

Evaluation of atmospheric concentrations of dl-PCBs comparing to PCDD/F compounds in Istanbul, Turkey

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ABSTRACT

In this study, the seasonal variation of atmospheric concentrations of PCDD/F and dl-PCB and the effect of meteorological factors on concentration were investigated. Ambient air samples were collected monthly between May 2011 and October 2013 by using high volume samplers. Based on these samples, average PCDD/F and dl-PCB concentrations were obtained as 1590 fg/m³ and 4855 fg/m³ respectively. PCDD/F congeners did show seasonal variations. 58% share in total PCDD/Fs belongs to winter season while 4% to summer season. No significant seasonal change has been observed for dl-PCBs. 92% (1397 fg/m³) of PCDD/Fs were detected in particulate phase while 20% (926 fg/m³) of dl-PCBs were found in particulate phase. Strong negative correlations were obtained between all homolog groups and T, UV, SR. Correlation between five-chlorinated dl-PCBs, the most abandoned homolog group, with T, UV and SR generated positive meaningful correlation. No meaningful correlations were observed with other parameters. Correlations with particle phase were found to be more meaningful compared to gas phase for both PCDD/F_s and dl-PCBs.

Keywords: Polychlorinated dibenzo-*p*-dioxin/furan, dioxin-like PCB, ambient air, active air sampler, meteorological parameters,

1. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are the two most important groups of persistent organic pollutants (POPs) which are regulated in Stockholm Convention (Stockholm Convention, 2009). Chemical properties and toxicity values of 12 compounds among PCB group (PCB77, PCB81, PCB105, PCB114, PCB118, PCB123, PCB126, PCB156, PCB157, PCB167, PCB169, PCB189) are similar to PCDD/Fs so that they are called dioxin-like PCBs (dl-PCBs). At high doses, they show similar adverse health effects on humans similar to like PCDD/Fs (Pereira, 2004). Their vapour pressures are low and, they have low octanol-air (K_{oa}) and high octanol-water (K_{ow}) coefficients (Mackay *et al.*, 2006). These properties affect many behavior and trends of PCBs such as gas/particle partitioning, transportation and abatement in the atmosphere, resistance against biological and chemical decompositions reactions, accumulations in the environmental and biological media. While PCDD/F compounds exist dominantly in particulate phase in the atmosphere, dl-PCBs exist in gaseous phase (Wethington and Hornbuckle 2005; Gambaro *et al.*, 2004). Low chlorinated PCBs tend to exist in gaseous phase because of their higher vapour pressures while higher chlorinated ones tend to exist

in particle phase because of their lower vapour pressures (Kouimtzis *et al.*, 2002; Mandalakis *et al.*, 2002; Eitzer and Hites, 1989; Oh *et al.*, 2001; Chao *et al.*, 2004).

Gas phase PCBs are generally removed from the atmosphere by hydroxyl radicals or photochemical reactions (Atkinson, 1987; Kwok *et al.*, 1994; Brubaker and Hites, 1997), while those in particle phase are removed by wet/dry deposition mechanisms (Lohmann and Jones, 1998).

Studies show that these chemical have been emitted into the environment mainly from combustion sources and PCB containing commercial products (Brown *et al.*, 1995; Simcik *et al.*, 1997). PCB-like semi volatile organic compounds, after emitted from sources, they are transported by atmospheric transportation mechanisms and accumulate in the environmental media such as soil, water bodies and sediments. They may desorb from those sinks and re-enter into the atmosphere because of their semi-volatility.

The most important sources of PCDD/Fs are combustion processes (waste combustion, open burning, domestic heating, internal combustion engines), chemical production processes, metal smelting, iron-steel smelting (Tuppurainen *et al.*, 1998; McKay, 2002; Buekens and Huang, 1998; Ni *et al.*, 2009; Li *et al.*, 2016; Liu *et al.*, 2013a). While PCDD/Fs are formed as unwanted by-products from thermal processes, the case is different for PCBs. The emissions of PCBs are generally originate from i) the storage of PCB containing wastes (electric transformers and capacitors, printer inks, resin products, hydraulic systems, vacuum pumps) and ii) thermal disposal of PCB containing wastes (Aries *et al.*, 2004; Choi *et al.*, 2008). Besides, recent studies show that thermal formation mechanisms of PCBs are somewhat similar to those of PCDD/Fs (Abad *et al.*, 2006; Weber *et al.*, 2001; Brubaker and Hites, 1998). Considering the fact that PCBs are precursors of the formations of PCDD/Fs, the sources causing the formation of PCDD/Fs will also be responsible for the formation of PCBs. For example, iron sintering (Liu *et al.*, 2013b) and metal production processes cause the formation and emission of PCDD/Fs as well as dl-PCBs (Ba *et al.*, 2009 a,b). Studies have shown that atmospheric concentrations of PCDD/Fs and dl-PCBs at industrial (Li *et al.*, 2012; Die *et al.*, 2015) and urban (Deng *et al.*, 2011; Li *et al.*, 2014) areas are higher than those at rural areas (Thuan *et al.*, 2013; Shih *et al.*, 2006).

Atmospheric concentrations of PCDD/Fs and dl-PCBs are greatly affected by diversity and intensity of sources, mechanisms of wet/dry depositions and meteorological parameters (pressure, mixing height, temperature, precipitation, UV-solar radiation, humidity).

In this study, atmospheric concentrations and behaviors of PCDD/ F and dl-PCB compounds were investigated. Their seasonal and spatial variations, gas/particle distributions were compared and their similarities and differences were determined. In addition, the relationship between meteorological parameters and congeners was investigated by statistical analysis.

