparison were conducted with others as shown in Table 1. In generally, the PCBs levels of Tianjin were lower than European cities (Halsall *et al.*, 1995; Mandalakis *et al.*, 2002; Manodori *et al.*, 2006; Menichini *et al.*, 2007), American cities (Brunciak *et al.*, 2001) and some industrial areas (Cetin *et al.*, 2007; Cindoruk *et al.*, 2007; Mari *et al.*, 2008), while higher than Asian and African urban and rural areas (Yeo *et al.*, 2003; Batterman *et al.*, 2009; Syed *et al.*, 2013) as well as background and forest areas (Oehme *et al.*, 1996; Horstmann and McLachlan, 1998; Menichini *et al.*, 2007; Li *et al.*, 2012b). These results reflected the different commercial PCBs application, emission intensity of the local sources, temperature and humidity among different regions. Compared with other regions of China, the levels of Tianjin were similar to a steel complex in Liaoning province (summer $66.60 \text{ pg}/\text{m}^3$, winter $42.47 \text{ pg}/\text{m}^3$) (Li *et al.*, 2011a) and urban areas of Xi'an (Han *et al.*, 2014), lower than northern South China Sea (Li *et al.*, 2012a) (Table 1), much lower than a transformer recycling area-Taizhou, Zhejiang province ($\Sigma 37\text{PCBs} = 17.6 \text{ ng}/\text{m}^3$) (Xing *et al.*, 2011), and higher than that of Chinese background levels (Wu *et al.*, 2011) (Table 1).

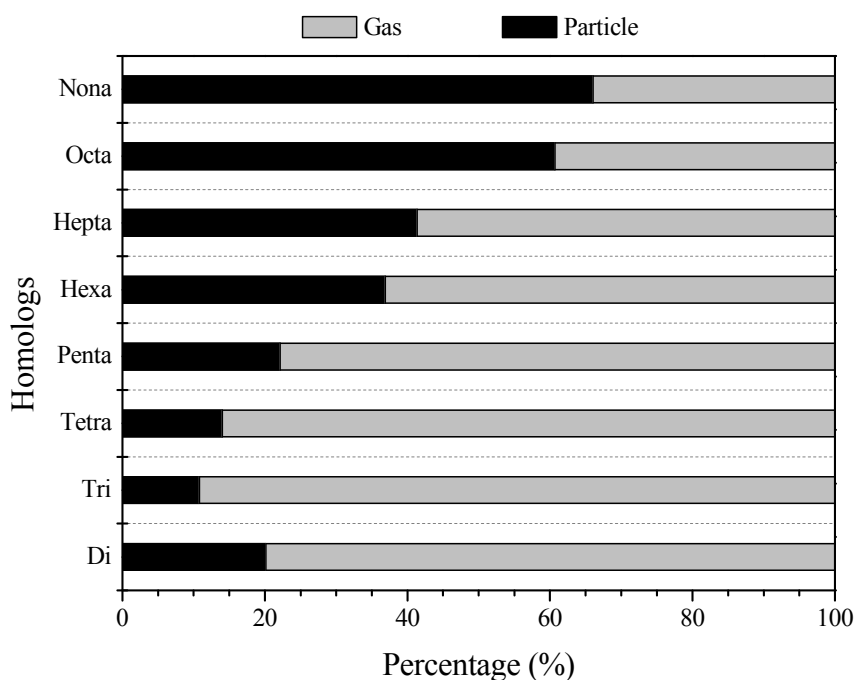


Fig. 3. Percentage of gas fraction and particle fraction to each PCB homolog.

Table 1. Comparison of concentrations of seven indicator PCBs in Tianjin atmosphere with others (Units: pg/m^3).

Area	Description	28	52	101	118	138	153	180	Sum	Reference
Tianjin, China	Urban	23.92	12.45	4.16	4.55	0.40	0.95	2.52	48.95	This study
Manchester	Urban	NA	NA	84.5	29.9	28.0	36.9	24.0	203.3	(Halsall et al., 1995)
London	Urban	NA	NA	117.0	52.9	23.0	26.2	12.0	231.1	(Halsall et al., 1995)
Baltimore	Urban	55.5	55.9	32.1	NA	18.4	31.5	4.6	142.5	(Brunciak et al., 2001)
Athens	Urban	30.46	25.13	21.04	9.94	3.36	7.04	NA	66.51	(Mandalakis et al., 2002)
Mestre ^a	Urban	30.3	23.3	NA	7.7	15.7	17.4	4.9	99.3	(Manodori et al., 2006)
Rome	Urban	39.6	48.3	34.0	42.9	18.8	17.2	5.35	205.9	(Menichini et al., 2007)
Izmir	Urban	53.6	42.1	18.7	12.7	18.4	15.9	7.7	169	(Cetin et al., 2007)
KwaZulu-Natal	Urban	5.46	1.37	5.60	12.15	8.04	5.94	0.43	38.99	(Batterman et al., 2009)
Kyonggi-do	Rural	12.2	6.1	3.7	ND ^c	1.1	1.2	0.5	24.8	(Yeo et al., 2003)
Melpitz	Rural	11	8	3	NA	1	2	1	25	(Mandalakis and Stephanou, 2007)
Izmir	Industrial	232.9	159.2	71.0	41.5	56.7	48.4	16.9	626.5	(Cetin et al., 2007)
Bursa	Industrial	47.39	29.12	4.26	3.2	0.61	4.09	0.17	88.84	(Cindoruk et al., 2007)
Catalonia	Industrial	66	42	24	2	13	14	5	169	(Mari et al., 2008)
Lombardy	Semi-rural	9.4	14.1	10.3	4.6	5.5	8.3	3.6	46.8	(Castro-Jiménez et al., 2009)
Punjab Province	Industrial	25	4.1	2.5	2.6	2.4	2.6	0.5	39.7	(Syed et al., 2013)
Arctic, Norway	Background	4.30	2.47	1.28	0.53	0.54	0.61	0.16	9.89	(Oehme et al., 1996)
Simbruini mountains	Background	7.75	7.83	4.98	6.33	2.78	2.39	0.65	32.71	(Menichini et al., 2007)
King George Island	Background	3.39	0.50	0.11	0.10	0.09	0.13	0.02	4.34	(Li et al., 2012)
Bayreuth	Forest	14	8	6	NA	3	5	1	36	(Horstmann and McLachlan, 1998)
Northern South China sea	Over sea	39.5	12.6	2.92	0.82	NA	1.23	NA	57.07	(Li et al., 2012)
Across China	Background	7.07	2.05	0.55	0.25	0.31	0.38	0.12	10.73	(Wu et al., 2011)

^a only gas phase PCBs were detected. ^b NA: not analyzed. ^c ND: not detected.

Relationship of Gas PCBs with Air Temperature Using Clausius–Clapeyron Equation

The atmospheric PCBs are predominantly found in gas compared with particles (Cindoruk and Tasdemir, 2007). Other than long-range transport and instantaneous discharge, volatilization from contaminated surfaces is an important source for atmospheric PCBs (Kim and Masunaga, 2005).

The atmospheric PCBs concentrations have been shown to be depending on temperature controlled volatilization from soils, vegetation and water bodies (Simcik et al., 1999; Mandalakis and Stephanou, 2007). The Clausius–Clapeyron (C.C) equation was used to investigate the relationship between gas PCBs and environmental temperature (Halsall et al., 1999).

$$\ln P = \left(\frac{-\Delta H_v}{R} \right) \left(\frac{1}{T} \right) + \text{const} \quad (1)$$

where P is the partial pressure of PCBs (atm), ΔH_v is the enthalpy of vaporization (kJ/mol), and R is the ideal gas constant (8.314 J/mol/K). Simcik *et al.* (1999) defined ΔH_v as ΔH_{SA} (energy necessary to cause vaporization from surface to air). The slope and ΔH_{SA} obtained from regressed results were used to evaluate the relative importance of short- and long-range transport (Wania *et al.*, 1998). Long-range transport leads to shallower slopes, while re-volatilization results in steep slopes. The gas PCBs concentrations were converted into partial pressures and the natural logarithms of these values ($\ln P$) were regressed against reciprocal mean temperature ($1/T$) of each sampling event. Vapor pressure of coeluting PCBs was calculated by averaging the vapor pressures of individual congener (Mandalakis *et al.*, 2002).

