Short-term variation in ambient concentrations and gas/particle partitioning of organochlorine pesticides in Izmir, Turkey

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Abstract

Twenty successive daytime and nighttime air samples were collected and analyzed for 23 currently used and/banned organochlorine pesticides (OCPs) between 14 and 23 May 2003 in Izmir, Turkey. Average individual OCP concentrations ranged from $5 \pm 4 \, \mathrm{pg \, m^{-3}}$ (p,p'-dichlorodiphenyldichloroethane) to $391 \pm 306 \, \mathrm{pg \, m^{-3}}$ (chlorpyrifos) and they were within the ranges previously measured at different sites.

Most of the OCPs did not exhibit strong diurnal cycling. The temperature dependence of gas-phase atmospheric concentrations of OCPs investigated using Clausius–Clapeyron plots was statistically significant for β-HCH and endosulfan sulfate ($p < 0.1$) and was not significant for other compounds (0–21% of the variability in their gas-phase concentrations). In addition to temperature, the effect of wind speed and direction was also investigated using multiple linear regression analysis and these three parameters together explained the 2% (aldrin) to 72% (endosulfan II) of the variability in gas-phase OCP concentrations. Results of the multiple regression analysis indicated that wind speed was a statistically significant factor for most of the OCPs and wind direction was important for some compounds. The temperature-dependent diurnal cycling of most OCPs was probably masked by the higher wind speeds observed during daytime periods with high temperatures, different source sectors and ongoing sources. The lack of correlation for heptachlor, aldrin, p,p'-dichlorodiphenyldichloroethylene (p-p'-DDE), and p,p'-dichlorodiphenyltrichloroethane (p-p'-DDT) with temperature, wind speed and direction suggested that their concentrations were affected by long-range transport.

The partitioning of OCPs between particle and gas phases was investigated and compared to K_{OA} (octanol/air partition coefficient) absorption model. The overall agreement between experimental and modeled log K_p (gas/particle partition coefficient) values was good ($p < 0.01$, slope = 0.94). Prediction of absorption model for particulate percentages was excellent for β-HCH, endosulfan I, and p-p'-DDT. However, the model underpredicted the particulate percentages for α,γ-HCHs, chlorpyrifos, and dieldrin, and overpredicted those for p-p'-DDE.

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1. Introduction

Organochlorine pesticides (OCPs) are a broad class of semivolatile organic compounds (SOCs) that were widely used as insecticides in the past. The atmosphere is a major pathway for the transport, deposition, degradation, and cycling of past and present SOCs. Past SOCs are defined as those that have been banned/restricted. They do not have any point sources around a sampling site. However, present SOCs have ongoing uses and point/diffuse sources around a sampling site (Lee et al., 2000).

It has been shown that the ambient concentrations of SOCs are affected by seasonal temperature variations and long-range transport (Sofuoglu et al., 2001; Lee and Jones, 1999; Cortes et al., 1998; Hoff et al., 1998; Honrath et al., 1997; Hillery et al., 1997; Wania et al., 1998). As the temperature rises, gas-phase air concentrations increase as a result of volatilization from previously contaminated surfaces such as soil, atmospheric particles, water, and vegetation. Short-term studies have indicated that ambient gas-phase SOCs also respond to short-term temperature changes resulting in rapid movement between environmental compartments (i.e., diurnal cycling) (Lee et al., 1998, 2000). Advection and ongoing sources are other important factors affecting the variation of ambient gas-phase OCP concentrations.

Izmir Metropolitan City is the center of a highly industrialized area by the Aegean Sea shoreline of Turkey. Izmir is located in a basin surrounded by mountain series of ~ 1000–1500 m height with only the west end open to the Aegean Sea. The climate is Mediterranean with warm and rainy winters, hot and dry summers. The major air movements over the area are mainly from northerly directions. The city with 2.7 million population has sizeable economic, industrial, and agricultural activities emitting high quantities of air pollutants. The use of most of the OCPs was banned/restricted in Turkey as in many countries due to persistent contamination of the environment. However, some OCPs (chlorpyrifos and endosulfan) are currently used. The average annual use of chlorpyrifos and endosulfan in Izmir area between 1998 and 2002 was estimated as 890 and 6700 kg, respectively (Ministry of Agriculture, 2003).

OCP levels have been widely measured around the world. However, very little information exists on their environmental levels in different compartments (surface waters, sediment, and biota) in Turkey (Turgut, 2003; Ayas et al., 1997) and there are no previous studies on atmospheric OCP concentrations.

The objectives of this study were to: (1) measure OCP concentrations and their short-term variation, (2) investigate their relationship with temperature and wind speed and direction, and (3) investigate their gas/particle partitioning.

2. Experimental

2.1. Sample collection

Twenty ambient air samples were collected between 14 and 23 May 2003 on a 4 m high sampling platform located on the Kaynaklar campus of the Dokuz Eylul University, Izmir, Turkey. The sampling site is located ~ 10 km southeast of Izmir's center. The campus is relatively far from any settlement zones or industrial facilities. There are residential areas located ~ 2 km southwest and a highway 0.5 km south of the sampling site. Land cover in the immediate area is a young coniferous forest. There are steel plants, a petroleum refinery, and a petrochemical industry located 45 km to the northwest. The nearest industrial facility is a cement work about 10 km at the north and an open road gravel storage site nearly 3 km at the east. Samples were collected during successive daytime (8.00 a.m.–8.00 p.m.) and nighttime (8.00 p.m.–8.00 a.m.) periods. Meteorological data were obtained from a 10 m high tower located at the same site (Table 1).

Air samples were collected using a modified high-volume sampler, Model GPS-11 (Thermo-Andersen Inc.). Particles were collected on 10.5-cm diameter quartz filters. The gas-phase compounds were collected in a modified cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF). Concurrently, particulate samples were collected on 11-cm diameter glass fiber filters using another high volume sampler to determine total suspended particulate (TSP) matter and its organic matter (OM) content. Average sampling time was 12 h. The average sampling volumes were 223 ± 8 and 41 ± 4 m^3 for pesticide and TSP samples, respectively.