2. EXPERIMENTAL/METHODOLOGY

2.1 Study Area

Ambient air samples were collected at three sampling stations in Istanbul as shown in Fig. 1. Site 1 may be characterized by industrial+urban pollutant sources where there are many small scale industrial settlements (industrial zones) and considerable city traffic load especially from the intercity bus station which is the biggest of Turkey. Site 2 may be

characterized by only urban pollutant sources where the traffic (motor vehicles) is the dominant pollution source. Site 3 may be considered as rural area which is far from city center and having no industrial activity in the immediate vicinity. However, medical and incineration plant are present at 8 km NE of the sampling station (Fig.1, Site 4)

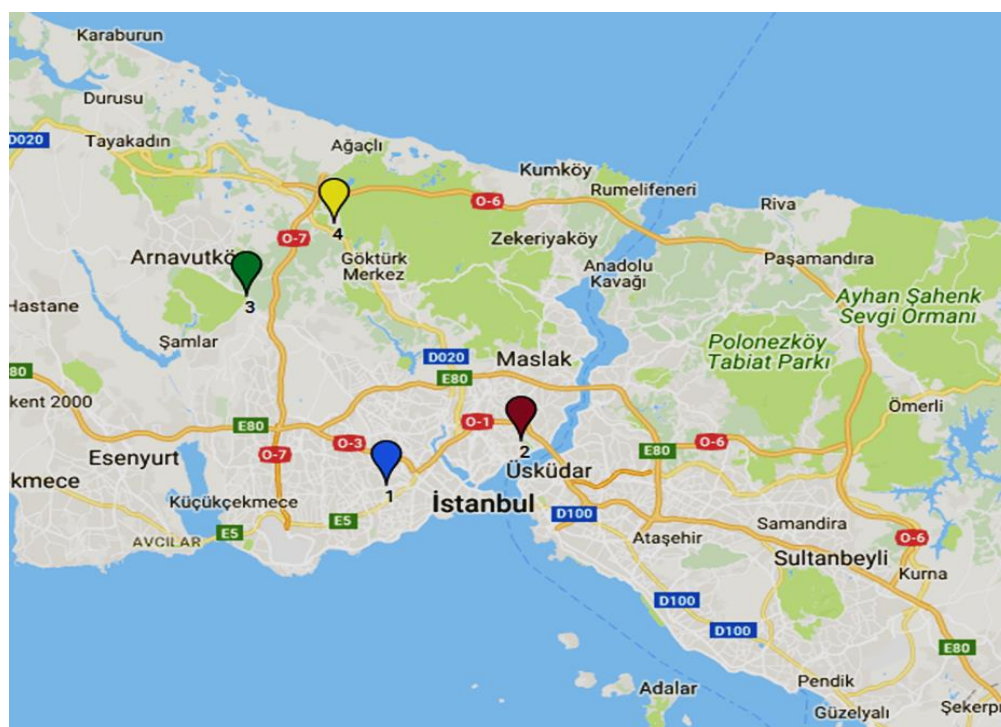


Figure. 1. Characteristics of sampling locations

2.2 Sampling and analysis

Ambient air samples were collected monthly between May 2011 and May 2013 by using high volume samplers (TCR Techora-Echo). High volume air samplers were operated at $0.225 \text{ m}^3 \text{ min}^{-1}$ flow rate for the period of 5-7 days at each sampling station. Total volumes of air samples were between $746\text{-}2242 \text{ m}^3$. Quartz fiber (QF) and polyurethane foam (PUF) filters were used for the sampling of gas and particle phases. Meteorological parameters were also measured and recorded by wireless weather stations (Davis Vantage Pro 2) at each sampling station (Table 1). Sampling and analyses were conducted in accordance with the reference method EPA TO-9A (US EPA, 1999). Detailed information about analytical process was reported in the literature (Gunes *et al.*, 2014; Gunes and Saral., 2014; Saral *et al.*, 2015).

Table 1. Meteorological parameters related to sampling campaign

	T (C°)	UV (index)	SR (W/m ²)	WV (m/s)	RH (%)	P (mb)	R (mm)	Mixing Height (m)	TSP (µg/m ³)
Spring	15,4 (10,7-23)	1,6 (0,9-2,1)	213 (111-257)	3 (2,0-3,6)	67 (58-80)	1015 (1010-1025)	12 (0,1-41)	374	88 (68-135)
Summer	24 (21-26)	2,1 (1,8-2,6)	252 (229-304)	3,7 (2,7-5,4)	77 (71-84)	1010 (1005-1012)	4,7 (0,1-20,1)	530	50 (36-60)
Autumn	15 (7-21)	0,9 (0,4-1,1)	116 (53-175)	3 (2,3-4,3)	79 (70-86)	1017 (1012-1018)	10 (1,8-32)	639	65 (43-117)
Winter	6,8 (3-10)	0,5 (0,2-0,8)	68 (37-114)	4 (3,1-5,1)	79 (74-83)	1016 (1011-1020)	14 (11-18)	541	60 (33-114)

T: Temperature, UV: Ultra Violet, SR: Solar Radiation, WV: Wind Velocity, RH: Humidity, P: Pressure, R: Rain, TSP: Total Suspended Particle

3. RESULTS AND DISCUSSION

Average PCDD/F concentration was obtained as 1590 fg/m³ (ranging between 893 and 2700 fg/m³) having median value of 1178 fg/m³ and standard deviation (SD) of ±972. Corresponding average international toxicity equivalent quantity (I-TEQ) value was calculated as 112 fg/m³ I-TEQ with the median of 85 fg/m³ and SD of ±54. Average dl-PCB concentration was obtained as 4855 fg/m³ (ranging between 3529 and 5773 fg/m³) with the median of 5263, SD of ±1176. The average of I-TEQ values of dl-PCBs were calculated as 11 fg/m³ with a range between 7 to 15 fg/m³. Contribution of dl-PCBs to total TEQ was calculated as 9% (Fig.2).

At this time there is no ambient air concentration standard for PCDD/F in Turkey. The average value obtained in this study (112 fg/m³ I-TEQ) was compared to the standard given for Japan (Japan's Environmental Quality Standards, 1996) which is 600 fg I-TEQ/m³ and found to be fairly lower than an ambient standard. Average I-TEQ value was found within the range (100-400 fg I-TEQ/m³) reported for urban areas by Lohmann and Jones (2000).

Studies in the literature reported dl-PCB concentrations of 6 fg I-TEQ/m³ for industrial regions and 2 fg I-TEQ/m³ for residential areas in Anshan city, China (Li *et al.*, 2010). Another study in China reported winter and summer PCDD/F concentrations of 83.4 and 63.4 fg TEQ/m³, respectively (Tian *et al.*, 2015). Li *et al.*, (2011) reported PCDD/F concentration of 74 fg TEQ/m³ for industrial regions. Martinez *et al.*, (2010) evaluated the transportation by wind. They determined dl-PCB concentration of 23 fg I-TEQ/m³ when the wind blows from industrial region and 12 fg I-TEQ/m³ when the wind blows from residential region. Another study recorded 26.2 pg/m³ of dl-PCB concentration in the vicinity of an iron-steel plant and 3.3 pg/m³ in urban area (Choi *et al.*, 2008).

