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Dry deposition fluxes and velocities of polychlorinated biphenyls (PCBs) associated with particles

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Abstract

The interest in atmospheric deposition by the scientific community has increased a great deal over the past several years because of its significant contribution to the pollution budget of many natural waters. Dry deposition is an effective removal mechanism for polychlorinated biphenyls (PCBs) from the atmosphere. This study focuses on the understanding of the particulate dry deposition of PCBs in urban areas. In this paper, 43 chromatographic PCB congener peaks which represent 50 individual or coeluting congeners were evaluated.

The PCB dry deposition fluxes were measured using a smooth, greased, knife-edge surrogate surface holding greased Mylar strips in Chicago, IL. The average PCB dry deposition flux measured ($190 \pm 80\,ng\,m^{-2}\,day^{-1}$) was similar to those measured in other urban areas. Ambient air samples were also collected simultaneously with flux samples. The average apparent dry deposition velocity, calculated by dividing the fluxes to the particle phase concentrations was $5.2 \pm 2.9\,cm\,s^{-1}$. This value is in good agreement with the values calculated using similar techniques.

Keywords: PCBs; Dry deposition; Particle deposition; Deposition velocity; Surrogate surface

1. Introduction

PCBs have been detected in almost all environmental matrixes (air, soil, water, biota and human tissue) (Hippelein et al., 1996; Asplund et al., 1994; Dahle et al., 1995) and in many locations around the world (Watanabe et al., 1996; Hermanson and Hites, 1989; Doskey and Andren, 1981; Halsall et al., 1999; Hoff et al., 1992; Kaupp et al., 1996; Brunciak et al., 2001). The atmosphere serves as an important pathway for global transport of PCBs. Particle deposition (Zannetti, 1990; Noll et al., 1990), gaseous air–water exchange (Hornbuckle et al., 1994, 1995; Jeremiason et al., 1994; Zhang et al., 1999) and wet deposition via rain and snow (Franz 1994; Poster and Baker, 1996) are the major atmospheric removal mechanisms for PCBs.

Atmospheric dry deposition results from the transport and accumulation of particle contaminants onto a surface during the periods of no precipitation. Dry deposition has gained a great deal of interest from researchers due to its effects on the environment and consequently there have been significant efforts to measure or estimate dry deposition using a variety of techniques (Ogura et al., 2001; Pryor and Barthelmie,

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2000; Drooge et al., 2001; Yang et al., 1999; Fang et al., 1999; Bidleman, 1988; Grainer and Chevreuil, 1997; Miller et al., 2001; Shahin et al., 1999; Pirrone et al., 1995; Hoff et al., 1996). The amount of dry deposition is a function of contaminant concentration and characteristics, atmospheric conditions and the receptor surface (Hoff et al., 1996; Zannetti, 1990; Holsen et al., 1991; Murphy et al., 1981).

The dry deposition flux can be calculated based on measured ambient air concentrations and reported dry deposition velocities. Mass balance is another approach used to determine the flux magnitude and direction. This approach is based on determining the relative inputs and outputs of a chemical from a water body (Baker et al., 1993; Strachan and Eisenreich, 1989; Jeremiason et al., 1994). The third method of determining the dry deposition flux is direct measurement with surrogate surfaces. To date different types of surrogate surfaces have been used including a bucket, filter paper, Teflon plates, petri dishes, and a variety of greased surfaces (Tasdemir and Caglar, 2002). The drawbacks of these direct measurement studies are (1) extension to natural surfaces is difficult and (2) no universally accepted sampling and analysis methods exist (Sehmel, 1980; Vardar et al., 2002). Holsen et al. (1991), Tasdemir (1997) and Franz et al. (1998) used surrogate surfaces to determine the PCB fluxes in Chicago, IL. The PCB dry deposition flux was measured using a smooth plate, covered with greased strips, with a sharp leading edge pointed into the wind-by-wind vane. The collection surface was designed based on wind tunnel studies to have minimum flow disruption and therefore, an estimation of the lower limit for dry deposition flux would be provided (Holsen et al., 1991). The deposition plate with greased strips has been successfully used as a surrogate surface to directly assess particulate fluxes of both organic and inorganic air pollutants (Noll et al., 1990; Tasdemir, 1997; Yi et al., 1997; Franz et al., 1998; Shahin et al., 1999; Odabasi et al., 1999; Vardar et al., 2002).