2.2. Sample preparation and analysis

Prior to sampling, quartz filters were wrapped loosely with aluminum foil and they were baked overnight at $450\,^{\circ}$C in a muffle furnace to remove any organic residues. They were then allowed to cool to room temperature in a desiccator. PUF cartridges were cleaned by Soxhlet extraction using 1:1 acetone:hexane mixture for 12 h. After extraction the cartridges and resin were wrapped loosely with aluminum foil and dried in an oven at $70\,^{\circ}$C. Cleaned cartridges were stored in glass jars capped with Teflon-lined lids.

Collected samples were Soxhlet extracted with a mixture of dichloromethane (DCM): petroleum ether (PE) (20:80) for 12 h. All sample extracts were concentrated and transferred into hexane using a rotary evaporator and a high purity stream of nitrogen. After volume reduction to 2 ml and transfer into hexane, samples were cleaned up on an alumina-silicic acid column containing 3 g silicic acid (3% water) and 2 g

Table 1
Summary of meteorological, TSP, and OM data

Sample number	Date	Wind direction	Relative humidity (%)	Wind speed (m s^{-1})	Temperature (°C)	TSP (μg m^{-3})	OM (μg m^{-3})	OM (%)
1	05.14.2003	WNW	53	2.8	23.5	72	59	81
2	05.14.2003	ESE	69	1.4	18.2	73	45	62
3	05.15.2003	WNW	47	2.2	25.0	84	44	52
4	05.15.2003	N	64	0.8	20.1	101	52	51
5	05.16.2003	WNW	43	3.4	26.4	127	54	43
6	05.16.2003	N	63	0.9	20.8	95	39	41
7	05.17.2003	WNW	45	3.5	25.7	95	59	62
8	05.17.2003	N	68	1.2	20.0	89	18	20
9	05.18.2003	WNW	58	5.0	23.2	109	57	52
10	05.18.2003	NW	79	1.7	18.0	90	35	39
11	05.19.2003	NW	64	5.1	21.9	108	59	55
12	05.19.2003	WNW	74	4.3	17.2	77	37	48
13	05.20.2003	N	56	5.5	22.5	107	47	44
14	05.20.2003	NW	72	1.0	18.5	125	87	69
15	05.21.2003	ESE	53	3.1	24.2	93	55	59
16	05.21.2003	WNW	72	2.4	16.9	48	27	57
17	05.22.2003	ESE	51	6.0	22.6	73	34	47
18	05.22.2003	SSE	72	3.8	17.3	25	14	55
19	05.23.2003	SE	50	3.8	21.5	43	25	58
20	05.23.2003	SE	83	2.2	15.7	33	24	73
Average			62	3	21	83	44	53
SD			12	2	3	29	18	13

alumina (6% water) (Odabasi et al., 1999; Sofuoglu et al., 2001). The column was prewashed with 20 ml DCM followed by 20 ml PE. The sample in 2 ml hexane was added to the top of column, heptachlor, aldrin, p,p′-dichlorodiphenyldichloroethylene (p-p′-DDE), polychlorinated naphthalenes, and polychlorinated biphenyls (PCBs) were eluted with 25 ml PE (fraction 1). Polycyclic aromatic hydrocarbons (PAHs) and the other 20 OCPs were eluted with 20 ml DCM (fraction 2). For both fractions the solvent was exchanged into hexane, and the final sample volume was adjusted to 1 ml by nitrogen blow-down. Decachloro biphenyl (PCB 209) was used as the internal standard for fraction 2. Before analysis, samples were spiked with 25 ng PCB 209.

Samples were analyzed for OCPs with an Agilent 6890N gas chromatograph (GC) equipped with a micro-electron capture detector (μ-ECD). A capillary column (DB5-ms, 30 m, 0.25 mm, 0.25 μm) was used. The initial oven temperature was held at 50°C for 1 min and raised to 100°C at 25°C min^{-1}, 100–300°C at 5°C min^{-1}, and held for 7 min. The injector and detector temperatures were 250°C and 320°C, respectively. High-purity helium and nitrogen were used as carrier and detector make-up gases, respectively. Fractions 1 and 2 were run separately. OCPs in fraction 2 were quantified using the internal calibration procedure. Since fraction 1 also

contained the PCBs, PCB-209 could not be used as the internal standard for this fraction. Therefore, OCPs (heptachlor, aldrin, p-p′-DDE) in fraction 1 were quantified using the external calibration procedure. α-Chlordane and endosulfan I were coeluted from the chromatographic column used. Therefore, they were reported as α-chlordane + endosulfan I.

Prior to sampling for TSP, glass fiber filters were wrapped loosely with aluminum foil and they were baked overnight at 450°C in a muffle furnace to remove any organic residues. They were then allowed to cool to room temperature in a desiccator and were weighed using a micro-balance capable of weighing 0.1 mg. After sample collection filters were kept in a desiccator overnight and they were reweighed. TSP was determined by subtracting the initial weight from the final weight. To determine the OM content of the particles, filters were then baked for 1 h at 450°C in a furnace, allowed to cool to room temperature in a desiccator, and weighed. OM was determined by subtracting the final weight (after baking) from the initial weight (before baking). It is possible that the determination of OM content by this method may be interfered by the weight loss of glass fiber filters at high temperatures. The hourly weight loss of filters at 450°C with time was monitored for 12 h. It was observed that the maximum weight loss (3 mg) occurs within a 2 h period and the weight loss

decreases to $0.3\,mg\,h^{-1}$ and becomes stable for the remaining period. Since this experiment did not indicate when the weight loss stops, concurrent blank filters were run for each sample to minimize the interference from weight loss of filters at high temperatures in OM determination. Determined OM contents were corrected using the weight loss in blank filters during baking. The average weight loss of blank filters (0.3 mg) was significantly lower than the average weight loss of the samples (2.2 mg) indicating that the interference was not significant in OM determination.