Fig. 4 showed the regressed results for selected indicator PCBs and all the sampling events. The C.C slopes for PCB-28, 52, 101, 138 and 180 were -3183, -4130, -6375, -4520 and -6471, respectively. Assuming the hypothesis proposed by Wania, these congeners were mainly originated from re-volatilization of local sources (Wania *et al.*, 1998). The LMW congeners with higher volatility may be more related to advection of distant air mass compared to volatilization of local sources, therefore have the shallower slopes (Castro-Jiménez *et al.*, 2009). Haugen *et al.* (1999) reported the similar trends of C.C slopes for indicator PCBs in south Norway. Currado and Harrad (2000) pointed out the C.C slopes of PCBs increased with the increasing molecular weight in Birmingham, U.K.

We calculated the C.C slopes for all the PCB congeners and they ranged from -1350 for PCB18 to -8675 for PCB201. The average annual C.C slope for all the congeners was -4933.64 ± 1888.09 , the steep slope of -4933.64 indicated the atmospheric PCBs of Tianjin were mainly originated from local sources emissions. The steep slope of -4933.64

was in the range of -4500- -8000 for eastern rural area in Germany (Mari *et al.*, 2008), higher than -3888 for urban site in Korea (Yeo *et al.*, 2004), -567.85 for Bursa (Cindoruk *et al.*, 2007) and -3851 for sub-alpine in Italy (Castro-Jiménez *et al.*, 2009), but lower than -6323 for Birmingham (Currado and Harrad, 2000).

In generally, the C.C slopes of PCB homologs and ΔH_{SA} increased with the increasing chlorines atoms (Fig. S2) and they were well correlated ($R = 0.71$, $p < 0.05$). The slopes for di-, tri-, tetra-, penta-, hexa-, hepta, octa- and nona-PCBs were -1331, -4666, -6660, -7222, -7527, -7671, -5668 and -8809, respectively. The corresponding ΔH_{SA} were 11.06, 38.79, 55.37, 60.04, 62.58, 63.78, 47.12 and 73.24 kJ/mol, respectively. The ΔH_{SA} (in kJ/mol) values were in the range of 38–66 for a rural site in Germany (Mandalakis and Stephanou, 2007), 19–87 for New Jersey (Brunciak *et al.*, 2001) and 27–112 for Birmingham (Currado and Harrad, 2000). It should be mentioned, the slope for octa-PCBs was relatively lower, possibly explained by the lack of paired PCBs data in both particle and gas phase (Hoff *et al.*, 1998).

Meanwhile, multiple regression analysis based on modified C.C plot of the relationship between wind direction (WD), wind speed (WS) and $\ln P$ for both individual homolog groups and Σ PCB was conducted. No significant relationships exist between $\ln P$ and any of these variables, which may be explained the strong influence of local source emissions determined by temperature. The related yield new equations from C.C equation were shown as follow. Currado and Harrad (2000) also adopted the same analysis method in the study on atmospheric PCBs from Birmingham, UK.

$$\ln P = m_1 \left(\frac{1}{T} \right) + m_2 \ln WS + b \quad (2)$$

$$\ln P = m_1 \left(\frac{1}{T} \right) + m_3 \sin WD + m_4 \cos WD + b \quad (3)$$

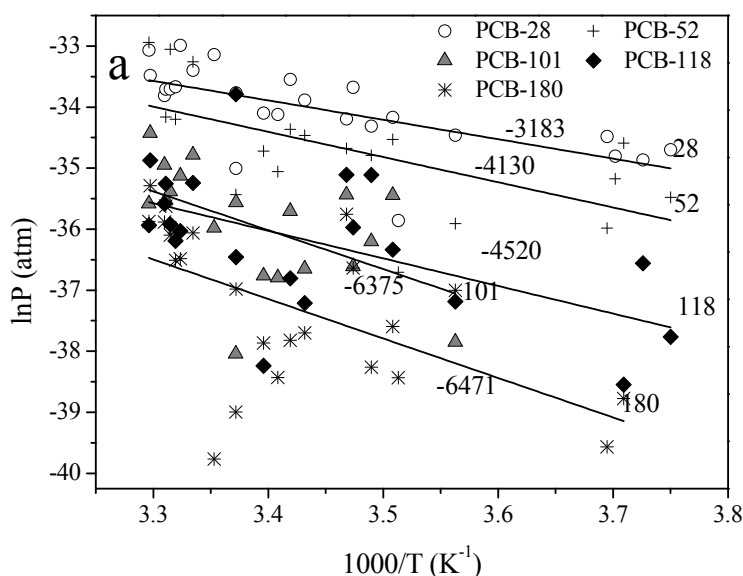


Fig. 4. Regressed results of Clausius-Clapeyron equation for the indicator PCB congeners.

Junge-Pankow Model

The subcooled liquid vapor pressure (P_L^0) and aerosol surface area (θ) have been used in an adsorptive model reviewed by Pankow (Pankow, 1987):

$$\phi = c\theta / (P_L^0 + c\theta) \quad (4)$$

where Φ is the particle-bound PCBs fraction (%), θ is the particle surface area per volume of air (m^2/m^3), and c is a constant depends on the heat of condensation of the chemical and particle surface properties. θ was 4.2×10^{-5} for clean continental background, 1.5×10^{-4} for rural region and 1.1×10^{-3} for urban region (Harner and Bidleman, 1998). The value of 1.1×10^{-3} for urban region was chosen in this study. The 0.172 Pa m for c assumed by Junge (Lohmann *et al.*, 2000) was employed in this study. The θ and c can't be measured directly and only be estimated, which is one drawback of this model. Although the experimental estimate of these parameters using non environmental temperature or mixture of compounds complicates this model, it also provides another error source (Falconer and Harner, 2000). The fraction of particle bound PCBs to total atmospheric PCBs were underestimated for PCB congeners with $P_L^0 > 10^{-3.85}$ Pa and overestimated for PCB congeners with $P_L^0 < 10^{-3.85}$ Pa by Junge-Pankow model (Fig. 5). The predicted values were correlated with measured values ($R = 0.71$, $p < 0.001$). The non-equilibrium state of gas/particle partitioning and the lack of data of particle bound LMW PCBs would be the explanation of relative lower coefficient.

Correlation of $\log K_p - \log P_L^0$ and $\log K_p - \log K_{OA}$

A parameter K_p ($\text{m}^3/\mu\text{g}$) was successfully used to parameterize gas/particle partitioning of SVOCs (Yamasaki *et al.*, 1982; Pankow, 1987; Cincinelli *et al.*, 2014), extensively

accepted by some researchers, was calculated for each PCB congener using Eq. (5):

$$K_p = (F/A)/TSP \quad (5)$$

where F and A are the particle and gas PCBs concentrations (pg/m^3), TSP is the concentration of total suspended particles ($\mu\text{g}/\text{m}^3$). Only data points where the PCBs were above the detection limit in both gas and particles were included in the calculations. The $\log K_p$ was regressed against the temperature corrected $\log P_L^0$ and some useful information was extracted from the slope m_r and intercept b_r (Yamasaki *et al.*, 1982).

$$\log K_p = m_r \log P_L^0 + b_r \quad (6)$$

By itself, Eq. (4) does not indicate whether the partitioning process is primarily adsorptive to surfaces, adsorptive into some phases, or combination of them. The slope m_r indicated the degree of equilibrium and should be -1 for equilibrium status (Pankow and Bidleman, 1992; Pankow, 1994). Some lab and field data showed the slope shallower than -1 , which were identified as non-equilibrium regardless of sampling artifacts and analysis error (Cotham and Bidleman, 1995; Simcik *et al.*, 1998; Tasdemir *et al.*, 2004; Cindoruk *et al.*, 2007).

