The determination of gas phase dry deposition fluxes and mass transfer coefficients (MTCs) of polychlorinated biphenyls (PCBs) using a modified water surface sampler (WSS)

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Abstract

Gas phase PCB dry deposition and concentration samples were collected simultaneously between July 2004 and May 2005 at a suburban site in Bursa, Turkey. A modified water surface sampler (WSS) was employed to collect gas phase fluxes while a high-volume air sampler (HVAS) was used for concentration samples. The WSS was able to collect both particle and gas phase PCB deposition samples. The collected PCBs on water surface were captured by a filter and an XAD-2 resin column during water cycle. The average of gas phase PCB deposition flux, determined by analyzing the XAD-2 resin column, was 79.3±40.5 ng m\(^{-2}\) d\(^{-1}\) and its percentage in total (gas+particle) PCB flux was about 60. The average of gas phase PCB concentration measured concurrently with flux samples was 224.4±160.2 pg m\(^{-3}\) and its ratio to the total (gas+particle) PCB concentration was 85%. This difference was likely due to the different deposition characteristics of gases and particulates. Dominant PCB homolog groups were 3–4 chlorobiphenyls (CBs) for both ambient air and gas phase deposition samples. Mass transfer coefficients (MTC, \(K_g\)) for air-side were determined using gas phase flux and ambient air concentration values. The average overall \(K_g\) ranged between 0.21 and 0.96 cm s\(^{-1}\) with an average of 0.60±0.19 cm s\(^{-1}\).

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Keywords: Air–water exchange; Water surface sampler (WSS); Overall \(K_g\); SOCs; Turkey

1. Introduction

Semi volatile organic compounds (SOCs) in air partition between gas and particle phases, are inclined to atmospheric transport and deposition to regions far from their sources (Jurado et al., 2004; Hillery et al., 1998). Polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) are of SOCs and some of them persist in the atmosphere. SOCs may be removed from the atmosphere by dry/wet deposition and air–water exchange processes (Tasdemir et al., 2005; Jurado et al., 2004; Totten et al., 2001; Park et al., 2001; Miller et al., 2001; Franz et al., 1998). PCBs may cycle between air and water bodies depending on their physical and chemical properties, meteorological factors and contact surface characteristics (Gustafson and Dickhut, 1997; Hoff et al., 1996; Finlayson-Pitts and Pitts, 1986).

An increasing trend on the investigation of air–water exchange fluxes of PCBs has been noticed in recent years (Wethington and Hornbuckle, 2005; Sundqvist

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et al., 2004; Bruhn et al., 2003; Totten et al., 2001; McConnell et al., 1996; Hornbuckle et al., 1994). In order to determine the air–water exchange flux, measurements of both air and water concentrations have been commonly used and the two-film model was employed in the calculations (Schwarzenbach et al., 1993). The two-film model and mass balance approaches have been used to estimate atmospheric loading/vaporization flux of SOCs to/from water bodies (Hoff et al., 1996; Pirrone et al., 1995). According to the two-film model, net flux \( F_g \) (Eq. (1)) is limited by the rate of molecular diffusion through thin films of air and water and net flux is driven by the fugacity difference between air and water (Odabasi et al., 2001; Schwarzenbach et al., 1993).

\[
F_g = K_g \left( C_g - C_w H / RT \right)
\]

where \( C_w \) and \( C_g \) are the water and air concentrations of contaminant (ng m\(^{-3}\)), respectively, \( H \) is the Henry’s law constant (L atm mol\(^{-1}\)), \( R \) is the universal gas constant (0.082 atm L mol\(^{-1}\) K\(^{-1}\)), \( T \) is the temperature at air–water interface (K), \( K_g \) is the gas phase overall mass transfer coefficient (m d\(^{-1}\)).