2.3. Quality control

Procedural recoveries of OCPs were determined externally ($n = 6$) and they ranged from $40 \pm 11\%$ (endosulfan II) to $128 \pm 22\%$ (endosulfan sulfate). Eighteen of the individual OCPs had recoveries $> 70\%$ (Table 2). Since the recoveries were generally high, sample amounts were not corrected for procedural recoveries.

Instrumental detection limits (IDLs) were determined from sequential injections of diluted standard solutions of the analyzed compounds. The quantifiable amounts of OCPs ranged from 9 (α,β,γ-HCHs, aldrin, t-nonachlor, p-p′-DDE) to 75 fg (chlorpyrifos, heptachlor epoxide, c-nonachlor) for 1 µl injection volume (Table 2). Blank PUF cartridges and filters were routinely placed in the field to determine if there was any contamination during sample handling and preparation. For the compounds detected in blanks the limit of detection (LOD, ng) of the method was defined as the mean blank mass plus three standard deviations. IDLs were used for the compounds that were not detected in blanks. LODs for OCPs ranged from 9 pg (α,γ-HCHs, t-nonachlor) to 12.6 ng (endosulfan sulfate) for PUFs and from 9 pg (t-nonachlor) to 12.9 ng (endosulfan sulfate) for filters (Table 2). In general, OCP amounts in the samples were substantially higher than LODs. Sample quantities exceeding the LOD were quantified and blank-corrected by subtracting the mean blank amount from the sample amount.

Table 2
Procedural recoveries (average $\pm$ SD), blank amounts, instrumental detection limits (IDL), and limits of detection for the method (LOD)

Pesticide	Recovery (%)		Blank amounts (ng)		IDL (ng)	LOD (ng)	
	PUF	Filter	PUF	Filter		PUF	Filter
α-HCH	91 ± 4	885	nd	0.3	0.009	0.009	0.450
β-HCH	102 ± 10	95 ± 3	6.7	2.9	0.009	9.6	3.0
γ-HCH	94 ± 4	92 ± 7	nd	0.6	0.009	0.009	0.820
δ-HCH	106 ± 11	104 ± 15	nd	nd	0.038	0.038	0.038
HEPCHL	74 ± 7	74 ± 6	1.8	1.5	0.038	2.1	1.8
CHLPYR	98 ± 17	98 ± 6	3.7	2.8	0.075	6.9	3.1
ALD	77 ± 8	77 ± 7	3.0	2.6	0.009	3.9	2.8
HEP EPOX	91 ± 13	87 ± 6	2.4	nd	0.075	5.6	0.075
γ-CHL	87 ± 8	84 ± 4	nd	nd	0.019	0.019	0.019
α-CHL + ESLF I	64 ± 1	74 ± 6	0.6	1.0	0.028	4.0	1.6
t-NONA	69 ± 8	62 ± 10	nd	nd	0.009	0.009	0.009
p-p′-DDE	80 ± 8	81 ± 6	1.0	0.7	0.009	1.3	1.1
DIELD	87 ± 15	84 ± 9	0.4	nd	0.019	2.3	0.019
END	89 ± 17	79 ± 14	nd	0.2	0.019	0.019	1.2
ESLF II	40 ± 11	42 ± 4	nd	nd	0.019	0.019	0.019
p-p′-DDD	85 ± 12	84 ± 6	nd	nd	0.019	0.019	0.019
END AL	54 ± 19	62 ± 15	nd	nd	0.038	0.038	0.038
c-NONA	68 ± 16	80 ± 5	nd	nd	0.075	0.075	0.075
ESLF SUL	126 ± 22	128 ± 22	2.0	6.6	0.038	12.6	12.9
p-p′-DDT	86 ± 5	76 ± 10	nd	nd	0.019	0.019	0.019
END KET	122 ± 24	122 ± 24	nd	nd	0.019	0.019	0.019
MEOCL	117 ± 17	110 ± 8	nd	nd	0.075	0.075	0.075

nd: not detected.

$\alpha,\beta,\gamma,\delta$-Hexachlorocyclohexane isomers ($\alpha,\beta,\gamma,\delta$-HCH), heptachlor (HEPCHL), chlorpyrifos (CHLPYR), aldrin (ALD), heptachlor epoxide (HEP EPOX), γ-chlordane (γ-CHL), α-chlordane (α-CHL), endosulfan I (ESLF I), *trans*-nonachlor (t-NONA), p,p′-dichlorodiphenyldichloroethylene (p-p′-DDE), dieldrin (DIELD), endrin (END), endosulfan II (ESLF II), p,p′-dichlorodiphenyldichloroethane (p-p′-DDD), endrin aldehyde (END AL), *cis*-nonachlor (c-NONA), endosulfan sulfate (ESLF SUL), p,p′-dichlorodiphenyltrichloroethane (p-p′-DDT), endrin ketone (END KET), methoxychlor (MEOCL).

OCP standards were obtained from Accustandard (New Haven, CT, USA). The calibration standard solution contained 23 OCPs and PCB 209 as the internal standard. Five levels of calibration standards (1.2, 12, 40, 80, and $120 \, \text{ng ml}^{-1}$ for 21 OCPs, 2.4, 24, 160, $240 \, \text{ng ml}^{-1}$ for endosulfan I and II, and PCB 209 at a fixed concentration of $25 \, \text{ng ml}^{-1}$) were used to prepare the calibration curves. For all compounds the linear fit was good ($r^2 > 0.99$).

ChemStation software was used for the identification of OCPs in the samples. Identification of individual OCPs was based on their retention times (within $\pm 0.05 \, \text{min}$ of the retention time of calibration standard).

A midrange calibration standard was analyzed for every 12-h period to confirm GC-ECD performance (i.e., peak area, retention time). Samples were analyzed occasionally as duplicates. Differences in duplicate samples were $<5\%$.