The P_L^0 was adjusted according to the mean temperature during sampling period using " $\log P_L^0 = M_L/T + b_L$ " and Falconer and Bidleman (1994) provided the m_L and b_L values for 180 PCB congeners. Considering the detection limit, chromatographic separation effect and gas/particle concentration for each congener, the P_L^0 was calculated for 13 congeners including PCB-85, 99, 114, 156, 167, 169, 172, 180, 194, 199, 201, 205 and 207.

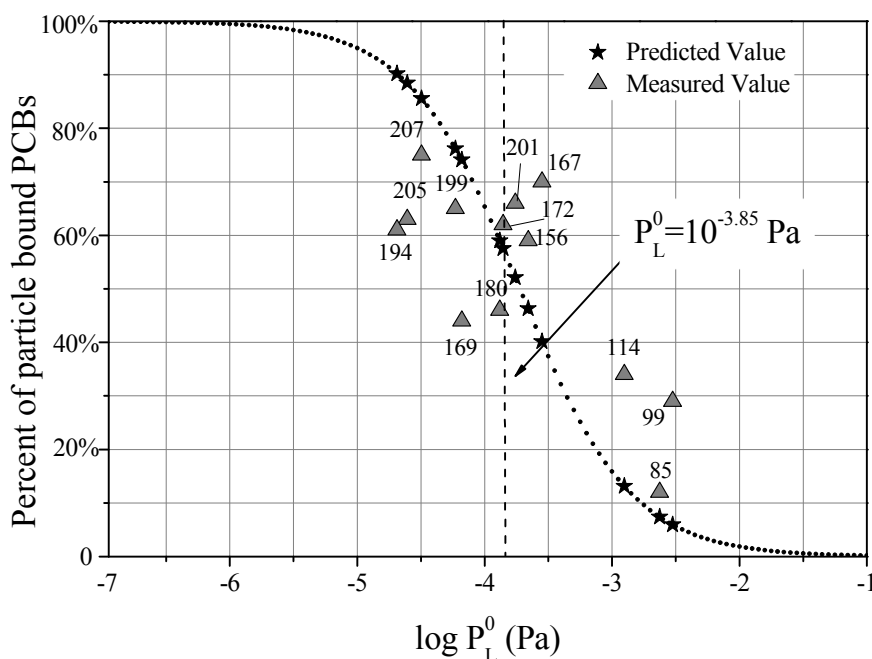


Fig. 5. Comparison between the measured fraction of particle bound PCBs and the predicted values by Junge-Pankow model.

The slope of the $\log K_p - \log P_L^0$ plot was -0.44 ($R = 0.72$) for all the sampling events, indicated the non-equilibrium state for PCBs gas/particle partitioning (Fig. 6(a)). Li *et al.* (2011b) reported some new industrial sources affected the soils PCBs pollution characterization of Tianjin. The PCBs emission of these sources would result in non-equilibrium state due to the time was needed for PCBs react between gas and particle before reach the state of equilibrium. In addition, Simcik *et al.* (1998) pointed out the changing of TSP concentrations, temperature and number of adsorption sites in particles surface, differences between enthalpies of desorption and volatilization and activity coefficients in organic matter would be the reasons for the slope deviation from -1 .

The slope of -0.44 was in the range of those for previous studies conducted in other urban and rural regions (Table 2), indicated the PCBs in Tianjin air would rather possibly resulted from continuous volatilization and emission of local sources. The summarized results in Table 3 showed that the slopes significantly deviated from -1 was more frequently observed for PCBs regardless of sampling locations.

The Junge-Pankow adsorption model uses P_L^0 as a

correlation parameter and the disadvantage was discussed by some researchers (Harner and Bidleman, 1998; Falconer and Harner, 2000). Pankow (1998) proposed that absorption of gas chemicals into an organic film containing particles makes an important contribution to the overall particle-gas partitioning process. The octanol-air partition coefficient (K_{OA}) is recognized as a key descriptor of chemicals partitioning between the atmosphere and organic phases. Recently, K_{OA} based approaches have been successfully employed to model surface-air partitioning of persistent organic pollutants to aerosols (Finizio *et al.*, 1997; Falconer and Harner, 2000; Lohmann *et al.*, 2000). As an alternative parameter, K_{OA} could eliminate the disadvantage of P_L^0 . In principle, K_{OA} be calculated as Eq. (7), where K_{OW} is the octanol-water partition coefficient, H is the Henry's law constant, T is absolute temperature, and R is the ideal gas constant.

$$K_{OA} = \frac{K_{OW} RT}{H} \quad (7)$$

$$H = H^* RT \quad (8)$$

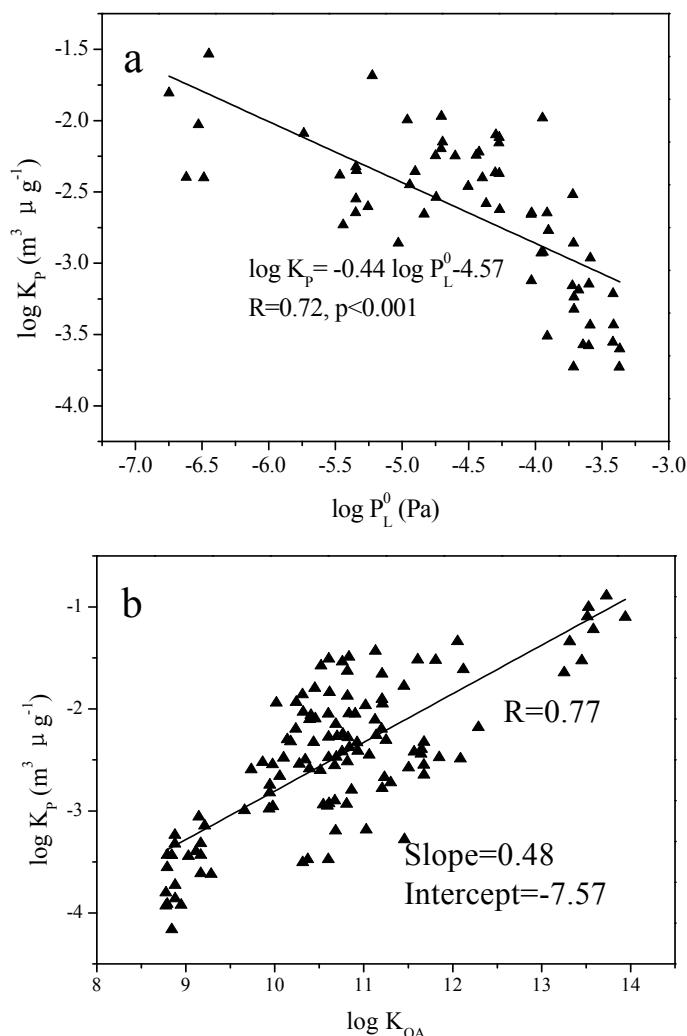


Fig. 6. Regression analysis of $\log K_p - \log P_L^0$ (a) and $\log K_p - \log K_{OA}$ (b) for all the sampling events in Tianjin.

Table 2. Regressed results of $\log K_P - \log P_L^0$ plots for Tianjin and other regions in the world.