Even though the net flux is zero at equilibrium, individual deposition and volatilization fluxes can be high enough to dominate the mass loadings of PCBs (Tasdemir et al., 2005; Bidleman, 1999). Therefore, it is crucial to consider the individual fluxes in each direction (Murphy, 1995). Deposition of SOCs has been measured directly using water surface samplers (WSSs) (Tasdemir et al., 2007, 2005; Odabasi et al., 2001, 1999; Shahin et al., 1999). Water was the collection media in the WSSs for measurement of gas phase SOC fluxes. WSSs with different configurations were used to successfully measure directly deposition fluxes of some inorganics and organics (Seyfioglu and Odabasi, 2006; Tasdemir and Gunez, 2006a,b; Raymond et al., 2004; Shahin et al., 2002; Pryor and Barthelmie, 2000; Odabasi et al., 1999; Yi et al., 1997). A constant level of water and short residence time were provided replenishing the water continuously in order to minimize the evaporation loss effects of water and SOCs (Tasdemir, 1997).

The overall objectives of this study were (i) to directly measure the gas phase PCB fluxes using a modified WSS,

### Table 1

<table>
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<tr>
<th>Date</th>
<th>Sampling duration (min)</th>
<th>WS (m s(^{-1}))</th>
<th>WD</th>
<th>T (°C)</th>
<th>RH (%)</th>
<th>P (mmHg)</th>
<th>Gas phase concentration (pg m(^{-3}))</th>
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<td>54.3</td>
<td>753</td>
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<td>69.5</td>
<td>749</td>
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<td>8/2–5/04</td>
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<td>1.4</td>
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<td>748</td>
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<tr>
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<tr>
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<td>64.5</td>
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<td>ND</td>
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<td>69.2</td>
<td>750</td>
<td>285.9</td>
</tr>
</tbody>
</table>

(ii) to characterize the atmospheric gas phase PCBs and depositional flux rates towards WSS, (iii) to calculate mass transfer coefficients of PCBs.

2. Materials and methods

2.1. Sampling program

Atmospheric samples were collected to measure gas phase PCB concentrations and gas phase PCB flux from July 2004 to May 2005. Samples were collected on a platform located on the roof of a three-story building (~10 m height) in the Uludag University Campus (N 40° 13′ 41.7″–E 28° 52′ 35.1″) in city of Bursa, Turkey (Fig. 1). The campus was about 20 km away from Bursa, an industrialized and crowded city, but it was close also to a highway and a town; therefore the downtown of the sampling site was supposed to be a suburban area and it was also used by other researchers for sampling (Tasdemir and Gunez, 2006a,b; Esen, 2006). Sampling duration and

Fig. 2. The water surface sampler (WSS).
meteorological data (wind speed, wind direction, temperature, relative humidity, pressure) were summarized in Table 1. Gas phase concentration and deposition samples were collected simultaneously. Average sampling duration was 40 h for dry deposition samples and 20 h for ambient air samples.

2.2. Sample collection

Gas phase deposition samples were collected by an aerodynamically designed water surface sampler (WSS) modified from previous studies (Tasdemir et al., 2007; Odabasi et al., 1999). A detailed illustration of the WSS was given in Fig. 2. The WSS was made of stainless steel plate having a diameter of 59.5 cm and a water depth of 0.5 cm. There was a leading edge (20 cm width) around the WSS to supply smooth contact of wind in order to minimize the turbulence effect. All tubings and connection apparatus were Teflon, glassware or stainless steel to prevent any adsorption or contamination. A detailed discussion on WSS sampling for SOC's can be found elsewhere and it is just summarized below (Tasdemir and Esen, 2007; Tasdemir et al., 2005, 2007; Odabasi et al., 1999). De-ionized (DI) water entered the collection surface (plate) from its center, and was collected by four weirs on the collection surface. Collected water having a retention time of 2–4 min on the collection surface, was passed through a filter unit for removing particulate phase and then an XAD-2 resin column for capturing dissolved phase PCBs by adsorption. Then clean water was pumped to water surface to maintain an uninterrupted cycle. Deposited PCBs associated with particles were assumed to be captured on the filter unit (Tasdemir and Holsen, 2005) while gas phase PCBs were collected in the XAD-2 resin column (Tasdemir et al., 2007).