Sampling artifacts associated with the glass fiber filters and PUF may influence the apparent gas–particle distributions of OCPs. Gas-phase OCPs may adsorb to the filter and particles collected on the filter or relatively more volatile compounds may be desorbed from the collected particles by continuing gas flow if the gas-phase concentration decreases or if the temperature increases during the sampling period. The extent of adsorption of gas-phase compounds is often estimated using a backup filter. Backup filters were not used in this study. However, a recent study indicated that the percent mass on the second filter was not significant (below 10%) for OCPs (Yeo et al., 2003). In the present study, since the sampling was conducted during relatively short periods (12 h, day or nighttime) the temperature fluctuations were also minimized. Therefore, it was assumed that sampling artifacts and their effect on the experimentally determined gas–particle distributions were not significant.

3. Results and discussion

3.1. Ambient organochlorine pesticide concentrations

Average individual OCP concentrations ranged from $5 \pm 4 \, \text{pg m}^{-3}$ (p,p′-dichlorodiphenyldichloroethane) to $391 \pm 306 \, \text{pg m}^{-3}$ (chlorpyrifos) (average $\pm$ SD) (Table 3). These concentrations were within the ranges previously measured at different sites. c-Nonachlor was not detected in any of the samples. Chlorpyrifos, a currently used pesticide had the highest average concentration and was followed by endosulfan sulfate (a degradation product of another currently used pesticide, endosulfan), β-HCH, methoxychlor, and α-CHL + endosulfan I (Table 3). α-HCH and γ-HCH concentrations were similar to those measured at other sites. However, average β-HCH concentration observed in this study

was higher than the ones reported for different sites. The average ratio of α-HCH to γ-HCH was 1.2 ± 0.5. It was reported that α-HCH/γ-HCH ratios were close to 1 in areas where lindane (γ-HCH) was used, and between 3 and 7 in areas where technical HCH was used or in remote areas (Lee et al., 2000; Murayama et al., 2003). α-HCH/γ-HCH ratios > 6 were reported for Arctic atmosphere (Halsall et al., 1998). The use of technical HCH and lindane has been prohibited for more than 20 years in Turkey. However, lindane is currently used in Europe (Lee et al., 2000). A recent study conducted using passive samplers at a continental scale reported that α-HCH/γ-HCH ratios were generally <1 in neighboring countries (Greece and Cyprus) and over the Europe (Jaward et al., 2004). Therefore, the relatively low α-HCH/γ-HCH ratios observed in this study can be attributed to the effect of regional sources.

Even though endosulfan has been used in greater quantities during recent years in the area (usage of endosulfans/chlorpyrifos = 7.5), chlorpyrifos concentrations were higher than endosulfan concentrations (ambient endosulfans/chlorpyrifos = 0.9 ± 1.0). When endosulfan sulfate is included, ambient endosulfans/chlorpyrifos ratio becomes 2.3 ± 1.9. However, this ratio is substantially lower than the ratio of 7.5 that was estimated for their usage. The relatively lower endosulfan concentrations observed may be due to different properties (i.e., vapor pressure, air/water partition coefficient, octanol/air partition coefficient, and reactivity in the atmosphere) of endosulfans and chlorpyrifos and as a result, their different transport, transformation and removal in the environment.

Fig. 1 shows the correlations between related OCPs. HCH isomers, endosulfan I, II and endosulfan sulfate, chlordane related compounds (heptachlor, heptachlor epoxide, and t-nonachlor) were correlated, indicating that their concentrations were affected by similar factors (local ongoing or regional sources, meteorological parameters). However, DDT and its degradation products DDE and DDD were not correlated probably due to their distant sources.

3.2. Effect of meteorological parameters on gas-phase OCP concentrations

It has been shown that the gas-phase air concentrations of SOCs have a strong relationship to ambient temperature (Lee and Jones, 1999; Cortes et al., 1998; Hoff et al., 1998; Honrath et al., 1997). As the temperature rises, gas-phase air concentrations increase as a result of volatilization from surfaces such as soil, atmospheric particles, water, and vegetation. The temperature dependence of gas-phase ambient concentrations of SOCs has been investigated using Clausius–Clapeyron plots (Lee and Jones, 1999; Cortes et al., 1998; Hoff et al., 1998; Honrath et al., 1997; Hillery

Table 3
Concentrations of OCPs (pg m^{-3}) in Izmir, Turkey and other sites

	Izmir, Turkey[a]			Galveston Bay, TX[b]	Niigata, Japan[c]	Hong Kong[d]	Chicago, IL[e]	Alert, Canadian Arctic[f]
	Range	Average ± SD	n					
α-HCH	4–462	111 ± 125	20	79	92	119	110	60
β-HCH	63–631	320 ± 176	20	4	23	41		0.8
γ-HCH	1–666	117 ± 157	20	135	32	36	150	10
δ-HCH	24–53	38 ± 15	3	47	3			
HEPCHL	2–24	7 ± 6	19	30		65		0.1
CHLPYR	38–1068	391 ± 306	20					
ALD	3–11	6 ± 3	14	6				
HEP EPOX	8–110	34 ± 35	14	13				1
γ-CHL	13–894	158 ± 262	15	38	64		130	0.5
α-CHL + ESLF I	96–342	171 ± 60	19	30[g]	78[g]	57[h]	120[g]	4[h]
t-NONA	2–387	50 ± 126	9	26			80	0.9
p-p'-DDE	8–35	20 ± 8	20	11	5	20		0.4
DIELD	3–114	35 ± 39	7	19				1
END	5–25	16 ± 10	3	1				0.2
ESLF II	3–30	20 ± 7	13					
p-p'-DDD	0.5–11	5 ± 4	6	2	<2		100	
END AL	19–149	48 ± 38	17					
c-NONA	nd	nd	0	4				0.1
ESLF SUL	46–1271	369 ± 375	16					
p-p'-DDT	5–75	29 ± 21	18	8	6	26	70	0.1
END KET	6–82	41 ± 26	8					
MEOCL	43–990	220 ± 255	20					0.3

Note: n, number of the samples above the detection limit; nd, not detected.