Dry deposition can be characterized by the deposition velocity, V_d (length/time) which is the ratio between contaminant dry deposition flux, F_p (mass length^{-2} time^{-1}) and contaminant particle phase concentrations, C_p (mass length^{-3}):

$$V_d = F_p/C_p. \quad (1)$$

Strictly speaking V_d is not a real velocity, however, it is referred to as a velocity because of its units (Zannetti, 1990). The one situation where V_d may be considered a real velocity is when gravitational settling controls deposition as is the case for large particles. Zhang et al. (2001) claim that impaction and interception are also important for larger size particles (d_p= 5 μm). For very small particles (d_p less than 0.1 μm), Brownian movement dominates the deposition velocity (Holsen et al., 1991; Zannetti, 1990). Particles in the intermediate size range have the lowest predicted deposition velocities because of the relative weakness of their Brownian motion and gravitational settling effects (Zannetti, 1990; Seinfeld, 1986).

In the literature, reported deposition velocities vary a great deal possibly due to the spatial fluctuations (urban and non-urban areas), temporal changes (winter and summer months), diurnal variations, surface type differences and micrometeorological conditions (such as wind velocity and direction, atmospheric stability) as well as experimental uncertainties (Finlayson-Pitts and Pitts, 1986). In general, it is expected that the dry deposition velocity increases with the chlorination content of PCB congeners. Higher chlorinated PCBs are primarily associated with the particle phase and they deposit mainly by gravitational settling which is significantly more effective than diffusional settling.

The overall objectives of this research were to measure the particle phase PCB dry deposition fluxes, and to determine the apparent dry deposition velocities for PCB homologs.

2. Materials and methods

2.1. Sampling program

Ten atmospheric deposition samples were taken from June to October 1995. The sampling program was conducted in Chicago, IL, which is a large urban industrialized area. Greased knife-edge surrogate surfaces (KSSs) were used to collect the ambient air PCB deposition fluxes.

2.2. Knife-edge surrogate surface

In this study, direct PCB flux measurements were performed using greased surfaces from which bounce-off losses for particulate matter were negligible (Holsen et al., 1991; Franz et al., 1998). The greased strips were previously successfully used for particle phase flux collections of both inorganics (Noll et al., 1990; Holsen and Noll, 1992; Yi et al., 2001) and organics (Odabasi et al., 1999; Franz et al., 1998; Vardar et al., 2002).

The KSS was made from polyvinyl chloride and its design is similar to those used in wind tunnel studies. It is about 21.6 cm long, 7.5 cm wide, and 0.55 cm thick with a sharp leading edge ($<10^\circ$) that is pointed into the wind by a wind vane. Mylar strips ($7.6 \times 2.5\,cm^2$) placed on top of the KSS were coated with approximately 2–3 mg of Apezion L grease (thickness $\sim$5 μm). The collection area was $5.7 \times 1.8\,cm^2$ for each strip. Fig. 1 shows a typical dry deposition KSS with strips. PCB concentrations in the atmosphere are low; thus, five

deposition plates (KSSs) each with up to five strips were used.

A summary of the preparation of Mylar strips for sampling is described below: Mylar, obtained from Graphic Arts Systems Cleveland, OH, were cut in strips ($7.6 \times 2.5\,cm^2$) and the area to be greased was marked with a sharp mechanical pen ($5.7 \times 1.8\,cm^2$). The strips were then cleaned several times with methanol and wiped with dust-free paper. This step was repeated with distilled water, and strips were then rinsed twice with DI water. Next, they were placed into the laminar-flow hood onto dust-free papers for drying. These Mylar strips were coated with 2–3 mg of Apezion type L grease ($\sim 5\,\mu m$ in thickness). Prior to coating the grease was melted on a hot plate and then coated on the marked surface with a small paintbrush. The Mylar strips were then put in a dust-free storage box for about 24 h for equilibrium before weighing (ATI Cahn Balance, Model C-38). The ungreased areas were covered with PVC covers to prevent any deposition to them during field sampling. Details of sample preparation are described elsewhere (Holsen et al., 1991; Tasdemir, 1997; Vardar, 1998; Paode et al., 1998; Odabasi et al., 1999).