Research area	Description	m_L	b_L	R	Reference
Tianjin, China	Urban	-0.44	-4.57	0.72	This study
Saronikos gulf, Greece	Coastal	-0.32	-4.01	0.65	(Mandalakis <i>et al.</i> , 2002)
Chicago, US	Urban	-0.64	-3.77	0.88	(Simcik <i>et al.</i> , 1998)
Manchester, UK	Urban	-0.67	-5.1	0.90	(Lohmann <i>et al.</i> , 2000)
Athens, Greece	Urban	-0.48	-4.59	0.84	(Mandalakis <i>et al.</i> , 2002)
Chicago, US	Urban, Land wind	-0.47	-4.06	0.53	(Tasdemir <i>et al.</i> , 2004)
Yokohama, Japan	Urban	-0.74	-5.42	0.85	(Kim and Masunaga, 2005)
Bursa, Turkey	Urban	-0.26 to -0.63	-	0.61–0.68	(Cindoruk and Tasdemir, 2007)
Singapore	Urban	-0.58	-4.72	0.85	(He and Balasubramanina, 2009)
Lake Michigan, US	Rural	-0.73	-5.18	0.85	(Cotham and Bidleman, 1995)
Austwick, UK	Rural	-0.52	-4.55	0.84	(Lohmann <i>et al.</i> , 2000)
Clapham, UK	Rural	-0.44	-3.98	0.86	(Lohmann <i>et al.</i> , 2000)
Kyonggi-do, Korea	Rural	-0.53	-4.33	0.92	(Yeo <i>et al.</i> , 2003)
Melpitz, Germany	Rural	-0.40	-3.60	0.57–0.95	(Mandalakis and Stephanou, 2007)

Table 3. Comparison of regressed results of $\log K_{OA} - \log K_P$ between Tianjin urban area and other regions in world.

Regions	description	m_r	b_r	R	References
Tianjin	Urban	0.48	-7.57	0.77	this study
Manchester, UK	Urban	0.32–0.65	-5.7 to -9.4	0.78–0.97	(Lohmann <i>et al.</i> , 2000)
Clapham, UK	Rural	0.19–0.57	-4.2 to -8.1	0.76–0.92	(Lohmann <i>et al.</i> , 2000)
Austwick, UK	Rural	0.20–0.74	-4.7 to -10	0.72–0.97	(Lohmann <i>et al.</i> , 2000)
Kyonggi-do, South Korea	Rural	0.44	-7.07	0.94	(Yeo <i>et al.</i> , 2003)
Bursa	Suburban	0.2–0.42	-	-	(Cindoruk and Tasdemir, 2008)
Bursa	Industrial	0.51	-7	0.82–0.96	(Cindoruk <i>et al.</i> , 2007)

where H' is the dimensionless Herry's law constant. The temperature dependence of H' is described by Eq. (9):

$$H' = \exp\left(\frac{-\Delta H_H}{RT} + \frac{\Delta S_H}{R}\right) \quad (9)$$

where ΔH_H and ΔS_H are enthalpy and entropy of phase transition from the dissolved phase to the gas phase. Bamford *et al.* (2000) provided the ΔH_H and ΔS_H values for 26 PCB congeners. The obtained H' by Eq. (9) were usually underestimated and the deviation extent increased for the chemicals with higher K_{OW} (Harner and Bidleman, 1996). Harner and Bidleman (1996) given an equation as Eq. (10) and provided the values of A and B for 19 PCB congeners.

$$\log K_{OA} = \frac{A}{T} + B \quad (10)$$

In this study, we calculated the KOA for 17 PCB congeners. The K_{OA} values for PCB-105, 118, 126, 153 and 180 were calculated as Eq. (10), while those for PCB-85, 99, 114, 156, 167, 169, 172, 194, 199, 201, 205 and 207 were calculated by Eq. (5). The slope and intercept of $\log K_{OA} - \log K_P$ plot were 0.48 and -7.57, respectively (Fig. 6(b)).

The summarized results in Table 3 indicated the slope and intercept of the $\log K_P - \log K_{OA}$ plot for Tianjin were in the range of values reported by other studies conducted in other rural and urban areas. The slope was higher than that of Bursa (Cindoruk and Tasdemir, 2008), consistent with those of rural site in Korea (Yeo *et al.*, 2003) and

industrial site in Bursa (Cindoruk *et al.*, 2007), and in the range of those of urban and rural sites in U.K. (Lohmann *et al.*, 2000). The slope of 0.48 was deviated significantly from the expected +1, indicated the non-equilibrium state of PCBs gas-particle partitioning for Tianjin, consistent with the result suggested by $\log K_P - \log P_L^0$ model. This deviated slope possibly resulted from the emission of the local sources and the data lack of particle PCBs. Cindoruk and Tasdemir (2008) and Lohmann *et al.* (2000) reported the lack of particle PCBs data would result in the deviated slope from +1.

Concentrations and Composition of Toxic Equivalency (TEQ) of Dioxin-Like PCBs (dl-PCBs)

In this study, 11 dl-PCBs except PCB-189 such as PCB-77, 81, 105, 114, 118, 123, 126, 156, 157, 167 and 169 and 189 were all detected in ambient air from Tianjin (Table 4). PCB-118 was the predominant dl-PCBs with the concentration as 4.54 pg/m^3 , the similar results were reported elsewhere such as Yokohama (Kim and Masunaga, 2005), a steel industrial complex in Northeast China (Li *et al.*, 2001b) and King George Island (Li *et al.*, 2012b). PCB-126 and -169 had the highest TEQ concentrations due to their higher TEF values. The TEQ concentrations ranged from 35.628 to 612.796 fg/m^3 with the mean value as 144.878 fg/m^3 , which was higher than that of Yokohama (2–14 fg/m^3) (Kim and Masunaga, 2005) and a steel industrial complex in northeast China (12 fg/m^3) (Li *et al.*, 2011a), which should be paid more attention by local government.

Table 4. TEQ concentrations of dioxin-like PCBs in air from Tianjin (Units: fg/m³).

IUPAC	TEF	Minimum	Maximum	Mean
PCB-77	0.0001	0.018	0.522	0.116
PCB-81	0.0003	0.053	2.276	0.386
PCB-105	0.00003	0.011	0.194	0.066
PCB-114	0.00003	0.008	0.223	0.076
PCB-118	0.00003	0.014	0.946	0.136
PCB-123	0.00003	0.004	0.053	0.008
PCB-126	0.1	31.956	465.816	94.853
PCB-156	0.00003	0.004	0.114	0.031
PCB-157	0.00003	0.002	0.005	0.003
PCB-167	0.00003	0.007	0.138	0.029
PCB-169	0.03	3.549	142.507	49.172
PCB-189	0.00003	0.002	0.002	0.002
Σdl-PCBs		35.628	612.796	144.878

CONCLUSIONS

The 26 air samples (gas and particle) including four seasons were collected for analysis of 86 PCB congeners from a highly industrialized coastal city-Tianjin. Gas and particle phase PCBs concentrations were measured. The average total PCBs concentration was 273.77 pg/m³ and showed a significant seasonal variation with summer > autumn > spring > winter. The PCBs were mainly existed in gas phase and the contribution of gas PCB congeners increasing with the decreasing chlorine atoms. The PCBs in both gas and particle phase also showed a significant seasonal variation. Tri-, tetra- and penta-PCBs were the predominantly PCB homologs in Tianjin atmosphere. The natural logarithm of partial pressures (ln P) of PCBs were well correlated with inverse absolute temperature (1/T) (R = 0.79). The steep slope (−4933.64) obtained from Clausius–Clapeyron (C.C) plot indicated the Tianjin atmospheric PCBs were mainly originated from local industrial sources. The slopes of C.C plots for PCB homologs increased with the decreased number of chlorine atoms. The fraction of particle bound PCBs to total atmospheric PCBs were underestimated by Junge-Pankow model for PCB congeners with $P_L^0 > 10^{-3.85}$ Pa and overestimated for congeners with $P_L^0 < 10^{-3.85}$ Pa compared with the measured values. Particle/gas partitioning coefficients (K_p) of PCBs were well correlated with the respective sub-cooled vapor pressures P_L^0 and the octanol-air partition coefficient K_{OA} . The slopes for log K_p versus log P_L^0 and log K_{OA} plots were −0.44 and 0.48, deviated significantly from the expected −1 and +1, indicated the state of non-equilibrium for gas/particle partitioning of atmospheric PCBs. Regressions for log K_p – log K_{OA} gave higher regression coefficients (R = 0.77) than regressions for log K_p – log P_L^0 (R = 0.72). The steep slope of C.C plot and regressed results of both P_L^0 and K_{OA} based models indicated that volatilization and emissions from local sources caused the non-equilibrium partitioning of PCBs. The average TEQ concentrations for all air samples in Tianjin was 144.878 fg/m³, was well above the values reported by other researchers, should be paid more attentions by local government.