[a] This study (particle + gas phase).
[b] Park et al. (2001) (gas phase).
[c] Murayama et al. (2003) (particle + gas phase).
[d] Louie and Sin (2003) (particle + gas phase).
[e] Sofuoglu et al. (2001) (gas phase).
[f] Halsall et al. (1998) (particle + gas phase).
[g] a-Chlordane.
[h] Endosulfan.

et al., 1997) and surface exchange models (Wania et al., 1998).

Studies by Lee et al. (2000, 1998) have reported that OCPs and other SOCs followed clear diurnal cycles for the first 5 days of their study when the stable atmospheric conditions were dominant. However, for the last 2 days as a more unstable and cooler weather started to influence the sampling site, OCP concentrations were controlled primarily by advection (Lee et al., 2000). Most of the OCPs did not exhibit strong diurnal cycling in the present study. Diurnal variation β-HCH was illustrated as an example in Fig. 2, which was apparent only for the period between samples 10 and 16.

The variation in atmospheric SOC concentrations can be quantified using the Clausius–Clapeyron equation

$$\ln P = (-\Delta H_v/R)(1/T) + \text{constant}, \tag{1}$$

where P is the gas-phase SOC partial pressure (atm), ΔH_v is the enthalpy of vaporization (kJ mol^{-1}), R is the

gas constant, and T is the average atmospheric temperature (K) during the sampling period. ΔH_v is the heat required for phase change of a pure compound. In real environments, Simcik et al. (1999) suggested that ΔH_v could be defined as the energy necessary to cause the phase transition from the surface of soil, water, or vegetation to the atmosphere.

The temperature dependence of gas-phase atmospheric concentrations of OCPs in this study was investigated using plots of $\ln P$ vs. $1/T$ (Eq. (1)). The regression of $\ln P$ against $1/T$ should be linear with a negative slope m and an intercept b (Currado and Harrad, 2000; Simcik et al., 1999):

$$\ln P = m(1/T) + b. \tag{2}$$

Partial pressures (atm) of individual compounds were calculated for each sample using gas-phase concentrations and the ideal gas law. Natural logarithms of calculated partial pressures were plotted against
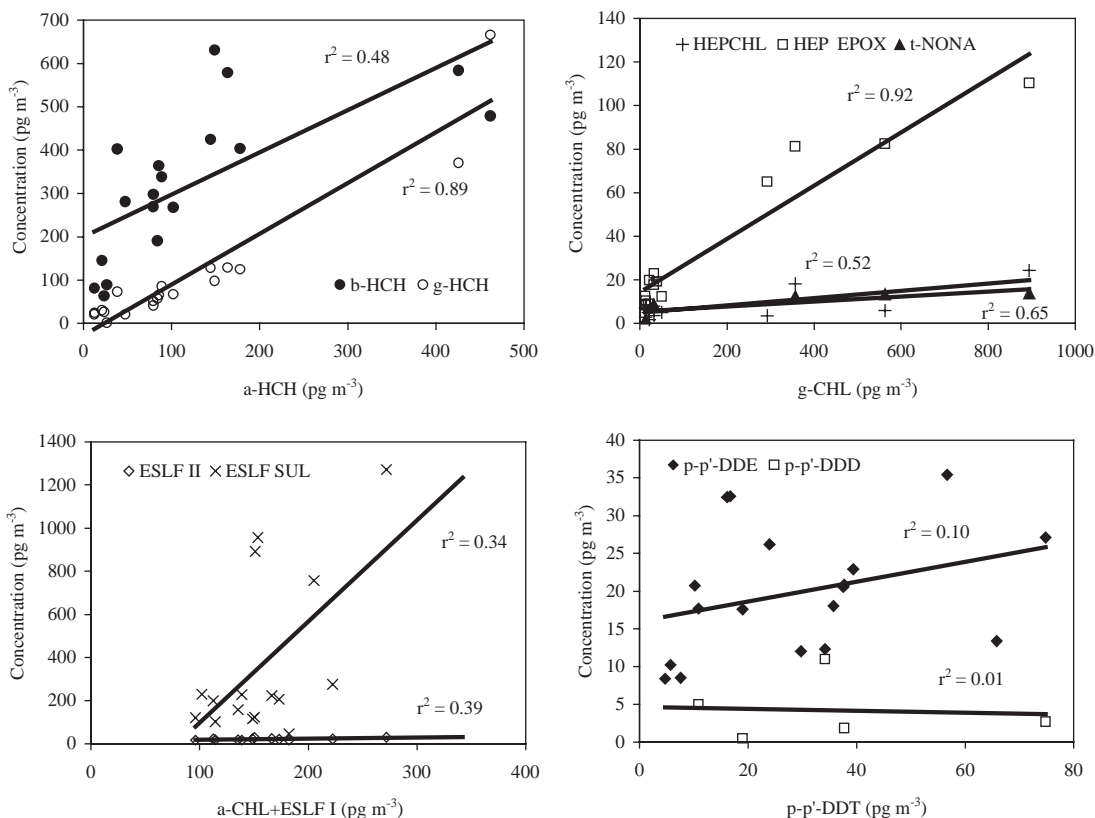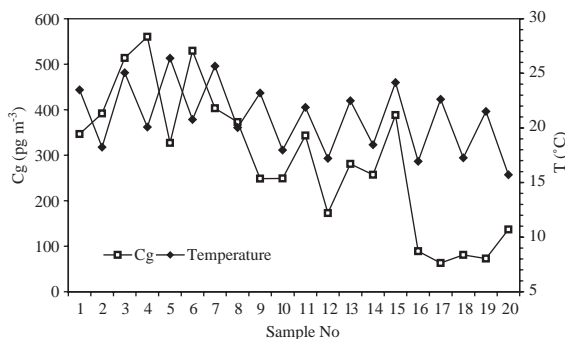
Fig. 1. Correlations between OCPs.