3.1. Spatial distribution of PCDD/F and dl-PCB concentrations

Order of magnitudes of the concentrations may be given as site 1 (urban-industrial) > site 2 (urban) > site 3 (rural) which was expected when the distribution of sources is considered as explained in Section 2.1 (Fig. 2). Motor vehicle traffic is thought to be the most important source of PCDD/Fs and dl-PCBs as site 1 and site 2 measurements indicated. Mass concentrations for PCDD/Fs measured at site 1 are compatible with the study conducted in Taiwan where measurements (3,5-5,7 pg m⁻³) were taken in the vicinity of a waste incineration plant (Chao *et al.*, 2004) and the study conducted in Shanghai in winter season (2.3 pg m⁻³) at an industrial area (Die *et al.*, 2015). Respective records of dl-PCBs at site 1 and site 2 are 5.77 and 5.26 pg m⁻³ which are compatible with the value of 5.4 pg m⁻³ in Toronto (Helm and Bidleman, 2003) and with the value of 5.4 pg m⁻³ in Netherland (Lopez Garcia *et al.*, 1996) both of which studies were conducted in urban sites away from city centers.

Site 3 is far away from the city center being at the edge of forest area and surrounded by villages. There is a highway near this station but the traffic load is light. 3.54 pg/m³ average concentration of dl-PCBs at this station is compatible with the study (3,3 pg m⁻³) conducted by Choi *et al.* (2008) for residential areas, but somewhat higher than the result of the study (1,2 pg/m³) conducted in the USA at rural and remote areas (Cleverly *et al.*, 2007). Average I-TEQ concentrations of dl-PCBs at sites 1 and 2 were found to be 15 and

10 fg I-TEQ/m³ respectively, which are somewhat greater than the study conducted at industrial area (steel plant) (6 fg I-TEQ/m³) by Li *et al.* (2010).

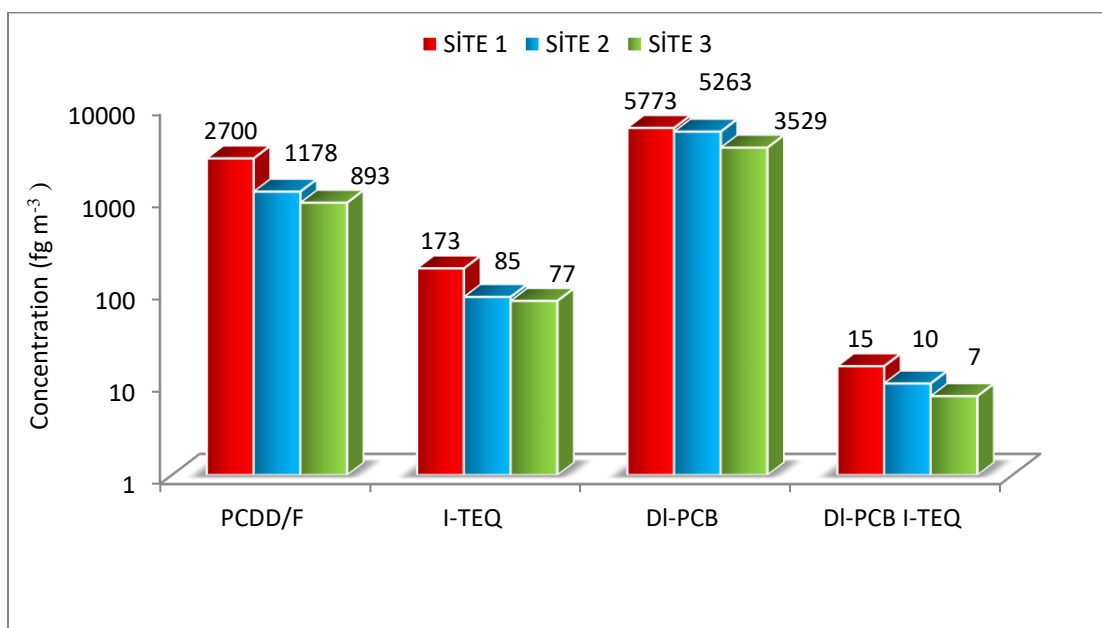


Figure 2. Spatial variation of PCDD/Fs and dl-PCBs

3.2. Congener profiles of PCDD/F and dl-PCB compounds

Statistical evaluations for PCDD/Fs and dl-PCBs were given in Table 2. The ratio of PCDD congeners is 38% and the rest (62%) is that of PCDFs in total PCDD/Fs concentration. This distribution is compatible with the literature stating that the congeners profile of atmospheric PCDD/Fs are dominantly characterized by PCDF congeners (Oh *et al.*, 2002; Lee *et al.*, 2007). The congeners contributing in highest ratios to total PCDD/F concentration are OCDD (22%) and 1,2,3,4,6,7,8-HpCDF (15%), 1,2,3,4,6,7,8-HpCDD (%11), OCDF (%10). Those dominant among PCDDs are OCDD (55%) and 1,2,3,4,6,7,8-HpCDD (29%). Primary sources of these congeners are motor vehicles with unleaded gasoline and diesel trucks (Cleverly *et al.*, 1997). The congener OCDD mainly originates from combustion most important sources of which are solid waste incineration, unleaded gasoline and diesel truck emissions, wood and heavy oil combustion processes (Cleverly *et al.*, 1997. Contribution of 2,3,7,8-TCDD is 0,7% being the most toxic one. Among PCDF congeners, 1,2,3,4,6,7,8-HpCDF contributes 25%, 1,2,3,4,7,8,9-HpCDF and OCDF contribute 16% to the total as the highest ones while 1,2,3,7,8,9-HxCDF shares 1% being the least contributing congener. Unlike 2,3,7,8-TCDD, 2,3,7,8-TCDF contributes with 5,6% share in total PCDF concentration. OCDD, HpCDF, HpCDD were determined as dominant congeners in studies conducted by Abad *et al.*(2007), Ariztizabal *et al.*(2011), OCDD, HpCDD, OCDF were reported as dominant congeners for rainy and dry season in another study conducted in Taiwan (Trinh *et al.*, 2018). OCDD, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD, OCDF were determined as dominant congeners at all sampling points. Only 2,3,4,7,8,9-HpCDF demonstrated 28% contribution in winter season at Site 1. This fact leads us to think that different fuels other than coal might be used for heating purpose in winter at the residential areas around site 1. Having this congener with about 2% contribution in other seasons at all sampling sites validates this thought.