In the previously used WSS by Tasdemir et al. (2005, 2006) and Odabasi et al. (1999), the water, entered the collection surface from its center, was overflown from the weirs located along the plates’ sides. Water was collected in the plate holder located under the plate before entering the filter unit (Tasdemir and Holsen, 2005). Some disadvantages related to the previous WSS would be evaporation loss from or absorption into the water under the plate holder. In order to minimize these artifacts a reservoir, covered by an aluminum foil to prevent any photochemical degradation of PCBs, was placed between the collection surface and the filter holder. “S” shaped connectors were employed to prevent any absorption or evaporation artifacts from the reservoir. Moreover, during the overflow from the triangle weirs, air–water exchange can be effective on the mass transfer (Baylar and Bagatur, 2001; Tasdemir et al., 2007). These disadvantages were attempted to be eliminated in our configuration (Fig. 2). The collection area of the sampler was increased in order to decrease sampling time by collecting more deposited PCBs; because longer sampling times may mask the relationship between measured fluxes and meteorological parameters. Another difference was the length of the leading edge illustrated in Fig. 2. The effect of WSS leading edge on deposition flux was investigated (Hsu, 1997). Hsu (1997) reported that when the leading edge length was 10 times increased, the measured deposition fluxes decreased 10–15%. Tasdemir et al. (2005) stated that the increase in the length of the leading edge located around the collection plate led to decrease in air–water exchange flux depending on decreasing air turbulence over water surface. In our study, the leading edge length was 20 cm and it was longer than the ones used by Tasdemir et al. (2005) which was 6 cm. Therefore, a relatively smooth water surface was provided to obtain an accurate deposition mechanism minimizing the wind effects. In our system, tubings were used as weirs to eliminate any absorption during overflow.

A modified high-volume air sampler (HVAS) (GPS11 Thermo Andersen, USA) equipped with a cartridge containing 10 g of XAD-2 resin sandwiched between two layers of PUF whose diameter was about 6 cm and thickness was 5 cm following the filter holder wherein a glass fiber filter (GFF) having 10.2 cm diameter was used (Esen et al., 2006). The average air volume passed through the HVAS was about 279±161 m³ (average±standard deviation, SD) at a rate of ~170 mL/min. The XAD-2 resin was used in the PUF cartridge to increase the adsorption capacity (Tasdemir et al., 2005; Odabasi et al., 1999).

2.3. Analytical procedure

PUF cartridges and XAD-2 resin were soxhlet extracted with de-ionized (DI) water followed by methanol (MeOH), dichlormethane (DCM), acetone/hexane (ACE/HEX) mixture for 24 h each, respectively. They were stored in a freezer until sampling. GFFs used in HVAS and WSS were wrapped loosely and put in a furnace whose temperature as over 450 °C overnight to remove any organic residuals on the filter. The followed analytical procedure was reported in details elsewhere (Tasdemir et al., 2005, 2007) and it was only summarized here. WSS samples including GFF and XAD-2 resin were extracted with MeOH for 24 h and DCM for 24 h in sequence (Tasdemir and Holsen, 2005). Extracts were merged subsequently and drained from Na₂SO₄ to remove any water residual. On the other hand, samples taken with the HVAS were extracted with DCM/PE (1/4) solvent for 24 h in a soxhlet. Both WSS
and HVAS samples were concentrated to 5 mL using rotary evaporator, and then reduced to 2 mL with a gentle stream of pure nitrogen. Fractionation of PCBs was achieved in a cleaning column containing silicic acid, alumina and Na₂SO₄ (Cindoruk and Tasdemir, in press; Odabasi et al., 1999; Cotham and Bidleman, 1995). Sulfuric acid cleaning was applied to prevent any contamination for chromatographic peaks. Field blank samples (n=8) were collected to determine the possible contamination during transport, sampling and analyzes. The same analytical procedure applied to the real samples was followed for field blank samples.

