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Monitoring atmospheric levels and deposition of dioxin-like pollutants in sub-alpine Northern Italy

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ABSTRACT

The objective of this work was to assess the atmospheric occurrence, seasonal variations and deposition of dioxin-like pollutants (17 PCDD/Fs + 12 DL-PCBs) in sub-alpine northern Italy. A total of 108 weekly integrated samples (aerosol + gas phases) were collected during a 1-year period (2005–2006) at the Ispra EMEP site (Northern Italy, 45°49'N, 8°38'E). Atmospheric loadings into Lake Maggiore were also estimated by implementing a deposition model. $\Sigma_{2,3,7,8}$ -PCDD/F atmospheric total concentrations were dominated by the aerosol-bound fraction which ranged from 50 to 3080 (1–215 WHO₉₈ TEQ) fg m⁻³. In contrast DL-PCB levels were dominated by the gas phase concentrations and varied from 1800 to 14800 (1–5 WHO₉₈ TEQ) fg m⁻³. The aerosol and gas phase concentrations of PCDD/Fs and DL-PCBs exhibited a similar seasonality (higher values in winter time for aerosol-bound contaminants and lower concentrations for gas phase contaminants) in spite of their different environmental sources and properties. Estimated total atmospheric (dry + wet) depositional fluxes of dioxin-like pollutants in sub-alpine northern Italy were ~0.2–~9.5 ng m⁻² d⁻¹, with wet deposition dominating. Total atmospheric inputs ($\Sigma_{2,3,7,8}$ -PCDD/Fs + DL-PCBs) into Lake Maggiore ranged from 14 to 304 g y⁻¹. Higher environmental concentrations of dioxin-like pollutants in sub-alpine northern Italy are expected in the cold season and in rainy days due to a combined effect of stagnant atmospheric conditions (low winds), household wood burning in the region and higher pollutant loads via rainfall in winter.

1. Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are two families of persistent organic pollutants (POPs). Among the 419 PCDD/F + PCB possible congeners, seventeen PCDD/Fs (2,3,7,8-chlorine substituted) and twelve PCBs (DL-PCBs) (CBs-81, -77, -105, -114, -118, -123, -126, -156, -157, -167, -169, -189), are considered dioxin-like pollutants, and of particular concern due to their accumulation and toxic effects in biota and humans (Safe, 1984, 1990; Van den Berg et al., 1998; Partzefall, 2002). Although PCBs have been removed from active use in nearly all countries since the mid-1970s, and primary (combustion) sources of PCDD/Fs are closely controlled (Lohmann et al., 2007), concerns regarding their global distribution and current ambient levels (human exposure) due to their high toxicity even at low levels remain. PCDD/Fs occur in the

environment as unintentional byproducts of chemical manufacturing and incineration processes (Harrad and Jones, 1992; Bruzy and Hites, 1996) whereas, current emissions of PCBs derive from urban/industrial centers, landfills, open burning of products containing PCBs, waste incinerations, accidental fires and re-volatilization from environmental reservoirs (Cousins and Jones, 1998; Breivik et al., 2002). After emission to the atmosphere, these contaminants participate in atmospheric processes that determine their inputs to environmental surfaces (e.g. waters, soils, vegetation) and their atmospheric transport (Wania and Mackay, 1996; Lohmann et al., 1999). Various regional or global monitoring networks/programs (e.g. TOMPs, UK; AMAP, Arctic region; EMEP in EU; IADN in North America, and GAPS, at global scale) have established ambient levels, deposition/transport and in some cases identify spatial-temporal trends of POPs (Blanchard et al., 2008; Pozo et al., 2009; Gioia et al., 2009, Aas and Breivik, 2010; Hung et al., 2010). PCDD/Fs and DL-PCB are infrequently included in monitoring programs, due to the difficulties in sampling and analyses at trace or ultra-trace levels and the associated high economic cost. As a result, there are many “non monitored areas” as well as little information on dioxin-like compound ambient

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concentrations. For instance, South-Western Europe remains largely uncovered by the EMEP POPs monitoring network (Fig. S1, supplementary material (SM)).

The objective of this work was to assess the atmospheric concentrations, seasonal variations and deposition of dioxin-like pollutants in a sub-alpine area of northern Italy as well as to quantify the atmospheric loading into neighboring Lake Maggiore. To achieve this goal, a monitoring and research station was established at the Joint Research Center (JRC) Ispra EMEP site in northern Italy near Lake Maggiore (Fig. 1). PCB (non-DL) atmospheric concentrations and deposition fluxes over one year and a limited data set (short-term sampling campaign) on PCDD/F and DL-PCB concentrations in air and bulk deposition have been reported for this site (Castro-Jiménez et al., 2008, 2009). PCDD/Fs have been reported in the Milan area and two other regions in northern Italy (i.e. Piemonte and Trieste) with a focus on urban and industrial impacted sites (Fattore et al., 2003; Colombo et al., 2009; Onofrio et al., 2011). However, no long-term study on dioxin-like pollutants has ever been conducted in the studied area.