Dominant PCB congeners among dl-PCBs were detected to be two of 5-chlorinated ones as PCB118 with 51% contribution and PCB105 with 20%, and one of 4-chlorinated ones as PCB77 with 10% contribution. Similar congener profiles were reported in the literature (Choi *et al.*, 2008; Cleverly *et al.*, 2007, Trinh *et al.*, 2018). The congener with the least contribution was a 6-chlorinated PCB169 with 1,2%. The highest percentage in total I-TEQ concentration is 87% which belongs to PCB126 (5-Cl), followed by PCB169 (6-Cl) with 5%, PCB77 (4-Cl) with 2% and PCB118 (5-Cl) with 2%. PCB118, PCB105 and PCB77 again shared the highest contributions when considering sampling sites and seasons individually. Martinez *et al.* (2010) reported PCB118, PCB105 and PCB77 as the dominant congeners at urban and industrial (steelwork) areas. Similar congener profile was also obtained in a survey conducted to search the effect of Asian dusts on ambient air PCB concentrations (Chi *et al.*, 2008). Other studies did report almost the same congener profiles of dl-PCBs in the ambient air (Helm and Bidleman, 2005; Cleverly *et al.*, 2007; Choi *et al.*, 2008; Castro-Jiménez *et al.*, 2008). Again, PCB118, PCB105 and PCB77 shared respective contributions of 50%, 20% and 15% in Eastern Asian countries (Trinh and Chang, 2018).

Table 2. Statistical coefficients related to PCDD/F and PCB compounds

Congeners (fg m ⁻³)	SITE 1						SITE 2						SITE 3					
	N	Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max		
2,3,7,8-TCDD	28	14	12	12	1,6	34	8	6	7	2	24	4	3	3	2	12		
1,2,3,7,8-PcDD	28	36	26	32	2	115	17	12	19	3	75	10	7	10	2	40		
1,2,3,4,7,8-HxCDD	28	25	22	18	4,54	69	14	11	12	3	52	11	9	7	3	24		
1,2,3,6,7,8-HxCDD	28	38	28	36	2,4	138	22	16	22	4	91	15	11	13	2	46		
1,2,3,7,8,9-HxCDD	28	32	16	31	2,4	115	19	12	22	4	91	15	10	15	2	57		
1,2,3,4,6,7,8,-HpCDD	28	278	136	286	12,3	1033	158	87	186	6	839	98	47	106	8	363		
OCDD	28	488	213	524	38	1721	348	151	443	12	1957	161	87	179	8	655		
PCDD		910	455	938	63	3225	587	295	710	34	3128	315	174	332	27	1197		
2,3,7,8-TCDF	28	89	57	93	5	339	40	27	49	3	217	37	17	54	4	264		
1,2,3,7,8-PeCDF	28	92	47	106	4	427	42	25	54	2	231	34	21	40	3	162		
2,3,4,7,8-PeCDF	28	121	63	143	3	567	54	34	68	3	313	40	21	46	4	192		
1,2,3,4,7,8-HxCDF	28	131	72	146	7	631	56	34	65	6	287	52	34	47	4	186		
1,2,3,6,7,8-HxCDF	28	146	76	168	8	688	63	34	79	4	356	51	30	50	4	182		
1,2,3,7,8,9-HxCDF	28	15	11	11	5	44	8	6	5	1	17	7	6	3	4	14		
2,3,4,6,7,8-HxCDF	28	124	70	136	6	574	56	41	58	5	252	55	36	52	7	194		
1,2,3,4,6,7,8,-HpCDF	28	404	187	503	35	2410	148	88	192	4	908	161	107	149	19	589		
1,2,3,4,7,8,9,-HpCDF	28	422	44	1848	4	9471	25	16	29	1	133	27	26	17	5	77		
OCDF	28	245	161	290	15	1377	100	69	133	8	576	115	69	131	12	625		
PCDF		1789					591					578						
PCDD/F		2699					1178					893						

Congeners (fg m ⁻³)	SITE 1						SITE 2						SITE 3					
	N	Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max		
PCB 77	28	76	624	487	242	2542	494	448	239	237	1187	340	279	256	0,13	1171		
PCB 81	28	95	89	55	15	201	46	48	19	12	80	56	47	61	2,6	233		
PCB 126	28	131	106	118	17	412	88	68	90	4,7	350	55	39	43	6	148		
PCB 169	28	77	71	40	14	136	61	45	46	28	152	38	31	34	3,1	85		
PCB 105	28	1225	1140	459	383	2063	1040	1022	290	649	1635	727	767	263	76	1471		
PCB 114	28	121	107	69	46	305	87	61	56	40	278	66	64	31	6,6	145		
PCB 118	28	3314	2923	1216	1641	5693	2770	2581	939	1335	4564	1705	1627	712	174	3478		
PCB 123	28	82	79	39	28	166	67	62	37	22	160	51	48	31	4,7	121		
PCB 156	28	318	325	138	119	669	325	286	183	123	1072	217	191	118	25	479		
PCB 157	28	87	80	45	26	171	72	63	35	32	182	57	40	36	8	118		
PCB 167	28	152	157	59	63	302	144	130	71	53	337	98	97	53	7,56	179		
PCB 189	28	95	101	51	17	202	69	47	53	13	163	119	51	231	2,71	901		
Total DI-PCB		5773					5263					3529						

N: Sample Number , SD: Standard Deviation

3.3. Comparison of gas/particle partitioning of PCDD/F and dl-PCB compounds

92% (1397 fg/m³) of PCDD/Fs were detected in particulate phase and the rest 8% (129 fg/m³) in gas phase, while 80% (3780 fg/m³) of dl-PCBs were found in gas phase and the rest 20% (926 fg/m³) in particulate phase. Similar results were reported in the literature (Lohmann and Jones, 1998; Yeo *et al.*, 2003). Particulate phase percentage of PCDD/Fs is found to be greater in urban site (94%) compared to rural area (84%). Similar comparison was also reported by Chi *et al.*, (2008) where 65% and 77% percentages were recorded for PCDD/Fs at rural and urban areas, respectively. Similar trend was also detected for dl-PCBs in particulate phase as 36% at urban and 20% at rural areas. For both PCDD/Fs and dl-PCBs, particulate phase share increases as the number of chlorine increases. For example, particulate phase shares of TCDD (4-Cl), 1,2,3,4,6,7,8-HPCDD (7-Cl) and OCDD (8-Cl) were recorded to be 0,004, 0,12 and 0,23, respectively. Particulate phase fraction of PCB77 was 0,1 while that of PCB118 was 0,5. On the other hand, since vapour pressures of PCDDs are lower than PCDFs, particulate phase fraction (96%) of PCDDs is greater than that (89%) of PCDFs. This result is compatible with the result reported by Li *et al.*, (2008).