Quantification of the PCB congeners was conducted using a gas chromatograph (Agilent HP 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-ms, 30 m, 0.25 mm, 0.25 μm) (Agilent 19091s-433) was used. The instrument was tuned for every 48 h using perfluorotributylamine (PFTBA) (Odabasi, 2005). The calibration was performed injecting (1 μL) five levels (1–100 ng/mL) of standard solutions in hexane (Odabasi, 2005). PCB congeners were identified based on their retention times, target and qualifier ions. Quantification was based on internal standard calibration procedure. The operating conditions for PCB analysis were as follows: oven temperature program 70 °C (2 min), 25 °C/min to 150 °C, 3 °C/min to 200 °C, 8 °C/min to 280 °C, 10 min at 280 °C; carrier gas (helium), 1.2 mL/min; splitless (split valve open after 1 min) with purge flow 25 mL/min (Odabasi, 2005). The ions were monitored in two groups: Group 1: 152.0, 186.0, 220.0, 222.0, 224.0, 254.0, 256.0, 258.0, 290.0, 292.0, 326.0, 328.0, 360.0, 362.0. Group 2: 326.0, 328.0, 360.0, 362.0, 394.0, 396.0, 428.0, 430.0, 462.0, 464.0, 498.0, 500.0 (Odabasi, 2005).

All PCB congeners were separated based on their target and qualifier ions. The instrumental detection limit was approximately 0.15 pg for 1 μL splitless injection.

2.4. Quality assurance/quality control

PCB #14, PCB #65 and PCB #166 congeners were used as surrogate standards to determine the recovery efficiencies of each sample and each congener had a concentration of 5 ng mL⁻¹. The average recovery efficiencies (average±SD) for PCB#14, PCB#65 and PCB #166 were 50.6±11.9%, 73.4±19.8%, and 87.7±26.7% for WSS XAD-2 resin samples, and 55.68±17.18%, 74.48±15.20% and 99.87±29.16% for HVAS PUF cartridges, respectively.

Limit of detection (LOD) values were calculated for each congener as blank average concentration plus three times standard deviation (average±3σ) (Tasdemir and Holsen, 2005; Simcik et al., 1998). The ratios of average total PCB amount detected in blank samples to that in the samples were 0.7±1.8% and 11.2±5.1% for HVAS and WSS, respectively. The obtained LOD values for individual PCB congener ranging from not detected to 0.96 pg. Congener values under the LOD in the samples were neglected. The gas phase flux and PCB concentration values were corrected with field blanks in order to eliminate the background contamination and artifacts by subtracting the average blank amount from the sample values (Vardar et al., 2004; Odabasi et al., 1999; Simcik et al., 1998). Breakthrough from the XAD-2 resin column in the WSS system was checked using a second (back-up) column after the main (first) column. The amount of PCBs detected in the second column was similar to the amounts detected in the blank sample. PCB levels were less than the LODs; therefore, breakthrough could not be the case during the sampling campaign.

3. Results and discussion

3.1. Gas phase concentrations of PCBs

The gas phase concentrations of Σ₂₅ PCBs ranged between 92.0 and 698.6 pg m⁻³ with an average of 224.4±160.2 pg m⁻³ (Table 1). This value was in line with reported values for rural sites (Totten et al., 2006; Gouin et al., 2002) while it was lower than urban site concentrations (Totten et al., 2004; Tasdemir et al., 2004). Atmospheric PCBs measured in this study dominated in gas phase (Tasdemir et al., 2004; Yeo et al., 2003; Simcik et al., 1997). The gas phase PCB concentrations in the site were significantly correlated with air temperature at p<0.01. The PCB profile determined in the gas phase was dominated by lighter molecular weight congeners including especially 3–4 chlorobiphenyls (CBs) (Cindoruk and Tasdemir, in press; Gambaro et al., 2005; Totten et al., 2004). The possible sources for gas phase PCBs measured in the site were evaporation from landfill area, leachate treatment plant, and emissions originated from treatment sludge incineration plant. Back trajectory analyses computed by HYSPLIT (NOAA Air Resources Laboratory, 2006) indicated that dominant air movement was from NNE-ENE of sampling site where the mentioned PCB sources were settled. A detailed discussion on gas and particulate phase levels and distributions of PCBs in this site can be found elsewhere (Cindoruk and Tasdemir, in press).