Fig. 2. Diurnal variation of β-HCH and temperature.

reciprocal mean temperature for each sampling period. The mean temperature was obtained by averaging the temperatures measured in 1 min intervals over the each sampling period and ranged from 15.7°C to 26.4°C during the sampling program.

For the OCPs included in this study, the temperature dependence of gas-phase concentrations was statistically significant only for β-HCH and endosulfan sulfate ($p < 0.1$) and was not statistically significant for other compounds. The temperature accounted for 0 (hepta-

chlor epoxide, endrin aldehyde, p,p′-dichlorodiphenyl-trichloroethane (p-p′-DDT)) to 21% (endosulfan sulfate) of the variability in gas-phase concentrations.

Inferences can be done using the slope (m) and coefficient of determination (r^2) with regard to the importance of temperature in controlling the gas-phase ambient concentrations of SOCs and the relative importance of other factors (Lee et al., 2000). Generally steep slopes and high r^2 values indicate that temperature-controlled air–surface cycling and short-term transport influences the ambient gas-phase concentrations (Hoff et al., 1998; Wania et al., 1998). Relatively shallow slopes and low r^2 values suggest that other factors (i.e., advection, ongoing sources, wet and dry deposition, atmospheric reactions) and long-range transport influence concentrations (Lee et al., 2000). The relatively shallow slopes and low r^2 values for some OCPs observed in this study suggest that long-range transport influenced their gas-phase concentrations (Hoff et al., 1998; Wania et al., 1998) or temperature dependency was affected by confounding factors (advection and proximity of the sources).

Temperature could not explain the majority of the variation in atmospheric gas-phase OCP concentrations. Wind speed and direction could be other parameters

affecting the gas-phase OCP concentrations. Examination of the meteorological parameters suggested that advection may be an important factor. During the sampling program the variation of temperature and wind speed was similar. Nighttime periods with lower temperatures corresponded to lower wind speeds while daytime periods with higher temperatures corresponded to more advective (higher wind speeds) conditions (Table 1, Fig. 3). Therefore, advection probably masked the temperature-dependent diurnal cycling of most OCPs.

The effect of wind speed and direction on gas-phase atmospheric concentrations of individual OCPs was investigated adding these parameters into Eq. (2) and using multiple linear regression analysis (Hillery et al., 1997):

$$\ln P = m_1(1/T) + m_2 U + m_3 \cos WD + b, \qquad (3)$$

where U is the wind speed (m s^{-1}), WD is the predominant wind direction during the sampling period (deg), m_1, m_2, m_3, and b are the regression parameters. The results of multiple linear regression analysis are presented in Table 4. Temperature, wind speed, and wind direction together explained the 2% (aldrin) to 72% (endosulfan II) of the variability in gas-phase concentrations. The correlation was statistically significant for 10 OCPs ($p < 0.05$ or $p < 0.1$). For all OCPs except chlorpyrifos m_1 was negative indicating that their concentrations increased with temperature. m_1 was statistically significant for α,β,γ-HCHs, heptachlor epoxide, γ-chlordane, endosulfan sulfate, and methoxychlor. Their slopes were relatively steep and ranged between -9703 and $-21,411$ suggesting that their ambient concentrations were influenced by short-range or regional transport. The relatively shallow slopes obtained for other OCPs suggest that their concentrations affected by long-range transport. However, the positive value obtained for chlorpyrifos and shallow slopes for endosulfan I and II can be attributed to the influence of their ongoing sources. For most of the
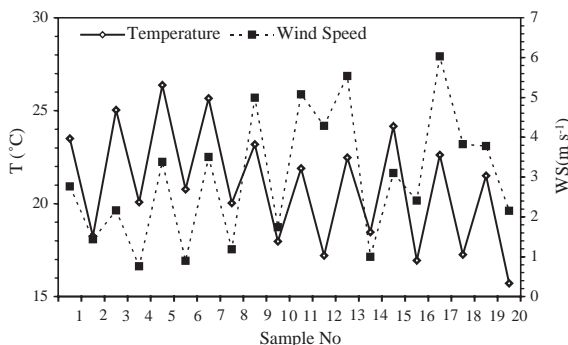
Table 4
Summary of regression parameters for Eq. (3)

	m_1	m_2	m_3	r^2	n
α-HCH	−10,630[b]	−0.29[a]	0.63[b]	0.52[a]	19
β-HCH	−9703[a]	−0.22[a]	0.45[a]	0.70[a]	20
γ-HCH	−13,697[a]	−0.40[a]	−0.06	0.47[a]	19
HEPCHL	−4184	−0.15	0.03	0.15	19
CHLPYR	1584	−0.26[b]	0.34	0.34[b]	20
ALD	−1082	0.01	−0.02	0.02	12
HEP EPOX	−13,190[b]	−0.45[a]	−1.04[a]	0.46[b]	14
γ-CHL	−19,829[a]	−0.46[a]	−2.23[a]	0.65[a]	15
α-CHL + ESLF I	−2658	−0.07	0.00	0.16	19
p-p′-DDE	−324	0.01	0.34	0.17	20
ESLF II	−4417	−0.06	0.35[a]	0.72[a]	12
END AL	−5293	−0.21[a]	−0.59[a]	0.42[b]	17
ESLF SUL	−21,411[a]	−0.33[a]	0.45	0.60[a]	16
p-p′-DDT	−549	−0.10	0.02	0.06	18
MEOCL	−12,839[a]	−0.30[a]	−0.31	0.31[b]	20

[a] $p < 0.05$.
[b] $p < 0.10$.