Annual mean Total Suspended Particle (TSP) concentration was determined as 67 µg/m³. Total Suspended Particulate concentrations at site 1, 2 and 3 were measured to be 164, 125 and 78 µg/m³, respectively. Seasonal variation of TSP was observed as spring: 87 µg/m³, summer: 59 µg/m³, autumn: 65 µg/m³ and winter: 66 µg/m³. Similar result was reported by Kuzu., (2016) on 3 February. Though TSP in spring was recorded to be relatively high, a weak correlation ($r: 0,4$; $r^2: 0,2$) was obtained between TSP and particulate phase PCDD/F concentration. This case may be explained by pollens released from trees causing higher TSP in the ambient air in spring. In summer, on the other hand, relatively stronger correlations were obtained between TSP and PCDD/Fs ($r: 0,88$; $r^2: 0,78$), and dl-PCBs ($r: 0,67$; $r^2: 0,45$). Especially at site 3, much higher summer correlations for both PCDD/Fs ($r: 0,92$; $r^2: 0,85$) and dl-PCBs ($r: 0,87$; $r^2: 0,76$) were obtained.

In winter, in which combustion for residential heating is dominant, correlations between TSP and PCDD/Fs was as ($r: 0,8$; $r^2: 0,64$) and dl-PCBs was as ($r: 0,72$; $r^2: 0,52$) which are relatively high. Emissions from combustion sources for heating which cause increase in the concentrations of both TSP and particle phase congeners support this result. Moreover Li *et al.*, (2010, 2016) state that biomass combustion cause increase in both TSP and particulate phase PCDD/F concentrations.

3.4. Seasonal variation of gas/particle partitioning of PCDD/F and dl-PCB

PCDD/F compounds did show seasonal variations. Considerable difference occurred between summer and winter. 58% share in total PCDD/Fs belongs to winter season being 4088 fg/m³ while 4% to summer as 276 fg/m³. The great difference between summer and winter figures may be explained by the dominant emissions from heating purpose combustion sources in winter. Similar results were reported by researchers in the literature (Li *et al.*, 2011; Huang *et al.*, 2011, Qin *et al.*, 2012; Chi *et al.* 2013). Unlike PCDD/Fs, dl-PCBs did not show significant seasonal variations. Concentrations in summer and winter were recorded as 4699 and 5225 fg/m³, respectively. Shares of summer and winter seasons in total concentration were calculated as 24% and 26%, respectively. Similarly, Fiedler *et al.* (1999) reported that the seasonal trend of dl-PCBs was the opposite of dioxins. P/G (particle/gas) ratio of PCDD/Fs for summer and winter were calculated as 2 and 25, respectively. Particulate and gas phase concentrations in summer were 190 and

107 fg/m³ while those in winter were 3930 and 158 fg/m³. Summer and winter shares of total gas phase concentration for PCDD/Fs were 20% and 30%, while those for particulate phase were 3% and 62%, respectively. Share of gas phase is higher in winter than in summer (Fig.3). This case could be explained by a source which becomes dominant in winter thought to be combustion for heating. This source also caused increase in particulate phase share in winter. Considering the sampling sites, the highest gas phase share for summer was detected at site 3 (22%) while the lowest was at site 2 (12%). As partially stated before, various ratios of P/G distribution of PCDD/Fs may be reasoned by the factors of temperature, physico-chemical properties of compounds (molecular weight, chlorine content, vapour pressure), sources and formation mechanisms.

G/P ratios of dl-PCBs were calculated as 6.4 for summer and 2.2 for winter. Gas phase concentrations in summer and winter were 4127 fg/m³ and 3724 fg/m³ while those for particulate phase were 647 fg/m³ and 1732 fg/m³ respectively (Fig.3). Seasonal variation of average gas phase concentrations was not significant with the figures of 26% and 24% for summer and winters shares. Unlike this study, other researchers (Chi *et al.*, 2008; Kim *et al.*, 2011; Min *et al.*, 2013.) have reported that more than 90% of dl-PCBs are in the gas phase in summer. Cetin *et al.* (2017) reported that the concentration of PCB (mostly non-dioxin-like PCB) increased with temperature in the study conducted in 4 different sampling periods in Istanbul. On the other hand, particulate phase shares in seasons showed somewhat remarkable change as 38% in winter and 14% in summer. Possible mechanisms and reasons stated in Section 3.4 are thought to be valid here. Moreover, summer time desorption of dl-PCBs was also stated by Halsall *et al.* (1995) and Tasdemir *et al.* (1997).

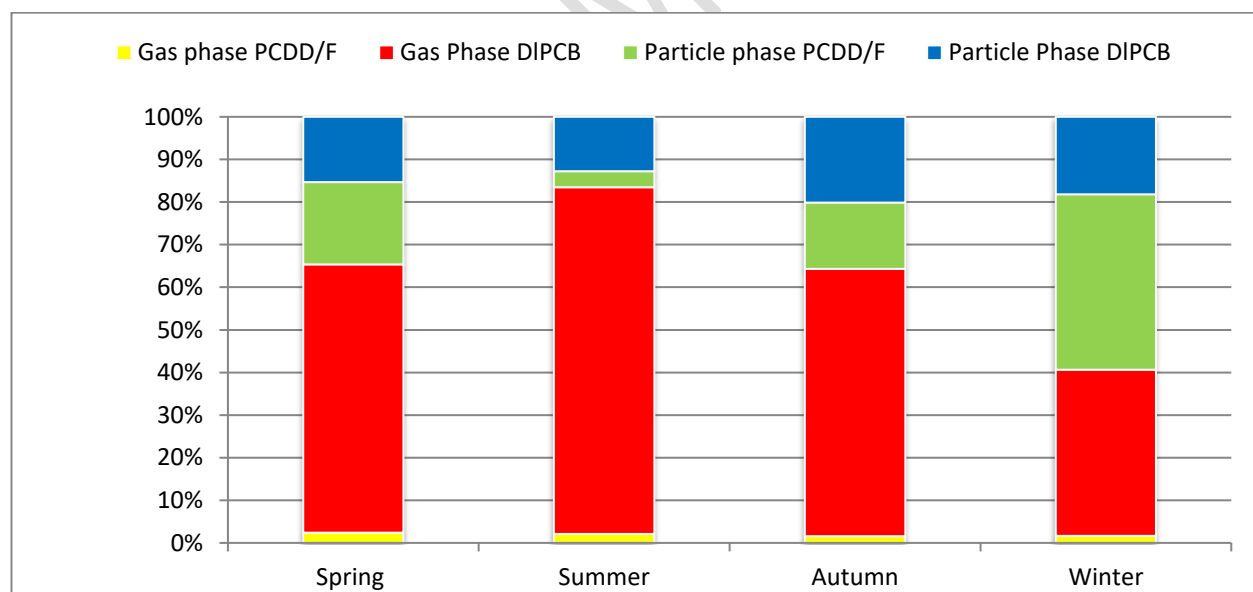


Figure 3. Seasonal variation of gas/particle concentrations of PCDD/F_s and dl-PCB_s