3.2. Gas phase deposition fluxes of PCBs

The fluxes of SOCs can be determined by direct measurements, mass balance or fugacity gradient calculations.
In many studies, air and water concentrations of PCBs are measured concurrently and air–water exchange fluxes based on concentration gradients and overall mass transfer coefficient (MTC) according to Eq. (1) have been calculated (Bruhn et al., 2003; Totten et al., 2003; Park et al., 2001; Hornbuckle et al., 1994; Schwarzenbach et al., 1993; Achman et al., 1993). In natural water bodies, the magnitude of flux change was studied based on background water and air concentrations. In our study, gas phase PCB deposition fluxes were measured directly by a modified WSS. The PCB concentration of the water recycled in WSS was assumed to be close to zero due to the use of XAD-2 resin and therefore, the maximum PCB transfer from ambient air to the water surface was observed with a minimal volatilization interference as a result of low retention time (Tasdemir et al., 2006).

PCB deposition fluxes, including particle and gas phases, can be measured with a WSS. The total (gas + particle) PCB fluxes measured in this study ranged between 47.3 and 262 ng m\(^{-2}\) d\(^{-1}\) with an average of 138.4 ± 70.6 ng m\(^{-2}\) d\(^{-1}\) (Fig. 3). On the other hand, the measured gas phase deposition fluxes determined by analyzing XAD-2 resin column, varied from 18.8 to 153.8 ng m\(^{-2}\) d\(^{-1}\) with an average of 79.3 ± 40.5 ng m\(^{-2}\) d\(^{-1}\) (Fig. 3). The average ratio of gas phase PCB flux to total PCB flux was 60.6%. Previous studies, in which a WSS used, also reported higher gas phase fluxes than particle fluxes for PCBs and PAHs (Tasdemir et al., 2006; Tasdemir and Holsen, 2005; Odabasi et al., 1999). The dominant mechanism was thought to be the gas phase deposition by which atmospheric PCBs were delivered to water surfaces (Totten et al., 2006). The gas phase PCB fluxes are assumed to be higher than particle phase fluxes because the PCBs in the air exist mostly in gas phase (Tasdemir et al., 2005). However, the ratio (gas/particle) for fluxes, 60.6%, was lower than when it was compared to the concentration ratio, 85%. This difference can be described not only by the gas phase concentrations but also the different deposition characteristics of gases and particles. Gravitational settling becomes effective for particles over 1 μm, while Brownian motion was in force for particles below 0.1 μm and gases (Finlayson-Pitts and Pitts, 1986).

The net air–water exchange fluxes given in Table 2 were mostly from water to air via volatilization. The net fluxes were measured by concurrently measurement of both water and air concentrations. According to the volatilization flux results, the contaminated water bodies are supposed to be appreciable sources for PCBs in air (Bamford et al., 2002; Park et al., 2002; Totten et al., 2001). For example, Park et al. (2002) reported only 7% for gas phase deposition flux while 93% for volatilization flux of PCBs in Texas, USA. The gas phase deposition fluxes presented in this study reflected only the atmospheric deposition process in dry air conditions and did not represent the net air–water exchange transfer.

<table>
<thead>
<tr>
<th>Fluctuation (ng m(^{-2}) d(^{-1}))</th>
<th>Location</th>
<th>Method</th>
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<td>Lake Michigan USA</td>
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<td>Air–water measurement</td>
<td>McConnell et al., 1996</td>
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<td>Air–water measurement</td>
<td>Sundqvist et al., 2004</td>
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<td>−70 to −360</td>
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<td>Air–water measurement</td>
<td>Gevao et al., 1998</td>
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<td>Bamford et al., 2002</td>
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<td>−2700 to +260</td>
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<td>Totten et al., 2001</td>
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<tr>
<td>830</td>
<td>Chicago, IL USA</td>
<td>WSS</td>
<td>Tasdemir et al., 2005</td>
</tr>
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<td>79.3 ± 40.5</td>
<td>Bursa, Turkey</td>
<td>WSS</td>
<td>This study</td>
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</table>

WSS: Water surface sampler. Negative values denote volatilization or water-to-air. Positive values denote deposition or air-to-water.
There have been limited studies exhibiting the dry deposition fluxes of gas phase PCBs. Only the results reported by Tasdemir et al. (2005) could be compared with our results, the difference between gas phase deposition fluxes for Chicago and Bursa could be due to the different concentration gradient and meteorological conditions.