ACKNOWLEDGEMENTS

This study was supported by National Natural Science Foundation of China (21407048) and the Fundamental Research Funds for the Central Universities (13MS79).

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

REFERENCES

- Bamford, H.A., Poster, D.L. and Baker, J.E. (2000). Henry's Law Constants of Polychlorinated Biphenyl Congeners and their Variation with Temperature. *J. Chem. Eng. Data.* 45: 1069–1074.
- Batterman, S., Chernyak, S., Gouden, Y., Hayes, J., Robins, T., Chetty, S. (2009). PCBs in air, soil and milk in industrialized and urban areas of KwaZulu-Natal, South Africa. *Environ. Pollut.* 157: 654–663.
- Bidleman, T.F. (1988). Atmospheric Process. *Environ. Sci. Technol.* 22: 361–367.
- Brevik, K., Sweetman, A., Pacyna, J.M. and Jones, K.C. (2002). Towards a Global Historical Emission Inventory for Selected PCB Congeners - A Mass Balance Approach: 1. Global Production and Consumption. *Sci. Total Environ.* 290: 181–198.
- Brunciak, P.A., Dachs, J., Franz, T.P., Gigliotti, C.L., Nelson, E.D., Turpin, B.J. and Eisenreich, S.J. (2001). Polychlorinated Biphenyls in the Atmosphere of Chesapeake Bay, USA. *Atmos. Environ.* 35: 5663–5677.
- Carlson, D.L. and Hites, R.A. (2005). Temperature Dependence of Atmospheric PCB Concentrations. *Environ. Sci. Technol.* 39: 740–747.
- Castro-Jiménez, J., Dueri, S., Eisenreich, S.J., Mariani, G., Skejo, H., Umlauf, G. and Zaldivar, J.M. (2009). *Environ. Pollut.* 157: 1024–1032.
- Cetin, B., Yatkin, S., Bayram, A. and Odabasi, M. (2007). Ambient Concentrations and Source Apportionment of PCBs and Trace Elements around an Industrial Area in Izmir, Turkey. *Chemosphere* 69: 1267–1277.

- Cindoruk, S.S. and Tasdemir, Y. (2007). Characterization of Gas/Particle Concentrations and Partitioning of Polychlorinated Biphenyls (PCBs) Measured in an Urban Site of Turkey. *Environ. Pollut.* 148: 325–333.
- Cincinelli, A., Pieri, F., Martellini, T., Passaponti, M., Bubba, M.D., Vento, S.D. and Katsoyiannis, A.A. (2014). Atmospheric Occurrence and Gas-particle Partitioning of PBDEs in an Industrialized and Urban Area of Florence, Italy. *Aerosol Air Qual. Res.* 14: 1121–1130.
- Cindoruk, S.S., Esen, F. and Tasdemir, Y. (2007). Concentration and Gas/Particle Partitioning of Polychlorinated Biphenyls (PCBs) at an Industrial Site at Bursa, Turkey. *Atmos. Res.* 85: 338–350.
- Cindoruk, S.S. and Tasdemir, Y. (2008). Atmospheric Gas and Particle Phase Concentrations of Polychlorinated Biphenyls (PCBs) in a Suburban Site of Bursa, Turkey. *Environ. Forensics* 9: 153–165.
- Cotham, W.E. and Bidleman, T.F. (1995). Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Air at an Urban and a Rural Site near Lake Michigan. *Environ. Sci. Technol.* 29: 2782–2789.
- Currado, G.M. and Harrad, S. (2000). Factors Influencing Atmospheric Concentrations of Polychlorinated Biphenyls in Birmingham, U.K. *Environ. Sci. Technol.* 34: 78–82.
- Falconer, R.L. and Bidleman, T.F. (1994). Vapor Pressures and Predicted Particle/Gas Distributions of Polychlorinated Biphenyl Congeners as Function of Temperature and Ortho-chlorine Substitution. *Atmos. Environ.* 28: 547–554.
- Falconer, R.L. and Harner, T. (2000). Comparison of the Octanol-air Partition Coefficient and Liquid-phase Vapor Pressure as Descriptors for Particle/Gas Partitioning Using Laboratory and Field Data for PCBs and PCNs. *Atmos. Environ.* 34: 4043–4046.
- Finizio, A., Mackay, D., Bidleman, T.F. and Harner, T. (1997). Octanol-air Partition Coefficient as a Predictor of Partitioning of Semi-volatile Organic Chemicals to Aerosols. *Atmos. Environ.* 31: 2289–2296.
- Gouin, T., Harner, T., Daly, G.L., Wania, F., Mackay, D. and Jones, K.C. (2005). Variability of Concentrations of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Air: Implications for Monitoring, Modeling and Control. *Atmos. Environ.* 39: 151–166.
- Guo, C.J., Wang, M.S., Lin, S.L., Mi, H.H., Wang, L.C. and Chien, G.P.C. (2014). Emissions of PCDD/Fs and PCBs during the Cold Start-up of Municipal Solid Waste Incinerators. *Aerosol Air Qual. Res.* 14: 1593–1604.
- Halsall, C.J., Lee, R.G.M., Coleman, P.J., Burnett, V., Jones, P.H. and Jones, K.C. (1995). PCBs in U.K. Urban Air. *Environ. Sci. Technol.* 29: 2368–2376.
- Halsall, C.J., Gevao, B., Howsam, M., Lee, R.G.M., Ockenden, W.A. and Jones, K.C. (1999). Temperature Dependence of PCBs in the UK Atmosphere. *Atmos. Environ.* 33: 541–552.
- Han, D.M., Ye, L., Zhang, C.Z., Li, W.L., Ma, W.L. and Li, Y.F. (2014). Gas-particle Partitioning of Polychlorinated Biphenyls in Air of Xi'an City. *China Environ. Sci.* 34: 2466–2471 (in Chinese).
- Harner, T. and Bidleman, T.F. (1996). Measurements of Octanol-air Partition Coefficients for Polychlorinated Biphenyls. *J. Chem. Eng. Data.* 41: 895–899.
- Harner, T. and Bidleman, T.F. (1998). Octanol–Air Partition Coefficient for Describing Particle/Gas Partitioning of Aromatic Compounds in Urban Air. *Environ. Sci. Technol.* 32: 1494–1502.
- Haugen, J.E., Wannia, F. and Lei, Y.D. (1999). Polychlorinated Biphenyls in the Atmosphere of Southern Norway. *Environ. Sci. Technol.* 33: 2340–2345.
- He, J. and Balasubramanina, R. (2009). A Study of Gas/Particle Partitioning of SVOCs in the Tropical Atmosphere of Southeast Asia. *Atmos. Environ.* 43: 4375–4383.
- Hillery, B.R., Basu, I., Sweet, C.W. and Hites, R.A. (1997). Temporal and Spatial Trends in a Long-term Study of Gas-phase PCB Concentrations near the Great Lakes. *Environ. Sci. Technol.* 31: 1811–1816.
- Hippelein, M. and McLachlan, M.S. (2000). Soil/Air Partitioning of Semivolatile Organic Compounds. 2. Influence of Temperature and relative Humidity. *Environ. Sci. Technol.* 34: 3521–3526.
- Hoff, R.M., Strachan, W.M.J., Sweet, C.W., Chan, C.H., Shackleton, M., Bidleman, T.F., Brice, K.A., Durniston, D.A., Cussion, S., Gatz, D.F., Harlin, K. and Schroeder, W.H. (1996). Atmospheric Deposition of Toxic Chemicals to the Great Lakes: A Review of Data through 1994. *Atmos. Environ.* 30: 3505–3527.
- Hoff, R.M., Brice, K.A. and Halsall, C.J. (1998). Nonlinearity in the Slopes of Clausius-Clapeyron Plots for SVOCs. *Environ. Sci. Technol.* 32: 1793–1798.
- Hornbuckle, K.C., Achman, D.R. and Eisenreich, S.J. (1993). Over-water and Over-land Polychlorinated Biphenyls in Green Bay, Lake Michigan. *Environ. Sci. Technol.* 27: 87–98.
- Horstmann, M. and McLachlan, M.S. (1998). Atmospheric Deposition of Semivolatile Organic Compounds to Two Forest Canopies. *Atmos. Environ.* 32: 1799–1809.
- Hung, H., Blanchard, P., Halsall, C.J., Bidleman, T.F., Stern, G.A., Fellin, P., Muir, D.C.G., Barrie, L.A., Jantunen, L.M., Helm, P.A., Ma, J. and Konoplev, A. (2005). Temporal and Spatial Variabilities of Atmospheric Polychlorinated Biphenyls (PCBs), Organochlorine (OC) Pesticides and Polycyclic Aromatic Hydrocarbons (PAHs) in the Canadian Arctic: Results from a Decade of Monitoring. *Sci. Total Environ.* 342: 119–144.
- Kim, K.S. and Masunaga, S. (2005). Behavior and Source Characteristics of PCBs in Urban Ambient Air of Yokohama, Japan. *Environ. Pollut.* 138: 290–298.
- Li, Q.L., Xu, Y., Li, J., Pan, X.H., Liu, X. and Zhang, G. (2012a). Levels and Spatial Distribution of Gaseous Polychlorinated Biphenyls and Polychlorinated Naphthalenes in the Air over the Northern South China Sea. *Atmos. Environ.* 56: 228–235.
- Li, Y.M., Geng, D.W., Liu, F.B., Wang, T., Wang, P., Zhang, Q.H. and Jiang, G.B. (2012b). Study of PCBs and PBDEs in King George Island, Antarctica, using PUF Passive Air Sampling. *Atmos. Environ.* 51: 140–145.
- Li, Y.M., Zhang, Q.H., Wang, P., Yang, H.B., Jiang, G.B. and Wei F.S. (2011a). Evaluation of Atmospheric Sources of PCDD/Fs, PCBs and PBDEs around a Steel