3.5. Relationships between meteorological parameters and congeners

In this Section, relationships between atmospheric concentrations of PCDD/F and dl-PCB compounds to meteorological parameters were evaluated. Table 3 summarizes the

seasonal averages (with max and min) of those parameters. Strong negative correlations were obtained between all homolog groups and T, UV, SR as given in Table 3.

Negative correlation between PCDD/Fs and T may be explained by increasing fossil fuel consumption with decreasing T in winter. High r^2 values support this idea. Another strong negative correlation between PCDD/Fs and UV-SR may be explained by decomposition of PCDD/Fs via photochemical reactions under high UV and solar radiation together with the lack of fossil fuel combustion in summer. No significant correlation was observed with WV, RH and rain while moderately positive correlation were obtained between concentration and pressure. High pressure causes descending air masses, decreased transportation and eventually accumulation of pollutants in the atmosphere.

There exist significant negative correlations between gas phase concentrations of 4-5 chlorinated PCDD/Fs and T, UV and SR, while no meaningful correlations were detected with higher chlorinated ones. Effect of combustion of fossil fuels in winter may be the cause of negative correlation between low chlorinated ones and temperature. Negative correlation with UV and SR may be explained by recessive effect of these parameters with dominant effect of emission sources in winter, while the opposite way in summer. As stated before, photochemical reactions caused by UV and SR might also cause decomposition of these congeners.

Lee *et al.*, (2008) also reported negative correlations between PCDD/Fs and UV – SR. In another lab scale study, a strong negative correlation was also reported between PCDD/Fs and ozone together with UV (Atkinson, 1997). No meaningful correlations were obtained between PCDD/Fs with wind velocity and rain both of which might be the main removal mechanisms from the atmosphere for those pollutants. Correlations with particle phase were found to be more meaningful compared to gas phase. Strong negative correlations were observed between all homologs with T, UV and SR while positive correlation with pressure. Multiple regression with T, UV and SR generated strong negative correlation (r : -0.78, r^2 : 0.62, p : 0,00) with all homologs.

Correlation between five-chlorinated dl-PCBs, the most abandoned homolog group, with T UV and SR generated positive meaningful correlation. No meaningful correlations were observed with other parameters. For gas phase concentrations, a positive correlation was detected between five-chlorinated group with T, UV and SR. The reason for this situation was explained in detail in the following section.

Negative correlation was detected between pressure and gas phase concentration with relatively smaller regression coefficient indicating that a variety of factors affect this relation. High pressures were generally recorded in winter months with low temperatures and this causes transport towards and increase in particulate phase concentration. A very weak negative correlation was observed between gas phase and rain which may indicate wet deposition and eventually decrease in gas phase concentration.

Negative correlations were observed between particulate phase concentrations of all homolog groups of dl-PCBs with T, UV and SR. Increasing chlorine content showed increase in correlations. Though wind velocity and humidity were reported to be effective on the atmospheric concentrations of dl-PCBs (Burgoyne and Hites, 1993; Hornbuckle and Eisenreich, 1996), no meaningful relations were observed (including rain, and PCDD/Fs also) between in this study. An exception may be stated as in the case of January 2012 in which sampling period a snow just after the rainfall considerably affected the atmospheric concentrations of these compounds. The average TSP concentration was determined as

69 $\mu\text{g}/\text{m}^3$ in December 2011 and 33 $\mu\text{g}/\text{m}^3$ in January 2012. Similarly, Chan and Kwok (2001) and Trinh et al. (2018) determined the TSP concentration lower in the rainy season than in the dry season. The PCDD/F particle phase concentration was determined to be 6658 fg/m^3 and 1680 fg/m^3 for December 2011 and January 2012, respectively. This can be explained by the removal of the particulate phase PCDD/F compounds from the atmosphere by rainfall and snowfall. Since PCDD/Fs existed in particulate phase by 90%, they have been removed in relatively much more fraction by wet deposition. Moreover, it was determined that the effect of rain and snow on dl-pcb concentration is negligible. The gas phase concentration of DI-PCBs decreased by 26% in January 2018. Similarly, Trinh et al. (2018) reported that TSP and PCDD/F concentrations were lower in the rainy season than dry season unlike dl-PCB compounds. Negative correlations were observed between PCDD/Fs and mixing height with the correlation and regression coefficients of (r: -0.66; r^2 : 0.53) in winter and (r: -0.68; r^2 : 0.51) in summer. It is well known that as mixing height increases concentration decreases.

3.6. The effect of meteorological parameters on atmospheric gas phase concentrations of PCDD/Fs and DI-PCBs

The variation of the atmospheric gas phase concentrations of the semi volatile organic compounds depending on the temperature was investigated by using Clausius-Clapeyron equation (Eq.(1)) by many researchers (Sofuoglu et al., 2004 ; Bozlaker et al., 2008; Kuzu et al., 2014). These researchers also investigated the effects of wind speed and wind direction on the gas phase concentration of these compounds by using Eq. (1) and multiple regression analysis.

$$\ln P = m(1/T) + b \quad (1)$$

Where, P partial pressures of congeners (atm), m slope, T average atmospheric temperature (K), b intercept. The effect of ultraviolet radiation (UV), wind speed and rainfall as well as temperature on gas phase concentration of PCDD/Fs and dl-PCBs was investigated by using Eq. (2) with the multiple linear regression analysis in this study and the results are shown in Table 4.

$$\ln P = m_1 (1/T) + m_2 UV + m_3 WR + m_4 R + b \quad (2)$$

Where, P partial pressures of congeners (atm), T average atmospheric temperature (K), UV ultraviolet radiation (index), WR wind rate (m/s), R rainfall (mm), m_1 , m_2 , m_3 , m_4 and b regression parameters. Since negative slope values were determined for all homologous groups of dl-PCBs it is thought that the gas phase concentrations increase with increasing temperature.