2. Experimental

2.1. Sampling location description

Air samples were collected at the EMEP monitoring and research station at the JRC Ispra Site, north Italy (Fig. 1). A detailed description of the area has been published elsewhere (Castro-Jiménez et al., 2009).

2.2. Air sampling

Sampling strategy and methodology have been detailed in Castro-Jiménez et al. (2009). Briefly, integrated weekly air samples were collected from April 2005 to April 2006 using high volume samplers according to the U.S. EPA TO-9A Method (US EPA, 1999a). Two identical samplers were used interchangeably and 108 samples (54 aerosol + 54 gas phase) were collected during the sampling period ($860 \pm 27 \text{ m}^3$ average sample volume). Quartz fiber filters (QFFs) were used for the collection of the particle air phase whereas polyurethane foam (PUF) was employed for the gas phase. Table S1 (SM) shows sampling details together with the meteorological parameters for each sampling event.

2.3. Analytical determination

QFFs and PUFs were Soxhlet extracted separately with n-hexane/acetone (220:30 v/v) for 48 h after being spiked with ^{13}C -labelled DL-PCB and PCDD/Fs internal standards. Extract purification was executed with an automated clean-up system (Power-Prep). This method, previously used in our laboratory, has proven a high quality purification of the studied POPs (Castro-Jiménez et al., 2008). Two fractions were collected: one containing mono-ortho PCBs, and one containing non-ortho PCBs and PCDD/Fs. Purified extracts were evaporated to $\sim 0.5 \text{ ml}$ by using a TurboVap and then to dryness under gentle nitrogen flow. Prior to injection, $30 \mu\text{L}$ of a toluene solution containing syringe ^{13}C -labelled standards (PCBs 111, -170 and 1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD)



Fig. 1. Sampling site location close to Lake Maggiore (Northern Italy).

were added to the fractions to determine the recoveries of the internal standards. Analysis of PCDD/Fs and PCB was performed according to EPA1613 and EPA (US EPA, 1994, 1999b). All organic solvents were dioxin analysis grade. Analysis of (1) mono-ortho PCBs and (2) non-ortho PCBs and PCDD/Fs was performed by two different couplings of high-resolution gas chromatograph (HRGC) – high-resolution mass spectrometer (HRMS). A HT-8 and BP-DXN capillary columns, both 60 m long, 0.25 mm i.d. (inner diameter) and 0.25 μm film were used, respectively (see Text S1 in SM for instrument details and GC and MS operating conditions).

2.4. Quality assurance/quality control

The QA/QC procedures followed are detailed in supporting information (Text S2, SM). Summarizing, field and procedural blanks were regularly collected and analyzed together with the samples. Blank values were at method detection limit (MDL) levels so concentrations reported were not corrected for blanks. MDL were calculated on the basis of a signal to noise ratio of 3/1 in real samples (therefore taking into account the matrix effect and the influence of both processing and analytical steps). MDL values ranged from 1 to 38 and from 0.03 to 2.3 fg m^{-3} for DL-PCBs and PCDD/Fs, respectively, depending on the congener and the sample. Breakthrough was evaluated during the sampling campaign and results indicated that this artifact was not significant under the field conditions encountered. Sampling reproducibility was assessed by operating two samplers (A and B) simultaneously in selected sample events. The relative standard deviation (RSD) varied from 1 to 24% when comparing $\sum\text{PCDD/F}$ and $\sum\text{DL-PCB}$ results in the samples gathered simultaneously, except for only one sample which showed a higher variability ($\sim 40\%$) but only for the DL-PCBs (Table S2, SM). Standards (natives + ^{13}C -compounds) were introduced in the chromatographic sequence to evaluate possible variations during the time of analyses. Chromatographic peaks of target compounds were only considered when complying with the following QA/QC criteria: (1) the retention time of target compound were $\pm 3\text{s}$ of those observed for the corresponding standards; (2) experimental isotopic ratio of natives compounds were within $\pm 20\%$ of the theoretical ratio and (3) peaks were at least 3 times higher than the noise. Average method recoveries ranged from 24 ± 5 to $58 \pm 7\%$ and from 46 ± 7 to $87 \pm 11\%$ for DL-PCB and PCDD/Fs depending on the congener and the sample. Results were corrected by recoveries (isotopic dilution method).