- Industrial Complex in Northeast China Using Passive Air Samplers. *Chemosphere* 84: 957–963.
- Li, Z.Y., Kong, S.F., Chen, L., Bai, Z.P., Ji, Y. Q., Liu, J.W., Lu, B., Han, B. and Wang, Q.W. (2011b). Concentrations, Spatial Distributions and Congener Profiles of Polychlorinated Biphenyls in Soils from a Coastal City-Tianjin, China. *Chemosphere* 85: 494–501.
- Liu, D., Xu, Y., Li, J., Chaemfa, C., Tian, C.G., Liu, X., Luo, C.L. and Zhang, G. (2014). Organochlorinated Compounds in the air at NAE0, an Eastern Background Site in China: Long-range Atmospheric Transport versus Local Sources. *Aerosol Air Qual. Res.* 14: 1258–1268.
- Lohmann, R., Harner, T., Thomas, G.O. and Jones, K.C. (2000). A Comparative Study of the Gas-particle Partitioning of PCDD/Fs, PCBs, and PAHs. *Environ. Sci. Technol.* 34: 4943–4951.
- Mai, B.X., Zeng, E.Y., Luo, X.J., Yang, Q.S., Zhang, G., Li, X.D., Sheng, G.Y. and Fu, J.M. (2005). Abundances, Depositional Fluxes, and Homologue Patterns of Polychlorinated Biphenyls in Dated Sediment Cores from the Pearl River Delta, China. *Environ. Sci. Technol.* 39: 49–56.
- Mandalakis, M., Tsapakis, M., Tsoga, A. and Stephanou, E.G. (2002). Gas-particle Concentrations and Distribution of Aliphatic Hydrocarbons, PAHs, PCBs and PCDD/Fs in the Atmosphere of Athens (Greece). *Atmos. Environ.* 36: 4023–4035.
- Mandalakis, M. and Stephanou, E.G. (2007). Atmospheric Concentration Characteristics and Gas-particle Partitioning of PCBs in a Rural Area of eastern Germany. *Environ. Pollut.* 147: 211–221.
- Manodori, L., Gambaro, A., Moret, I., Capodaglio, G., Cairns, W.R.L. and Cescon, P. (2006). Seasonal Evolution of Gas-phase PCB Concentrations in the Venice Lagoon Area. *Chemosphere* 62: 449–458.
- Mari, M., Nadal, M., Schuhmacher, M.J. and Domingo, L. (2008). Monitoring PCDD/Fs, PCBs and Metals in the Ambient Air of an Industrial Area of Catalonia, Spain. *Chemosphere* 73: 990–998.
- Menichini, E., Iacovella, N., Monfredini, F. and Turrio-Baldassarri, L. (2007). Atmospheric Pollution by PAHs, PCDD/Fs and PCBs Simultaneously Collected at a Regional Background Site. *Chemosphere* 69: 422–434.
- Murayama, H., Takase, Y., Mitobe, H., Ohzeki, T., Shimizu, K. and Kitayama, Y. (2003). Seasonal Change of Persistent Organic Pollutant Concentrations in Air at Niigata Area, Japan. *Chemosphere* 52: 683–694.
- Ockenden, W.A., Breivik, K., Meijer, S.N., Steinnes, E., Sweetman, A.J. and Jones, K.C. (2003). The Global Recycling of Persistent Organic Pollutants is Strongly Retarded by Soils. *Environ. Pollut.* 121: 75–80.
- Oehme, M., Haugen, J.E. and Schlabach, M. (1996). Seasonal Changes and Relations between Levels of Organochlorines in Arctic Ambient Air: First Results of an All-year-round Monitoring Program at Ny-Ålesund, Svalbard, Norway. *Environ. Sci. Technol.* 30: 2294–2304.
- Offenberg, J.H. and Baker, J.E. (1997). Urban Contamination of the Chicago/Coastal Lake Michigan Atmosphere by PCBs and PAHs during AEOLOS. *Environ. Sci. Technol.* 31: 1534–1538.
- Pankow, J.F. (1987). Review and Comparative Analysis of the Theories on Partitioning between Gas and Aerosol Particulate Phase in the Atmosphere. *Atmos. Environ.* 21: 2275–2283.
- Pankow, J.F. and Bidleman, T.F. (1992). Interdependence of the Slopes and Intercepts from Log-log Correlations of Measured Gas-particle Partitioning and Vapor Pressure—I. Theory and Analysis of Available data. *Atmos. Environ.* 26: 1071–1080.
- Pankow, J.F. (1994). An Absorption Model of Gas/Particle Partitioning of Organic Compounds in the Atmosphere. *Atmos. Environ.* 28: 185–188.
- Pankow, J.F. (1998). Further Discussion of the Octanol/Air Partition Coefficient K_{oa} as a Correlating Parameter for Gas/Particle Partitioning Coefficients. *Atmos. Environ.* 32: 1493–1497.
- Panshin, S.Y. and Hites, R.A. (1994). Atmospheric Concentrations of Polychlorinated Biphenyls in Bloomington, Indiana. *Environ. Sci. Technol.* 28: 2003–2013.
- Park, Y.K., Kim, W. and Jo, Y.M. (2013). Release of Harmful Air Pollutants from Open Burning of Domestic Municipal Solid Wastes in a Metropolitan Area of Korea. *Aerosol Air Qual. Res.* 13: 1365–1372.
- Simcik, M.F., Franz, T.P., Zhang, H.X. and Eisenreich, S.J. (1998). Gas-particle Partitioning of PCBs and PAHs in the Chicago Urban and Adjacent Coastal Atmosphere: State of Equilibrium. *Environ. Sci. Technol.* 32: 251–257.
- Simcik, M.F., Basu, I., Sweet, C.W. and Hites, R.A. (1999). Temperature Dependence and Temporal Trends of Polychlorinated Biphenyl Congeners in the Great Lakes Atmosphere. *Environ. Sci. Technol.* 33: 1991–1995.
- Syed, J.H., Malik, R.N., Li, J., Zhang, G. and Jones, K.C. (2013). Levels, Distribution and Air-soil Exchange Fluxes of Polychlorinated Biphenyls (PCBs) in the Environment of Punjab Province, Pakistan. *Ecotox. Environ. Safe.* 97: 189–195.
- Tasdemir, Y., Vardar, N., Odabasi, M. and Holsen, T.M. (2004). Concentrations and Gas/Particle Partitioning of PCBs in Chicago. *Environ. Pollut.* 131: 35–44.
- Tseng, Y.J., Mi, H.H., Hsieh, L.T., Liao, W.T. and Chien, G.P.C. (2014a). Atmospheric Deposition Modeling of Polychlorinated Dibenzop-dioxins, Dibenzofurans and Polychlorinated Biphenyls in the Ambient Air of Southern Taiwan. Part I. Dry Depositions. *Aerosol Air Qual. Res.* 14: 1950–1965.
- Tseng, Y.J., Mi, H.H., Hsieh, L.T., Liao, W.T. and Chien, G.P.C. (2014b). Atmospheric Deposition Modeling of Polychlorinated Dibenzop-dioxins, Dibenzofurans and Polychlorinated Biphenyls in the Ambient air of Southern Taiwan. Part II. Wet Depositions and Total Deposition Fluxes. *Aerosol Air Qual. Res.* 14: 1966–1985.
- Wania, F., Haugen, J.E., Lei, Y.D. and Mackay, D. (1998). Temperature dependence of atmospheric Concentrations of Semivolatile Organic Compounds. *Environ. Sci. Technol.* 32: 1013–1021.
- Wethington, D.M. and Hornbuckle K.C. (2005). Milwaukee, WI, as a Source of Atmospheric PCBs to Lake Michigan.