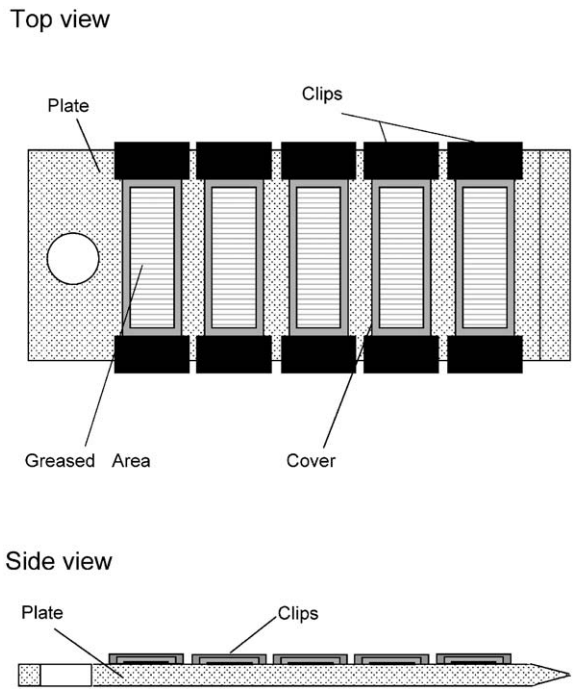

Fig. 1. Greased knife-edge surrogate surface (KSS).

2.3. Sampling site and strategy

Table 1 summarizes the sampling information. The sampling site was on the roof of a four-storey building (~ 12 m height) located on the IIT campus, in Chicago. The campus is in a mixed institutional, residential and commercial area on the south side of Chicago. The sampling site was surrounded by low-rise buildings, landscaped areas and large parking lots. The KSS sampler and meteorological tower on the roof were out the roof wake boundary (Yi et al., 1997) and has been used in previous studies (Tasdemir, 1997; Paode et al., 1998; Franz et al., 1998; Odabasi et al., 1999).

Daily samples were usually taken from 8:00 a.m. to 8:00 p.m. when there was no rain. Each sampling period lasted at least 5 days to collect sufficient sample for analysis. The temperature, wind speed, wind direction and relative humidity were obtained from a meteorological tower located on the top of the building.

2.4. Analytical procedures

KSS samples were spiked with PCB surrogate standards (PCB #14, PCB #65 and PCB #166) before extraction in order to determine analytical recovery efficiencies. The greased strips were extracted with 4:1 (v/v) petroleum ether (PE):dichloromethane (DCM) (20% v/v DCM in PE) for 24 h. The extract was then concentrated with a rotary evaporator to 5 ml. Fifteen

Table 1
Summary of sampling information (1995)

Sample no.	Sampling date	Sampling time (min)	Wind speed ($m\,s^{-1}$)	Temperature (°C)	Relative humidity (%)
1	6/29–7/6	3680	3.6	23.7	52.7
2	7/8–7/13	4020	3.0	26.9	57.7
3	7/14–7/21	3880	3.7	30.1	53.5
4	7/25–7/30	3750	2.9	29.1	64.7
5	8/15–8/23	4305	2.8	27.3	63.3
6	8/24–8/31	4515	2.8	27.7	68.3
7	9/6–9/14	4920	3.6	19.3	57.0
8	9/15–9/25	4770	3.3	15.8	53.5
9	10/4–10/13	4615	3.2	20.6	39.3
10	10/15–10/23	3825	4.5	14.8	35.3

Note: Wind speed, temperature and relative humidity values are the averages over the sampling period.

ml of hexane was added and the sample again concentrated to 5 ml. This step was repeated twice to replace DCM:PE with hexane, and then the sample in hexane was concentrated to 2 ml with gentle stream of nitrogen. Extracts were cleaned by passing them through a 0.5 cm × 20 cm column containing deactivated silicic acid (3% water), deactivated alumina (6% water) and Na_2SO_4. The sample was eluted with PE solvent. The solvent was again exchanged to hexane and the PCB samples were further cleaned by extraction with concentrated H_2SO_4. The sample was concentrated to approximately 1 ml under a gentle stream of pure nitrogen. Internal standards (PCB 30 and 204) were added for volume correction before quantification by gas chromatography (GC). Sample analysis for PCBs were performed with a Hewlett-Packard (HP) 5890 GC with ^{63}Ni electron capture detector (ECD) and a 25 m × 0.25 mm ID DB-5 capillary column with a 0.25 μm film thickness. Hydrogen was the carrier gas (2.4 ml min^{-1} at 80°C) and 5% methane in argon was the make-up gas (50 ml min^{-1}). Injections were splitless, and injection port and detector temperatures were set at 240°C and 375°C, respectively. The oven program was: inject at 80°C, program at 10°C min^{-1} to 160°C, 2°C min^{-1} to 250°C, 5°C min^{-1} to 280°C, then a 2 min hold. Total run time was 61 min. Data were collected and analyzed with HP ChemStation software. Congeners were identified and quantified by comparison to standard solutions (Ultra Scientific Lot Number K0888 and K0889; Catalog Number: CUS-1820 and CUS-1821, NIST Test No: 732/221797).