Deposited PCB congeners were classified according to homolog numbers. The average gas phase deposition fluxes and concentrations of homologues were presented in Fig. 4. The sum of 3 and 4-CBs accounted for 62% of the total gas phase PCB flux. For higher molecular weight PCBs, the fluxes were lower due to the fact that PCBs occur almost exclusively in the particle phase (Palm et al., 2004; Totten et al., 2004). A well-correlated relationship was obtained between gas phase homolog concentrations and flux values ($p < 0.01$). When winds blew from the sectors where possible PCB sources were located, depositional fluxes were measured in high levels supported by back trajectory analysis for the site.

### 3.3. Mass transfer coefficient (MTC)

The magnitude of gas transfer is a function of concentration differences between atmosphere and surface, chemical characteristics of compound, and atmospheric conditions (Tasdemir et al., 2007; Hornbuckle et al., 1994). Air–water exchange can be described by stagnant two-film model including diffusion process (Schwarzenbach et al., 1993). The air–water exchange flux is estimated according to Eq. (1) using air/water concentrations and MTC ($K_g$, $K_w$). Several factors causing uncertainties affect the flux calculations and air–water fugacity (i.e. physical processes in water, turbulence at air–water interface, boundary layer stability, surface conditions such as breaking waves and bubble injection) (Sundqvist et al., 2004; Bruhn et al., 2003; Odabasi et al., 2001). MTC is of importance in terms of air–water

#### Table 3

<table>
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<th>Compound</th>
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<td>WSS Tasdemir et al., 2005</td>
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<td>0.74</td>
<td>PAHs</td>
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<td>WSS Odabasi et al., 1999</td>
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<td>Siskiwit Lake, USA</td>
<td>Mass balance balance McVeety and Hites, 1988</td>
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<td>Izmir, Turkey</td>
<td>WSS Seyfioglu and Odabasi, 2006</td>
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<td>0.25</td>
<td>PBDE</td>
<td>Izmir, Turkey</td>
<td>Gas stripping</td>
</tr>
<tr>
<td>0.6±0.2</td>
<td>PCBs</td>
<td>Bursa, Turkey</td>
<td>WSS This study</td>
</tr>
</tbody>
</table>

![Fig. 4. The homolog distribution of gas phase PCB concentrations and dry deposition fluxes.](image)

![Fig. 5. The calculated overall mass transfer coefficient (MTC) of PCBs.](image)

![Fig. 6. The mass transfer coefficient variations of PCB congeners.](image)
The overall gas phase PCB MTCs ($K_g = F_g / C_g$), calculated from the concurrently measured gas phase deposition fluxes ($F_g$) and air concentrations ($C_g$), were calculated for each sample and plotted in Fig. 5. The overall $K_g$’s ranged between 0.21 and 0.96 cm s$^{-1}$ with an average of 0.6±0.19 cm s$^{-1}$. This value is in line with reported value of 0.54 cm s$^{-1}$ for PCBs measured by WSS (Tasdemir et al., 2005). The variation of $K_g$ may be attributed to the meteorological conditions especially temperature and wind speed. However, an insignificant correlation was obtained from the correlation analysis between $K_g$ and wind speed ($p>0.1$). Odabasi et al. (1999) reported an average $K_g$ value of 0.74 cm s$^{-1}$ for 6 PAH compounds, members of SOCs, (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene) using a similar WSS. The MTC value measured with WSS for HCHO (formaldehyde), which is an organic compound, was 0.58 cm s$^{-1}$ (Table 3) (Seyfoglu and Odabasi, 2006).