OCPs m_2 had also negative values and they were statistically significant for nine OCPs. This indicated that their gas-phase concentrations decreased as the wind speed increased and supported the hypothesis that advection masked the temperature-dependent diurnal cycling of most OCPs. The regression parameter related to wind direction (m_3) varied between negative and positive values and it was statistically significant for six OCPs (Table 4). Negative values for m_3 indicate that relatively higher gas-phase concentrations were observed when the wind was from southerly directions while positive values point northerly directions for high concentrations. Based on statistically significant m_3 values, north of the sampling site may be an important source sector for α,β-HCHs and endosulfan II while south may be an important source sector for heptachlor epoxide, γ-chlordane and endrin aldehyde. The lack of correlation for heptachlor, aldrin, p-p′-DDE, and p-p′-DDT with temperature, wind speed and direction suggests that their gas-phase concentrations were affected by long-range transport.

3.3. Gas/particle partitioning

Partitioning of SOCs between the gas and particulate phases is parameterized using the gas/particle partition coefficient, K_p (m^3 μg^{-1}) (Harner and Bidleman, 1998):

$$K_p = (C_p/C_{TSP})/C_g, \qquad (4)$$

where C_p and C_g are the SOC concentrations in the particulate and gas phases, respectively (pg m^{-3}), and C_{TSP} is the concentration of total suspended particles in the air (μg m^{-3}).

Fig. 3. Diurnal variation of temperature and wind speed.

The octanol–air partitioning coefficient (K_{OA}) can be used to predict K_p with the assumption of predominant distribution process is absorption (Harner and Bidleman, 1998). The relationship between K_p and K_{OA} is

$$K_p = \frac{f_{OM} MW_{OCT} \zeta_{OCT}}{\rho_{OCT} MW_{OM} \zeta_{OM} 10^{12}} K_{OA}, \qquad (5)$$

where f_{OM} is the fraction of OM phase on TSP, MW_{OCT} and MW_{OM} are the mean molecular weights of octanol and the OM phase (g mol^{-1}), respectively, ρ_{OCT} is the density of octanol (0.820 kg L^{-1}), ζ_{OCT} is the activity coefficient of the absorbing compound in octanol, ζ_{OM} is the activity coefficient of the compound in the OM phase. With the assumptions that ζ_{OCT}/ζ_{OM} and $MW_{OCT}/MW_{OM} = 1$, Eq. (5) can be written as:

$$\log K_p = \log K_{OA} + \log f_{OM} - 11.91. \qquad (6)$$

The K_p values defined in Eqs. (4) (experimental) and (6) (modeled) were calculated for OCPs that could be detected in both gas and particulate phases and for those experimentally determined K_{OA} values were available (α-HCH, β-HCH, γ-HCH, chlorpyrifos, endosulfan I, dieldrin, p-p$'$-DDE, and p-p$'$-DDT). Measured f_{OM}, C_{TSP}, C_g, C_p and K_{OA} values taken from previous studies used in the calculation of K_p. The influence of temperature (T, K) on K_{OA} is taken into account using the following equation with the regression parameters (A and B) given by Shoeib and Harner (2002):

$$\log K_{OA} = A + B/T. \qquad (7)$$

The parameters A and B were not available for chlorpyrifos. Therefore, for this compound the K_{OA} value was obtained as the ratio of octanol/water partition coefficient (K_{OW}) to dimensionless Henry's law constant (H') (McConnell et al., 1997). H' values as a function of temperature were calculated using the regression parameters given by McConnell et al. (1997).

Plots of $\log K_p$ vs. $\log K_{OA}$ have been used in field and laboratory studies to evaluate the gas–particle partitioning of SOCs in urban and rural particulate matter (Shoeib and Harner, 2002; Falconer and Harner, 2000). A good correlation between $\log K_p$ and $\log K_{OA}$ and a slope near 1 indicates that octanol is a good surrogate for the partitioning of SOCs into aerosol OM (Falconer and Harner, 2000). Even though strong correlations were observed between $\log K_p$ and $\log K_{OA}$, some of the previously reported slope values were significantly different than 1. Slope values of 0.99, 0.74, and 0.65 for OCPs, PCBs, and polychlorinated naphthalenes, respectively, were reported previously (Shoeib and Harner, 2002; Falconer and Harner, 2000; Harner and Bidleman, 1998). Recently, Goss and Schwarzenbach (1998) questioned the necessity of a slope of 1 for

equilibrium partitioning when $\log K_p$ is plotted vs. $\log K_{OA}$. Based on the theoretical considerations and experimental data from the literature, they concluded that the slope might deviate significantly from 1 for equilibrium partitioning. Deviations from a unity slope further indicate that atmospheric particles have sorbing properties different from that of octanol. Despite that these differences, $\log K_{OA}$ works as a useful predictor for a given class of compounds (e.g., PCBs) as indicated by the good linearity of the regression lines (Goss and Schwarzenbach, 1998).

Fig. 4 is a plot of experimental $\log K_p$ values vs. $\log K_{OA}$ values. For the plot containing all data, the correlation between $\log K_p$ and $\log K_{OA}$ was statistically significant ($p < 0.01$). However, the slope of the regression line (0.46) was < 1. Slope of the regression line may be variable for each sampling event. Therefore, focusing on sorption to particles collected over a single sampling period can reduce fluctuations in atmospheric conditions and particle characteristics. For 10 sampling periods having six or more experimentally determined K_p values, slope of the regression line varied between 0.26 and 0.82 ($r^2 = 0.49-0.91$). Plots for selected sampling events are presented in Fig. 4. The variation of slope values suggests that atmospheric particles for different samples have different sorbing properties. Good correlation between $\log K_p$ and $\log K_{OA}$ suggests that K_{OA} is a useful predictor for the partitioning of OCPs into aerosol OM.

Fig. 5 compares the experimentally determined and predicted $\log K_p$ values using Eq. (6). The correlation between experimental and modeled $\log K_p$ values was statistically significant ($p < 0.01$) and the slope of the regression line (0.94) was close to 1 indicating that the overall agreement between experimental and predicted values was very good.