2.5. Quality control/quality assurance

All reported values were blank corrected. In this study, 43 chromatographic peaks corresponding to 50 individual or coeluting congeners were analyzed. A similar mixture of PCB species were reported elsewhere (Hornbuckle et al., 1994; Falconer et al., 1995; Cotham and Bidleman, 1995; Tasdemir, 1997; Harner, 1996; Franz, 1996).

Analytical QA/QC included determinations of the congener specific method detection limit, peak separations and corresponding concentrations along with the appropriate blank and recovery checks. A mixture of calibration and surrogate standards were run before and during each set of samples in order to observe peak separations, areas, and retention times.

The limit of detection (LOD) was determined from the mean noise, in mass units, plus 3 standard deviations (3σ) (Simcik et al., 1998; Cotham and Bidleman, 1995; Falconer et al., 1995). Blank samples were used to calculate mean mass (ng) and σ. Detection limits for individual PCBs ranged from not detected to 0.8 ng for different matrixes employed in this study. Instrumental detection limit (IDL) was also determined from the minimum area detected from sample chromatograms (Franz, 1996). The GC employed in our study was able to detect areas of 10–15 U without interference from the background noise (> 5 × noise). In this study, the lowest reported area is about 100 U which means values of PCB congeners presented in this paper are at least 8 to 10 times bigger than the minimum GC detection limit.

In order to determine analytical recovery efficiencies, all collected samples were spiked with surrogate PCBs standards including PCB 14, 65 and 166 prior to extraction. Average recoveries were 67 ± 8% ($n = 12$), 78 ± 6% ($n = 12$), and 83 ± 5% ($n = 12$) for PCB 14, 65 and 166, respectively. The average recoveries for the field blanks were 81 ± 10% ($n = 3$), 77 ± 16% ($n = 8$), 88 ± 9% ($n = 5$) for greased surfaces, filters and PUF cartridges, respectively.

Possible sampling artifacts including contamination and PCB vapor absorption by the greased strips were minimized by employing field blanks (20% of the total number of the samples). The blanks were exposed to ambient air for the time period required to set up and collect the dry deposition samples (less than 20 min for each day). The amount of PCBs found in the greased surface blanks averaged 32.95 ± 9.09 ng ($n = 3$) which was about 28% of the PCB amount present in plate samples (119.74 ± 48.26 ng) prior to blank correction. PCB quantities exceeding the LOD in the sample were quantified and blank corrected. All calculations were congener specific. For example, for greased strips the field blanks were averaged to obtain a mean mass for each congener. These amounts were subtracted from the congener mass obtained from each sample.

3. Results and discussion

3.1. Particle phase PCBs fluxes

In this paper, Σ_{50}PCB refers to the summed contribution of 43 chromatographic PCB congener peaks representing 50 individual or coeluting congeners among the 2- to 10-chlorinated homologs. The particle PCB fluxes were corrected with field blanks in order to eliminate artifacts associated with partitioning of gas phase PCBs to the greased surfaces and any background contamination (Franz et al., 1998). Possible sampling artifacts associated with greased surfaces can be summarized below:

(1) Losses of PCBs from particles deposited onto the greased surfaces by evaporation. Myrczik (1997) performed a series of experiments to compare the PCB fluxes measured with long-term (5 days) and combined short-term (5 × 1 day) greased samples between August and October, 1996 in Chicago. The deposition fluxes obtained from short- and long-term were not statistically different from each other even though short-term

fluxes were slightly higher than long-term fluxes. Therefore, evaporative PCB losses from deposited particulates onto the greased surfaces were not significant. (2) Sorption of vapor phase PCBs by the greased surfaces (KSS). Absorption of vapor phase PCBs to the greased surface can be estimated from the octanol–air partition coefficient (K_{OA}) (Harner and Mackay, 1995) which is defined as

$$K_{OA} = C_O/C_A, \quad (2)$$

where C_O and C_A are the concentrations of the PCB in octanol and air, respectively. Temperature adjusted K_{OA} can be determined from

$$\log K_{OA} = A + B/T, \quad (3)$$

where A and B are from the study of Harner and Bidleman (1996). K_{OA} values were found to range between 2.7×10^7 and 5.42×10^{11} for PCB 8 and PCB 209, respectively, at 20°C. The results indicate that PCBs with higher molecular weights can be sorbed to the grease in greater quantities than can low molecular weight PCBs. Moreover, temperature has an important effect on K_{OA}, which increases with decreasing temperature (Harner and Bidleman, 1996).

The K_{OA} approach assumes that gas phase semivolatile organic compounds (SOCs) (i.e. PCBs) reach equilibrium with the grease during exposure and also that the partitioning characteristics of grease used in this study (Apezion L) are similar to octanol. If equilibrium conditions are reached, the predicted equilibrium deposition amount is about 30 times greater than the average of the field blanks and eight times greater than the PCBs in the samples prior to blank correction. Therefore, gas partitioning is probably not at equilibrium. In a recent study, PAH gas phase sorption by similar greased surfaces was measured (Li, 1992). They found an increasing trend in the PAH concentrations for exposures of 400 h indicating that gas phase PAHs did not reach equilibrium.

Although previous estimates indicated that deposition of gas phase PAHs onto grease was not significant compared to particle deposition (Odabasi et al., 1999; Shahin et al., 1999). The particle phase PCB flux values ranged between 105 and 390 ng m^{-2} day^{-1} and averaged about 190 ± 80 ng m^{-2} day^{-1} (Fig. 2). These results agree well with the measurements made at the same sampling site by Franz et al. (1998) which ranged from 37 to 880 ng m^{-2} day^{-1} with an arithmetic mean of $\sim$210 ng m^{-2} day^{-1}. On the other hand, Holsen et al. (1991) measured PCB dry deposition fluxes at the same sampling point with similar greased surfaces and their reported fluxes were on the average around 4500 ng m^{-2} day^{-1}. In an earlier study conducted in Chicago, particle phase PCB fluxes were reported to be $\sim$630 ng m^{-2} day^{-1} (Murphy et al., 1981). Murphy et al. (1981) employed filters that were wetted with propane and butanediols as a collection surface.

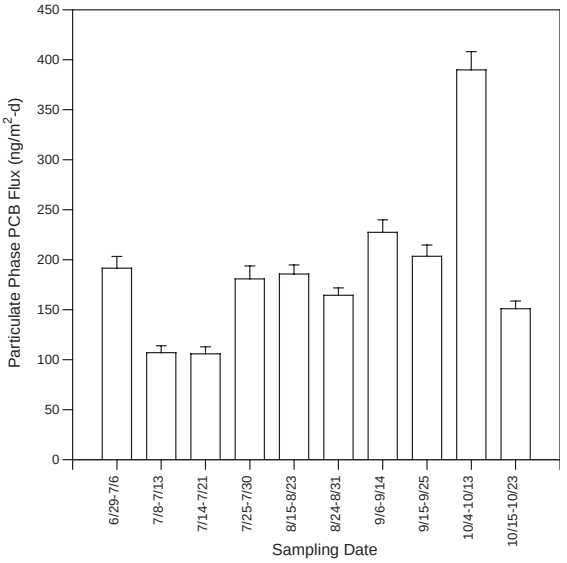

Fig. 2. Particulate phase PCB dry deposition flux values of each sample. Error bars represent one standard deviation.

PCBs enter the atmosphere from incinerators, landfills, or soil and air/water exchange (Murphy et al., 1981, 1985; Hornbuckle et al., 1994, 1995; Jeremiason et al., 1994; Zhang et al., 1999; Franz, 1994; Poster and Baker, 1996; Hsu et al., 2003; Garcia-Alonso and Perez-Pastor, 2003). Since there are some important PCB sources around Chicago, the atmospheric concentrations of PCBs are higher there than many other urban areas (Tasdemir et al., 2004; Green et al., 2000; Simcik et al., 1998; Cotham and Bidleman, 1995). As a result of the close proximity of atmospheric PCB sources, dry deposition fluxes were also expected to be higher in Chicago (Franz et al., 1998). In general, fluxes obtained in this study are higher than the ones reported for non-urban areas but they are comparable with those found in other urban areas (Table 2).