The variation of measured $K_g$ values for each PCB congener was shown in Fig. 6. The MTCs for each congener ranged from 0.25 (PCB-33) to 1.83 (PCB-151) cm s$^{-1}$ with average of 0.75±0.51 cm s$^{-1}$. Tasdemir et al. (2007) reported 0.40±0.36 cm s$^{-1}$ average MTC value for PCB congeners similar to this study. However, they reported a maximum MTC value of 2.05 cm s$^{-1}$ for PCB-28.

In another approach, gas phase PCB fluxes and gas phase PCB concentrations were regressed to obtain the slope of best-fit linear regression line giving the $K_g$ value (Fig. 7). The $K_g$ value obtained from the linear regression ($r^2=0.76, p<0.05$) was 0.14 cm s$^{-1}$. The average $K_g$ value calculated using individual PCB flux and concentration values was about 4 times greater than the $K_g$ value obtained from the regression plot but both values were in the same level.

4. Conclusion

There is still no commonly accepted dry deposition collection method for polychlorinated biphenyls (PCBs) which exist in both gas and particulate phases. This study demonstrated that the water surface sampler (WSS) was a good sampler to collect PCB deposition fluxes.

A modified WSS was utilized to directly measure gas phase deposition of PCBs. In fact, the WSS is able to capture both particulate phase and gas phase PCBs with a filter holder and an XAD-2 resin column. The measured gas phase PCB fluxes averaged about 79±40 ng m$^{-2}$ d$^{-1}$. The reported fluxes indicate only the absorption direction fluxes thus they are higher than the ones reporting net fluxes calculated using simultaneously measured air and water concentrations for natural surface waters.

Ambient air PCBs were sampled simultaneously with a modified high-volume sampler. The gas phase PCB concentrations changed between 92.0 and 698.6 pg m$^{-3}$ with an average of 224.4±160.2 pg m$^{-3}$. The average concentration, dominated in gas phase, was in line with reported values for non-urban sites while it was lower than urban site concentrations.

The overall gas phase mass transfer coefficients (MTC, $K_g$), as a function of gas phase PCBs and meteorological conditions, were determined using gas phase flux and ambient air concentration values. PCB homologs measured with hi-volume had similar patterns to the ones measured by a water surface sampler. This correlation between gas phase flux and concentration suggests that both samplers collect the same material. MTCs were calculated using the two-film theory along with the measured phase concentrations and corresponding $H'$s. The average overall $K_g$ ranged between 0.21 and 0.96 cm s$^{-1}$ with an average of 0.60±0.19 cm s$^{-1}$ indicating that most of resistance to mass transfer occurred on the water-side for PCBs. The average of overall MTC was in good agreement with ones calculated using a similar configuration of WSS.

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References


Odabasi M. Personal communication. Izmir, Turkey: Dokuz Eylul University; 2005.


Raymond HA, Yi SM, Moumen N, Han YJ, Holsen TM. Quantifying the dry deposition of reactive nitrogen and sulfur containing species in remote areas using a surrogate surface analysis approach. Atmos Environ 2004;38:2687–97.


Shahin UM, Holsen TM, Odabasi M. Dry deposition measured with a water surface sampler: a comparison to modeled results. Atmos Environ 2002;36:3267–76.


Simcik MF, Franz TP, Zhang H, Eisenreich SJ. Gas/particle partitioning of PCBs and PAHs in the Chicago urban and adjacent


Tasdemir Y, Esen F. Dry deposition fluxes and deposition velocities of PAHs at an urban site in Turkey. Atmos Environ 2007;41:1288–301.

Tasdemir Y, Gunez H. Dry deposition of sulfur containing species to the water surface sampler at two sites. Water Air Soil污染 2006a;175:223–40.

Tasdemir Y, Gunez H. Ambient concentration, dry deposition flux and overall deposition velocities of particulate sulfate measured at two sites. Atmos Res 2006b;81(3):250–64.