Generally, shallow slope values and low regression coefficients were determined for all homologous groups. Shallow slope and low r^2 values are explained by continuous sources, advection, wet/dry deposition, atmospheric reactions and long-distance transport of atmospheric air mass (Sofuoglu et al., 2004). According to Eq. (2), shallow and statistically insignificant m_1 values were determined for dl-PCBs. Shallow, negative slope values were determined for 4,5 and 7 Cl-PCBs. For this reason, it is considered that the atmospheric gas phase concentrations of dl-PCBs may be affected by long-range transport. Another reason may be a decrease in particulate matter concentration as temperature increases during the summer. Thus, PCBs may tend to be in the gas phase during the summer. A medical waste incineration plant located at a certain distance from the sampling points (20 km from sampling points 1 and 2 and 8 km from sampling point 3)

can be the reason for long range transport. This situation is supported by the dominance of low-chlorinated PCBs in incineration plants (Jansson *et al.*, 2011). In another study conducted in Istanbul, it was reported that non dl-PCB concentration increased with temperature and high negative slope values were explained by desorption from terrestrial areas (Kuzu *et al.*, 2014). Similarly, Cetin *et al.* (2017) reported that the PCB concentration increased with temperature. Statistically significant results were obtained for the 4, 5 and 7 chlorinated homologues of PCDD/F compounds. As the positive shallow m_1 values for the 4,5 Cl-PCDD/F homologs are determined, it can be said that these homologs are affected by the continuous sources. Negative and shallow slope values for 6-7Cl-PCDD/F can be explained by long-range transport, advection, wet/dry deposition and atmospheric reactions. According to the results of multiple regression, a shallow positive m_1 for mostly negative shallow negative PCDD/Fs was determined for dl-PCBs

According to multiple regression results, a shallow negative m_1 values were determined for dl/PCBs while a shallow positive m_1 values were determined for PCDD/F compounds. However, the results are not statistically significant. Positive m_2 values were determined for all PCDD/F and dl-PCB homologs except 4 and 5 chlorinated PCDD/F homologs and the results are statistically insignificant. For this reason it is thought that UV is not related to the gas phase concentration of these compounds. Negative m_3 values were determined for all PCDD/F homologs (except 8 chlorinated homologs) and 4 chlorinated PCB homologs. For this reason, at higher wind speeds these compounds are swept from the atmosphere by advection. However, the results are not statistically significant. Statistical results show that rainfall is not effective on the gas phase concentrations of PCDD/Fs and PCBs. Similarly, Trinh *et al.* (2018) reported that the scavenging effect of higher rainfall on the dl-PCB gas phase concentration is weak.

Table 4. Regression parameters for Eq. (1) and Eq. (2)

	m_1	m_2	m_3	m_4	p_1	p_2	p_3	p_4	r^2	m_1	P_1	r^2	n
4Cl-PCDD/F	3799	-0,15	-0,16	0,01	0,16	0,63	0,29	0,51	0,42	4916	0,00	0,36	23
5Cl-PCDD/F	2766	-0,11	-0,18	0,01	0,27	0,71	0,21	0,42	0,34	3625	0,01	0,25	23
6Cl-PCDD/F	66	0,15	-0,15	0,00	0,96	0,40	0,09	0,93	0,26	-1080	0,21	0,07	23
7Cl-PCDD/F	2576	0,76	-0,15	-0,01	0,30	0,02	0,22	0,16	0,53	-3250	0,02	0,25	20
8Cl-PCDD/F	3787	0,69	0,05	-0,01	0,11	0,07	0,82	0,50	0,33	28	0,99	0,00	15
4Cl-PCB	-507	0,1	-0,1	0,00	0,83	0,64	0,69	0,97	0,1	-1447	0,25	0,1	23
5Cl-PCB	-656	0,4	0,1	0,00	0,74	0,11	0,35	0,95	0,4	-3063	0,01	0,3	23
6Cl-PCB	1670	0,27	0,09	-0,01	0,33	0,20	0,34	0,47	0,1	-205	0,83	0,0	23
7Cl-PCB	-96,6	0,456	0,34	-0,014	0,99	0,57	0,34	0,61	0,2	-2141	0,40	0,3	14

Table 3. Statistical coefficients related to meteorological parameters and PCDD/Fs and DL-PCBs homologues