There were some studies of particle size distributions in the Chicago air (Noll et al., 1985, 1990; Holsen and Noll, 1992; Lin et al., 1994). The coarse particle mass was 0.8–1.3 times the fine particle mass for the Chicago site and the mass distributions of particles were distinctly different from each other depending on wind direction (Holsen and Noll, 1992). Miller et al. (2001) estimated that the average impacted area by enhanced dry deposition fluxes due to coarse particles could be no more than 100 km^2 surrounding the Chicago area. This idea was supported by Franz et al. (1998) who found that PCB deposition fluxes were about 2.5 times lower at over-water sites within 10 km from the shore in Chicago. A similar observation was made for metal deposition

Table 2
Particle phase PCB dry deposition fluxes (ng m^{-2} day^{-1})

Location	Flux	References
Mould Bay, Canada	2	Gregor et al. (1996)
Around Saginaw Bay, USA	17	Murphy et al. (1981)
Eastern Atlantic Ocean	1.7	Drooge et al. (2001)
South Heaven, MI, USA	140[a]	Franz et al. (1998)
Offshore Chicago, IL, USA	60[a]	Franz et al. (1998)
Waukegan, IL, USA	120	Murphy et al. (1981)
Paris, France	80	Grainer and Chevreuil (1997)
Tainan, Taiwan	4730	Lee et al. (1996a)
Chicago, IL, USA	190±80	This study

[a]Geometric mean.

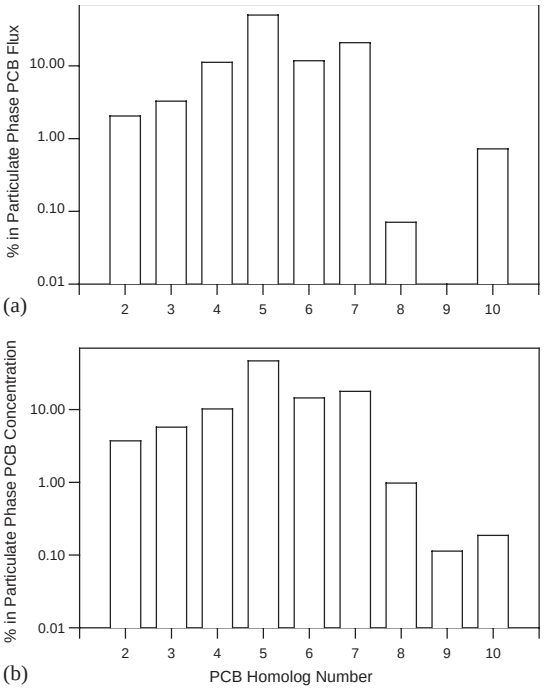

Fig. 3. Percentages of PCB homologs in particulate fluxes (a) and particulate concentrations (b).

fluxes. Metal deposition was about 20 times higher at Chicago compared to offshore sites (Paode et al., 1998). An important fraction of the flux that originates in Chicago may be deposited into Lake Michigan. Therefore, it is obvious that urban areas near surface waters are important sources for deposition of PCBs as well as other anthropogenic pollutants. Since, more than half of the world's population lives within 100 km of a coast, the majority of anthropogenic fluxes to surface waters occur in the coastal zone (Pryor and Barthelmie, 2000).

The deposition collected on the plates contained both low (less chlorinated) and high molecular weight PCB homologs. The maximum particle phase PCB flux was for mid-range molecular weight PCB homologs (Fig. 3a). PCB homologs patterns of the dry deposited material were similar to those observed on particulate PCBs collected simultaneously with a high-volume air sampler (Fig. 3b). However, a slight difference was observed for higher molecular weight PCBs (9- and 10-chlorinated biphenyls). This was probably related to the low levels of higher MW PCBs in the atmosphere because lower levels are more difficult to detect and identify. Their levels were at least one order of magnitude smaller than the lower MW PCBs.

The measured ambient vapour and particulate PCB concentrations collected by a high-volume air sampler which was used simultaneously with KSS indicated that the particulate PCB concentration was on the average ~5% of the total PCB concentration in the atmosphere (Tasdemir et al., 2004).