- Environ. Sci. Technol.* 39: 57–63.
- Wu, J.J., Teng, M., Gao, L.R. and Zheng, M.H. (2011). Background Air Levels of Polychlorinated Biphenyls in China. *Sci. Total Environ.* 409: 1818–1823.
- Xing, G.H., Liang, Y., Chen, L.X., Wu, S.C. and Wong, M.H. (2011). Exposure to PCBs, through Inhalation, Dermal Contact and Dust Ingestion at Taizhou, China – A Major Site for Recycling Transformers. *Chemosphere* 83: 605–611.
- Xing, Y.Y., Lu, L., Dawson, R.W., Shi, Y.J., Zhang, H., Wang, T.Y., Liu, W.B. and Ren, H.C. (2005). A Spatial Temporal Assessment of Pollution from PCBs in China. *Chemosphere* 60: 731–739.
- Yamasaki, H., Kuwata, K. and Miyamoto, H. (1982). Effects of Ambient Temperature on Aspects of Airborne Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol.* 16: 189–194.
- Yeo, H.G., Choi, M., Chun, M.Y. and Sunwoo, Y. (2003). Gas/Particle Concentrations and Partitioning of PCBs in the Atmosphere of Korea. *Atmos. Environ.* 37: 3561–3570.
- Yeo, H.G., Choi, M., Chun, M.Y., Kim, T.W., Cho, K.C. and Sunwoo, Y. (2004). Concentration Characteristics of Atmospheric PCBs for Urban and Rural Area. *Sci. Total Environ.* 324: 261–270.

Received for review, January 19, 2015

Revised, March 18, 2015

Accepted, March 28, 2015

Supplementary Materials

Table S1.

Statistic values of concentrations of the individual atmospheric PCB congener in Tianjin. (Units: pg m^{-3})

Fig. S1.

Contribution of different PCB homologues to total PCBs in Tianjin (error bar: standard deviation).

Fig. S2.

Regressed results of Clausius-Clapeyron plot for different PCB homologs.

Table S1 Statistic values of concentrations of the individual atmospheric PCB congener in Tianjin. (Units: pg m^{-3})