		T (°C)			UV (index)			SR (W/m ²)			WV (m/s)			H (%)			P (mb)			R (mm)				
		R	R ²	p	R	R ²	p	R	R ²	p	R	R ²	p	R	R ²	p	R	R ²	p	R	R ²	p		
PCDD/F	GAS PHASE	4CI	-0,6	0,37	0,002	-0,6	0,32	0,005	-0,5	0,25	0,014	0,007	0,00	0,97	-0,1	0,01	0,65	0,2	0,04	0,37	0,2	0,04	0,35	
		5CI	-0,75	0,6	0,00	-0,6	0,4	0,001	-0,6	0,3	0,003	0,00	0,00	0,94	0,1	0,00	0,61	0,6	0,3	0,01	0,1	0,00	0,51	
		6CI	0,29	0,09	0,17	0,39	0,15	0,06	0,48	0,23	0,02	-0,41	0,16	0,055	-0,6	0,36	0,003	-0,15	0,02	0,51	-0,05	0,00	0,81	
	PARTICLE PHASE	7CI	0,37	0,14	0,105	0,47	0,23	0,03	0,56	0,31	0,011	-0,27	0,07	0,25	-0,36	0,13	0,12	-0,15	0,02	0,53	-0,29	0,09	0,21	
		8CI	0,07	0,00	0,82	0,39	0,15	0,15	0,29	0,08	0,3	-0,15	0,02	0,6	0,33	0,11	0,23	-0,21	0,04	0,45	-0,1	0,01	0,76	
		4CI	-0,67	0,45	0,00	-0,61	0,37	0,002	-0,59	0,35	0,003	0,11	0,01	0,6	0,17	0,03	0,45	0,33	0,11	0,12	0,05	0,0	0,83	
	DL-PCB	GAS+PARTICLE PHASE	5CI	-0,75	0,56	0,00	-0,63	0,39	0,001	-0,59	0,34	0,003	0,02	0,0	0,93	0,519	0,01	0,61	0,55	0,31	0,006	0,14	0,02	0,51
			6CI	-0,78	0,61	0,00	-0,65	0,43	0,001	-0,58	0,34	0,004	-0,04	0,0	0,86	0,01	0,00	0,95	0,6	0,36	0,003	0,12	0,02	0,57
			7CI	-0,44	0,2	0,03	-0,5	0,25	0,015	-0,48	0,23	0,02	0,29	0,1	0,17	0,19	0,04	0,4	0,16	0,03	0,46	0,17	0,03	0,43
		CLE PHASE	8CI	-0,66	0,43	0,001	-0,53	0,29	0,009	-0,43	0,19	0,04	-0,11	0,01	0,63	-0,1	0,00	0,78	0,6	0,37	0,002	0,05	0,0	0,8
			4CI	-0,76	0,58	0,00	-0,68	0,46	0,00	-0,63	0,4	0,001	0,02	0,00	0,94	0,1	0,01	0,68	0,41	0,17	0,05	0,17	0,03	0,45
			5CI	-0,76	0,58	0,00	-0,65	0,42	0,001	-0,6	0,36	0,002	0,01	0,00	0,96	0,06	0,00	0,8	0,55	0,3	0,006	0,18	0,03	0,41
GAS PHASE		6CI	-0,76	0,58	0,00	-0,64	0,41	0,001	-0,56	0,31	0,006	-0,1	0,00	0,77	-0,02	0,00	0,91	0,6	0,36	0,003	0,11	0,01	0,62	
		7CI	-0,44	0,19	0,036	-0,5	0,25	0,015	-0,48	0,23	0,021	0,29	0,09	0,17	0,19	0,04	0,38	0,16	0,02	0,47	0,17	0,03	0,44	
		8CI	-0,65	0,42	0,001	-0,51	0,26	0,013	-0,4	0,16	0,16	-0,13	0,02	0,55	-0,1	0,01	0,001	0,64	0,42	0,001	0,02	0,00	0,92	
		4CI	0,26	0,1	0,24	0,5	0,1	0,25	0,34	0,12	0,11	-0,16	0,1	0,46	-0,44	0,2	0,04	-0,12	0,1	0,6	-0,1	0,1	0,7	
		5CI	0,5	0,24	0,02	0,6	0,34	0,003	0,6	0,32	0,005	0,2	0,04	0,36	-0,2	0,03	0,4	-0,44	0,2	0,034	-0,14	0,02	0,51	
		6CI	-0,1	0,1	0,7	0,11	0,1	0,62	0,1	0,1	0,75	0,2	0,1	0,41	-0,1	0,1	0,68	0,1	0,00	0,88	-0,12	0,1	0,58	
	7CI	0,28	0,1	0,32	0,23	0,1	0,44	0,3	0,1	0,35	0,13	0,1	0,65	-0,1	0,00	0,83	-0,2	0,1	0,5	-0,2	0,1	0,52		
	4CI	-0,25	0,1	0,26	-0,3	0,1	0,2	-0,24	0,1	0,3	-0,02	0,00	0,92	-0,12	0,01	0,57	0,14	0,02	0,56	0,23	0,1	0,28		
	5CI	-0,5	0,2	0,02	-0,35	0,12	0,1	-0,33	0,11	0,12	0,1	0,1	0,66	-0,1	0,1	0,65	0,2	0,03	0,65	0,1	0,1	0,64		
PARTICLE PHASE	6CI	-0,64	0,41	0,001	-0,67	0,44	0,001	-0,66	0,44	0,001	0,14	0,1	0,55	0,13	0,02	0,58	0,55	0,3	0,008	0,22	0,1	0,32		
	7CI	-0,71	0,5	0,002	-0,64	0,41	0,007	-0,6	0,33	0,02	0,34	0,1	0,2	0,2	0,1	0,42	0,51	0,26	0,05	0,1	0,1	0,77		
	4CI	0,2	0,0	0,43	0,1	0,0	0,56	0,2	0,0	0,32	-0,1	0,0	0,51	-0,3	0,1	0,14	-0,1	0,0	0,7	-0,1	0,0	0,7		
	5CI	0,43	0,2	0,04	0,5	0,3	0,015	0,51	0,3	0,014	0,2	0,1	0,4	-0,2	0,1	0,5	-0,4	0,2	0,06	-0,2	0,1	0,32		
	6CI	-0,3	0,1	0,13	-0,2	0,1	0,46	-0,2	0,1	0,45	0,2	0,1	0,45	0,0	0,0	0,99	0,3	0,1	0,19	-0,2	0,1	0,47		
	6CI	-0,1	0,0	0,95	-0,1	0,1	0,8	0,1	0,0	0,88	0,2	0,1	0,47	-0,1	0,0	0,83	0,1	0,1	0,7	-0,2	0,1	0,47		

T: Temperature, UV: Ultra Violet, SR: Solar Radiation, WV: Wind Velocity, H: Humidity, P: Pressure, R: Rain

4. CONCLUSIONS

Average atmospheric concentrations of PCDD/Fs was found to be about 30% of that of dl-PCBs. Increasing chlorine content increased the PCDD/Fs concentration in contrast to dl-PCBs. Seasonal variation is more apparent for PCDD/Fs. Concentration ratio of winter to summer was about 15, while that for dl-PCBs was 1,1. Therefore, it was thought that fossil fuel combustion sources for heating affected PCDD/Fs concentrations much more than dl-PCBs. Moreover, statistical coefficients of relation (r : 0,5, r^2 : 0,24, p : 0,002) determined between temperature and gas phase concentration of dl-PCBs implied that their desorption from sinks was not considerable. PCDD/Fs were found in gas phase in 8% while dl-PCBs were in 80%. Temperature, number of chlorine atoms and vapour pressure were observed to be the most important parameters affecting gas/particle partitioning of congeners. As number of chlorine increases and temperature decreases, fraction of particulate phase increased. In addition shallow, negative slope values were determined for 4,5 and 7 Cl-PCBs. For this reason, it is considered that the atmospheric gas phase concentrations of dl-PCBs were not affected by volatilization from soil and water surfaces.

Statistical relations determined between particulate phase concentrations and meteorological parameters were observed to be more meaningful compared to those for gas phase concentrations. Since particle phase fractions of PCDD/Fs were found to be much higher than those of dl-PCBs, statistical relations between meteorological parameters and PCDD/Fs were found to be more meaningful.

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