3.2. Apparent dry deposition velocities of PCBs

Apparent particle phase PCB dry deposition velocities were obtained from the measured particle PCB fluxes and concentrations ($V_d = F_p/C_p$). Particle depositional fluxes were obtained from the KSS while concentrations were obtained from the filter of a high-volume air sampler. In the literature, the calculated dry deposition velocities commonly used concentrations obtained from high-volume samplers. For example, Franz et al. (1998) used greased surfaces and high-volume air sampler to collect concentrations and fluxes of atmospheric PCBs and then dry deposition velocities were calculated. In another study, Odabasi et al. (1999) used the same high-volume air sampler and greased surfaces similar to those used in this study to collect atmospheric PAHs and determine their dry deposition velocities. Similarly, Vardar et al. (2002) used a greased surface and high-volume sampler to measure the dry deposition flux and concentrations of PAHs. These examples including our study's result ($r^2 = 0.835$) indicated high correlation between flux and concentration values. Therefore, the particle size distribution collected by the greased surfaces and high volume are probably similar (Franz et al., 1998). However, since this similarity cannot be confirmed we will use the term "apparent" deposition velocity in this paper.

The calculated average apparent dry deposition velocity for particle phase PCBs was 5.2±2.9 cm s^{-1} and it ranged between 1.4 and 10.5 cm s^{-1} (sample by sample). The variations in the apparent dry deposition

velocities are probably a direct function of particle size distribution and the meteorological conditions (i.e. wind direction, wind speed, temperature, atmospheric stability).

The average apparent dry deposition velocity determined from this study is comparable to the values obtained using similar techniques. Holsen et al. (1991) and Franz et al. (1998) collected samples in Chicago with the same type of sampler used in this study. Franz et al. (1998) reported that the range of their average values were between 4.4 and 7.2 cm s^{-1} for warm and cold months, respectively. Holsen et al. (1991) gave a range for the dry deposition velocity for coarse particles between 4.8 and 7.3 cm s^{-1}.

Table 3 summarizes some of the PCB dry deposition velocities cited in the literature. The reported values range over 2 orders of magnitude probably in part due to different sampling and calculation techniques. However, the difference is very small when similar collection techniques were used (Lee, 1991; Holsen et al., 1991; Franz et al., 1998, this study). There have also been some studies that determined the dry deposition velocities of other SOCs (Table 4) (McVeety and Hites, 1988; Hoff et al., 1996; Kaupp and McLachlan, 1999; Odabasi et al., 1999; Vardar et al., 2002; Franz et al., 1998; Sheu et al., 1996; Cakan, 1999).The agreement between the average dry deposition velocity obtained from this study and the reported values using similar techniques for other SOCs (i.e. PAHs and OCPs) is good (Odabasi et al., 1999; Vardar et al., 2002; Franz et al., 1998; Sheu et al., 1996; Cakan, 1999). However, some dry deposition velocities summarized in the literature are significantly smaller than the results found in this study. This difference is possibly due to dry deposition velocity estimation techniques in which coarse particles were not taken into consideration (Doskey and Andren, 1981; Hoff et al., 1996; Miller et al., 2001).

Coarse particles have been shown to be very important in deposition fluxes of SOCs in urban areas (Lee, 1991; Holsen et al., 1991; Sweet et al., 1993; Pirrone et al., 1995; Chen et al., 1996; Tasdemir, 1997; Lipiatou et al., 1997; Franz et al., 1998; Odabasi et al., 1999; Yang et al., 1999). Dry deposition samples taken in Chicago demonstrated that urban areas contained a significant amount of PCBs associated with coarse particles (Holsen et al., 1991). A similar result was found by Sweet et al. (1993). Their cascade impactor data indicated that some of the particulate PCBs were associated with coarse particles in Green Bay. Although the particle size distribution is one of the most important features controlling PCBs deposition velocities, only a small amount of data exists on particle size distributions of PCBs (Baker et al., 1993). Lee et al. (1996a) reported that more than 87% of the PCB dry deposition flux was