Fig. 6 shows the experimental particulate percentages and those predicted by the absorption model. Predicted particulate percentages were calculated using the fraction (ϕ) of the compound in the particle phase (Harner and Bidleman, 1998):

$$\phi = (K_p C_{TSP})/(1 + K_p C_{TSP}), \qquad (8)$$

where K_p (m^3 µg^{-1}) is the gas/particle partition coefficient and C_{TSP} is the concentration of total suspended particles in the air (µg m^{-3}). Prediction of absorption model was excellent for β-HCH, endosulfan I, and p-p$'$-DDT. However, the model underpredicted the particulate percentages for α,γ-HCHs, chlorpyrifos, and dieldrin, and overpredicted the particulate percentage for p-p$'$-DDE. The absorption model has been generally used assuming that the atmospheric particles contain 10–20% OM ($f_{OM} = 0.1-0.2$) (Shoeib and Harner, 2002; Falconer and Harner, 2000; Harner and Bidleman, 1998). Fig. 6 also shows the predicted particulate
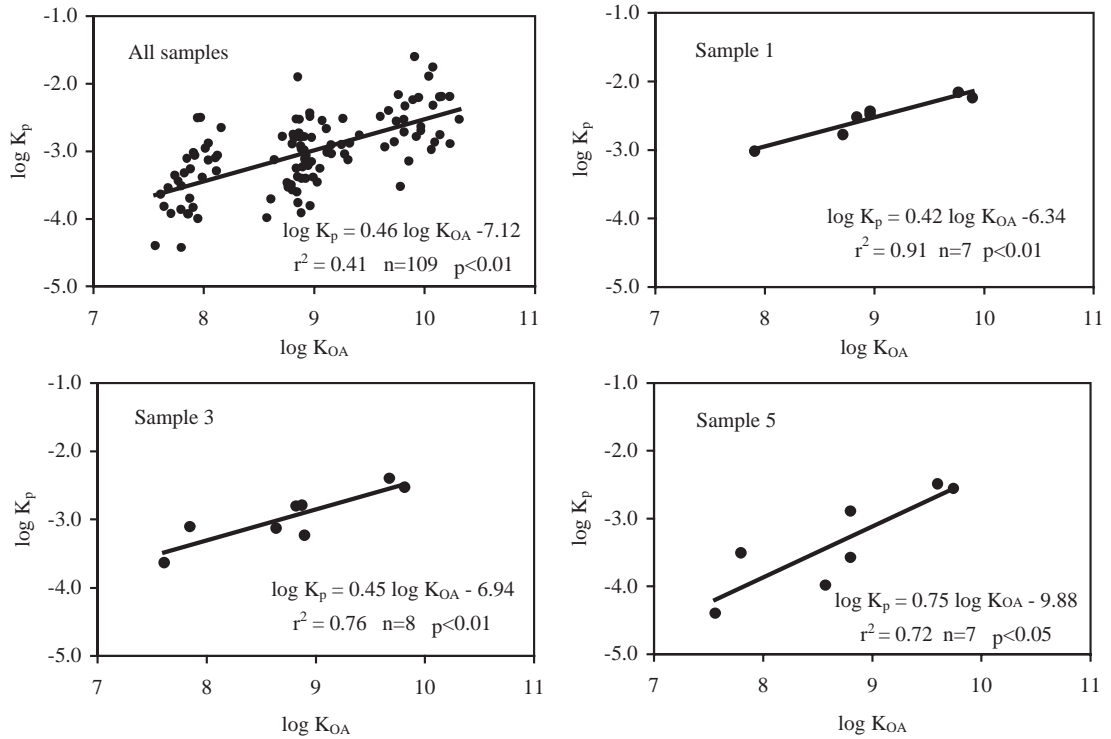
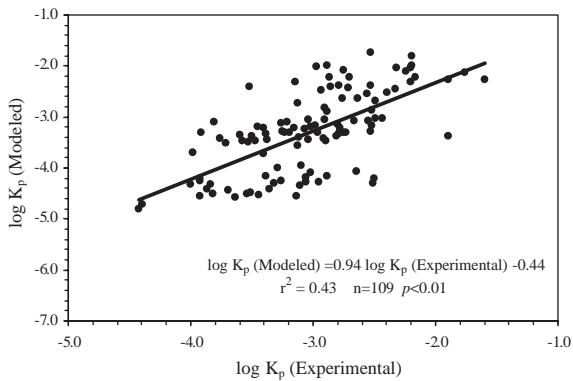Fig. 4. Plot of log K_p vs. octanol–air partition coefficients (log K_{OA}).

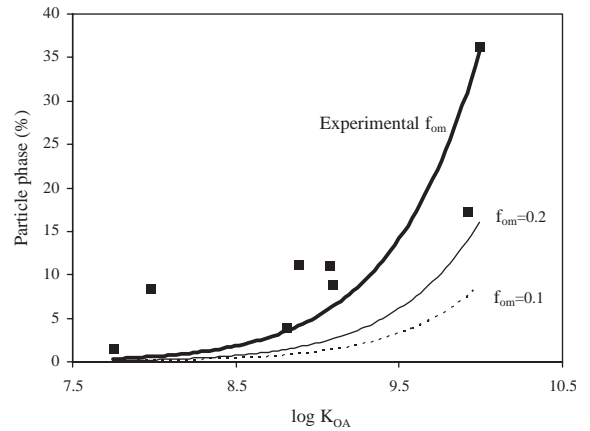Fig. 5. Comparison of experimental and estimated log K_p values.

Fig. 6. Comparison of experimental (filled squares) and modeled (solid and dashed lines) particulate-phase percentages.

percentages assuming 10% and 20% OM. When these assumptions were used, the model substantially under-predicted the experimental particulate percentages indicating the importance of using measured f_{OM} values. The measured average f_{OM} values (0.53) in this study were higher than typically expected. These high f_{OM} values can be attributed to the high pollen content of the air during the sampling period that was obvious from the yellow deposited material on the sampling platform and the filters.

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