PCB congeners	Gas phase			Particle phase		
	Minimum	maximum	Mean \pm SD ^a	Minimum	Maximum	Mean \pm SD ^a
PCB4+10	0.47	15.62	1.10 \pm 2.96	0.47	0.54	0.51 \pm 0.02
PCB7+9	0.24	20.97	1.83 \pm 4.32	0.24	0.27	0.26 \pm 0.01
PCB6	0.47	26.78	3.14 \pm 5.79	0.47	0.54	0.51 \pm 0.02
PCB5+8	0.38	57.51	5.09 \pm 12.48	0.38	0.44	0.42 \pm 0.02
PCB19	0.47	29.35	3.34 \pm 7.69	0.47	0.54	0.51 \pm 0.02
PCB12+13	0.98	38.36	5.05 \pm 10.33	0.98	2.73	1.25 \pm 0.43
PCB18	0.48	95.67	11.81 \pm 22.96	0.47	0.80	0.53 \pm 0.06
PCB15	0.47	8.11	1.29 \pm 1.75	0.47	3.11	0.38 \pm 0.15
PCB17	0.47	7.61	1.31 \pm 1.82	0.47	1.26	0.54 \pm 0.14
PCB16+32	0.26	30.28	13.64 \pm 10.55	0.24	1.34	0.34 \pm 0.28
PCB26	0.25	34.95	11.41 \pm 11.59	0.24	1.33	0.37 \pm 0.31
PCB31+28	0.42	54.49	21.82 \pm 14.25	0.39	7.77	2.05 \pm 2.23
PCB33+53	0.47	129.85	13.08 \pm 26.76	0.47	0.54	0.51 \pm 0.02
PCB22	0.18	13.65	4.53 \pm 5.00	0.18	0.20	0.19 \pm 0.01
PCB45	0.24	27.31	7.44 \pm 7.17	0.24	0.89	0.28 \pm 0.12
PCB52	0.24	65.20	11.74 \pm 17.54	0.24	2.69	0.43 \pm 0.54
PCB49	0.24	4.40	1.12 \pm 1.50	0.24	1.10	0.29 \pm 0.17
PCB47+48	0.38	111.02	18.90 \pm 34.44	0.38	1.17	0.45 \pm 0.15
PCB44	0.18	8.49	0.98 \pm 1.87	0.18	6.73	0.68 \pm 1.42
PCB37+42	0.26	32.23	14.54 \pm 10.78	0.24	3.05	0.52 \pm 0.71
PCB41+71+64	0.30	5.97	0.93 \pm 1.27	0.30	0.34	0.32 \pm 0.01
PCB100	0.18	26.91	5.07 \pm 7.73	0.18	2.87	0.39 \pm 0.66
PCB74	0.18	25.01	3.29 \pm 6.15	0.18	2.91	0.38 \pm 0.65
PCB76+70	0.24	64.32	10.37 \pm 16.62	0.24	0.77	0.28 \pm 0.10
PCB66+95	0.24	4.87	0.72 \pm 1.23	0.24	0.46	0.27 \pm 0.04
PCB91	0.18	8.54	1.40 \pm 2.46	0.18	2.51	0.28 \pm 0.45
PCB56+60	0.18	28.12	4.47 \pm 8.56	0.18	2.46	0.30 \pm 0.45
PCB92	0.18	16.00	2.26 \pm 3.39	0.18	0.67	0.23 \pm 0.11
PCB84	0.24	45.62	3.14 \pm 9.59	0.24	0.41	0.26 \pm 0.03
PCB89	0.18	30.30	6.53 \pm 9.05	0.00	7.01	1.65 \pm 2.24
PCB101	0.18	16.58	3.92 \pm 4.08	0.18	0.76	0.23 \pm 0.13
PCB99	0.18	14.85	4.08 \pm 3.87	0.18	4.85	0.70 \pm 1.23
PCB119	0.18	0.63	0.21 \pm 0.09	0.18	1.46	0.24 \pm 0.25
PCB83	0.18	3.42	0.83 \pm 0.85	0.18	0.56	0.22 \pm 0.08
PCB97	0.18	4.29	0.71 \pm 0.94	0.18	8.66	0.61 \pm 1.70
PCB81	0.18	14.97	1.02 \pm 3.04	0.18	1.64	0.26 \pm 0.35
PCB87	0.18	1.95	0.58 \pm 0.64	0.18	0.21	0.19 \pm 0.31
PCB85	0.12	51.33	19.09 \pm 18.42	0.13	2.53	0.64 \pm 0.63
PCB77	0.18	10.24	0.95 \pm 2.40	0.18	1.05	0.21 \pm 0.22
PCB110	0.18	3.61	0.69 \pm 1.11	0.18	0.18	0.18 \pm 0.19
PCB144+135	0.18	0.37	0.20 \pm 0.04	0.18	0.20	0.19 \pm 0.01
PCB123	0.12	3.40	0.13 \pm 0.69	0.12	0.12	0.12 \pm 0.01
PCB149	0.12	0.12	0.12 \pm 0.00	0.12	0.12	0.12 \pm 0.01
PCB118	0.24	31.27	4.07 \pm 6.29	0.24	2.51	0.47 \pm 0.57
PCB114	0.26	14.57	2.03 \pm 4.03	0.26	3.05	0.51 \pm 0.77
PCB131	0.26	2.90	1.46 \pm 0.89	0.26	0.85	0.32 \pm 0.36
PCB153+132	0.24	3.23	0.57 \pm 0.66	0.24	1.76	0.38 \pm 0.41
PCB105	0.18	6.29	0.59 \pm 1.19	0.18	2.27	0.32 \pm 0.45
PCB138+163	0.18	0.20	0.19 \pm 0.01	0.18	0.52	0.21 \pm 0.06
PCB126	0.13	0.47	0.21 \pm 0.07	0.18	4.47	0.73 \pm 1.09
PCB128	0.12	1.94	0.39 \pm 0.46	0.12	0.85	0.18 \pm 0.16
PCB167	0.12	3.90	0.63 \pm 0.84	0.12	2.06	0.33 \pm 0.42
PCB174	0.09	1.60	0.49 \pm 0.52	0.09	2.69	0.48 \pm 0.71
PCB171+202	0.15	0.47	0.17 \pm 0.06	0.15	2.76	0.46 \pm 0.72
PCB156	0.06	1.43	0.38 \pm 0.37	0.06	3.42	0.64 \pm 0.90
PCB157	0.06	0.06	0.06 \pm 0.00	0.06	0.20	0.10 \pm 0.03
PCB172	0.06	0.59	0.18 \pm 0.14	0.06	6.14	0.56 \pm 1.25
PCB180	0.06	8.52	1.96 \pm 2.27	0.06	2.85	0.55 \pm 0.72
PCB201	0.06	8.98	0.68 \pm 1.71	0.07	7.27	1.18 \pm 1.55
PCB169	0.06	4.68	1.09 \pm 0.98	0.06	3.04	0.55 \pm 0.79
PCB170+190	0.06	0.80	0.22 \pm 0.17	0.06	1.54	0.39 \pm 0.41
PCB199	0.06	1.12	0.21 \pm 0.27	0.07	11.38	1.50 \pm 2.65
PCB189	0.06	0.06	0.06 \pm 0.00	0.06	0.06	0.06 \pm 0.00
PCB207	0.06	0.40	0.15 \pm 0.09	0.06	3.68	0.65 \pm 0.91
PCB194	0.06	1.48	0.52 \pm 0.44	0.06	2.47	0.57 \pm 0.66
PCB205	0.06	0.76	0.41 \pm 0.16	0.26	4.43	1.15 \pm 1.25
PCB206	0.06	0.35	0.14 \pm 0.11	0.06	3.76	0.66 \pm 0.98

^aSD: Standard Deviation.

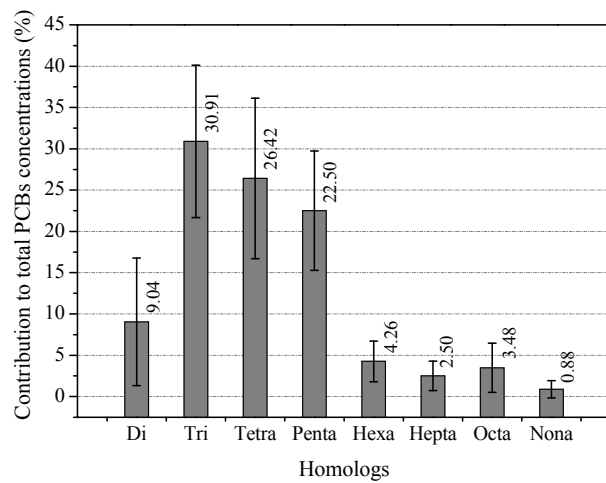


Fig. S1. Contribution of different PCB homologs to total PCBs in Tianjin (error bar: standard deviation).

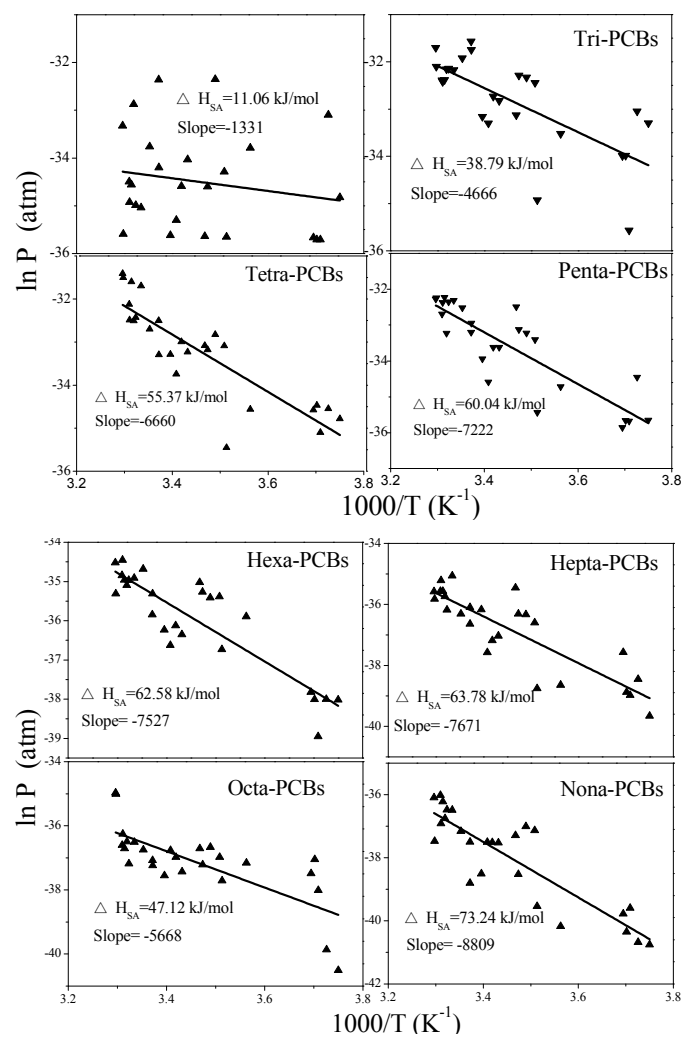


Fig. S2. Regressed results of Clausius-Clapeyron plot for different PCB homologs.