Table 3
Particle phase dry deposition velocities of PCBs

No.	Compound	V_d (cm s^{-1})	References
a	PCB	0.5	Doskey and Andren (1981)
b	PCB	0.12	Grainer and Chevreuil (1997)
c	PCB	1.1[a]–5.9[b]	Lee (1991)
d	PCB	0.09–0.58	Lee et al. (1996a)
e	PCB	0.27–0.93	Lee et al. (1996b)
f	PCB	5.0	Holsen et al. (1991)
g	PCB	4.4[c]–7.2[d]	Franz et al. (1998)
h	PCB	5.2±2.9	This study

a: Estimated employing the model suggested by Sehmel and Sutter for submicron particles.
b: Calculated based on the assumption of 20% Aroclor 1254, of which 50% would be deposited while ambient concentration is about 5 ng m^{-3}.
c: Greased dry deposition plates.
d: Greased dry deposition plates.
e: Greased dry deposition plates.
f: Greased dry deposition plates.
g: Greased dry deposition plates.
h: Greased dry deposition plates.
[a] For fine particles.
[b] For coarse particles.
[c] For summer months.
[d] For winter months.

Table 4
Particle phase dry deposition velocities of semivolatile organic compounds

No.	Compound	V_d (cm s^{-1})	References
a	PAH	1.0	McVeety and Hites (1988)
b	SOC	0.2	Hoff et al. (1996)
c	PAH and PCDD/F	0.05	Kaupp and McLachlan (1999)
d	PAH	6.7±2.8	Odabasi et al. (1999)
e	PAH	4.5±3.1	Vardar et al. (2002)
f	PAH	0.64[a]–2.2[b]	Franz et al. (1998)
g	PAH	0.67–1.8	Sheu et al. (1996)
h	OCP	5.0±2.0	Cakan (1999)

a: Calculated by a mass balance model.
b: Obtained using the model by Slinn and Slinn for small (0.5 μm) and large (5 μm) particles.
c: Calculated using selected deposition velocities and fractions for considered interval.
d: Greased dry deposition plates.
e: Greased dry deposition plates.
f: Greased dry deposition plates.
g: Greased dry deposition plates.
h: Greased dry deposition plates.
[a] For summer months.
[b] For winter months.

due to particles bigger than 10 μm. This conclusion supports the results obtained by Holsen et al. (1991) who studied particulate PCB fluxes and based on their calculations, the coarse particles were an important contributor to the dry deposition burden. The calculated mass median diameter (MMD) of coarse particles associated with PCBs was about 25 μm.

Coarse particles are prevalent in heavily populated cities and therefore, there is a greater chance for partitioning between coarse particles and PCBs (Hoff et al., 1996). Similar to the findings mentioned above, Sweet et al. (1993) stated that in Green Bay up to 50% of the particulate PCBs were associated with large particles ($d_p = 2$–$10\,\mu m$).

In general, PAHs, some of which behave similarly to PCBs, would not be expected to be in equilibrium with the particle phase in the urban air due to many local PAH sources. However, PAHs are expected to be closer to the equilibrium with particles in the rural areas. PAHs in the rural samples showed higher association with the coarse particles than urban samples. Rural data indicate that at equilibrium more than 50% of PAHs would be associated with coarse rural particles (Allen et al., 1996). This tendency to associate with larger particles could be due to mechanical processes such as atmospheric turbulence and dispersion. Since there are few or no point sources for PCBs to the atmosphere, they are theoretically in equilibrium with the gas phase in urban areas also. Thus, it is expected that PCBs will have high particle dry deposition velocities due to their association with coarse particles.

4. Conclusions

This study focused on the collection of the particulate phase PCB deposition fluxes to greased surrogate surfaces. The dry deposition flux of PCBs averaged $190\,ng\,m^{-2}\,day^{-1}$. This value is higher than the ones measured in non-urban areas. The main reasons for the discrepancy may be the varied concentrations of airborne PCBs, concentrations of particulate matter in the atmosphere, and size and characteristics of particles associated with the PCBs.

Homolog distributions from ambient particulate matter and flux samples matched well suggesting that both samplers (Hi-vol and greased deposition plates) were able to collect similar particles ($r^2 = 0.835$). In general, atmospheric particle associated PCBs were dominated by mid-range chlorinated homologs.

Apparent particle associated PCB dry deposition velocities were calculated from the measured particle PCB fluxes and concentrations ($V_d = F_p/C_p$). The apparent dry deposition velocity averaged $5.2 \pm 2.9\,cm\,s^{-1}$. This result indicated that PCBs were mainly associated with coarse particles.

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