2.5. Calculating atmospheric deposition

Atmospheric deposition was considered to be represented by the wet and dry deposition fluxes. Gaseous deposition (air to water flux) was not including in the calculation due to the lack of PCB and PCDD/Fs concentration data in the receptor surfaces. Deposition fluxes may be therefore underestimated for those chemicals with a significant gaseous fraction.

2.5.1. Dry deposition flux

The dry deposition flux (F_{DD} , $\text{pg m}^{-2} \text{d}^{-1}$) was estimated from the particle deposition velocity, V_d (m d^{-1}), and the PCDD/F and PCB concentrations in the aerosol phase (C_a , pg m^{-3}) as:

$$F_{\text{DD}} = C_a V_d \quad (1)$$

Particle deposition velocity depends on aerosol size distribution and atmospheric turbulence, which is influenced by wind speed. Deposition velocities of 0.2 cm s^{-1} have been reported for lake environments (Schottler and Eisenreich, 1997) and those varying from 0.39 to 0.52 cm s^{-1} for rural areas (Shih et al., 2006). In our

model, we assumed an average deposition velocity of 0.4 cm s^{-1} which was considered representative for a lake environment located in a rural/semi-rural area. A degree of uncertainty (factor of 2–3) is assumed due to the lack of measurements of V_d during the 1-year sampling campaign.

2.5.2. Wet deposition flux

The wet deposition flux (F_{WD} , $\text{pg m}^{-2} \text{d}^{-1}$) was calculated as the product of the precipitation rate P_o ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$) and the contaminant concentration in rain water C_r (pg m^{-3}) that includes both the atmospheric gas and particle phase contributions:

$$F_{\text{WD}} = C_r P_o \quad (2)$$

Contaminant concentrations in precipitation as the result of the scavenging of the atmospheric gas phase by rain drops (C_{rw}) was calculated using the dimensionless Henry' law constant ($H' = H/RT$) and the measured gas phase concentrations. Henry' law constants (H) values for PCB (Bamford et al., 2002) were corrected by temperature using Eq. (3):

$$\ln\left(\frac{H_T}{H}\right) = \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_T}\right) \quad (3)$$

Where H_T and H are the Henry' law constants ($\text{Pa m}^3 \text{mol}^{-1}$) at the sampling average temperature (T_T) and at standard temperature (T , 298.15°K), ΔH (kJ mol^{-1}) is the phase transition enthalpy of the compound and R ($\text{kJ }^\circ\text{K}^{-1} \text{mol}^{-1}$) is the gas constant. The correlation of H with temperature proposed by Paasivirta et al. (1999) was used for PCDD/Fs. The scavenging of the aerosol by rain was calculated by multiplying the aerosol concentrations (C_a) by the particle phase washout ratio (W_p), so Eq. (2) becomes:

$$F_{\text{WD}} = \left(\frac{C_g}{H'} + W_p C_a\right) P_o \quad (4)$$

The value of $W_p = 2 \cdot 10^5$ was selected for our calculations, consistent with McLachlan and Sellström (2009), Jurado et al. (2005), and Dueri et al. (2010).

3. Results and discussion

3.1. Ambient levels and seasonality

Figs. 2 and 3 show the $\sum 2,3,7,8\text{-PCDD/Fs}$ and $\sum\text{DL-PCBs}$ concentrations, respectively, in the atmospheric boundary layer aerosol (particle) and gas phases along the 1-year sampling period. Concentrations expressed as WHO₉₈ TEQ are also provided for comparative purposes. Single congener and homologue series ($\sum\text{Cl}_{4-8}\text{DD/F}$) concentrations in the case of dioxins are provided in Tables S3–S6 (SM). Atmospheric concentrations of $\sum 2,3,7,8\text{-PCDD/F}$ and $\sum\text{Cl}_{4-8}\text{DD/F}$ were dominated by the aerosol-bound fraction, levels ranging from 50 to 3080 (1–215 WHO₉₈ TEQ) fg m^{-3} and from 90 to 9500 fg m^{-3} , respectively (Fig. 2A, Table S3). Gas phase concentrations were lower and less variable, ranging from 12 to 67 (2–10 WHO₉₈ TEQ) fg m^{-3} and from 200 to 910 fg m^{-3} for $\sum 2,3,7,8\text{-PCDD/Fs}$ and $\sum\text{Cl}_{4-8}\text{DD/Fs}$, respectively (Fig. 2B, Table S4). Contrary to PCDD/Fs, DL-PCB atmospheric levels were dominated by gas phase concentrations ranging from 1800 to 14800 (1–5 WHO₉₈ TEQ) fg m^{-3} (Fig. 3B, Table S5). Aerosol phase concentrations varied from 410 to 7800 (0.1–15 WHO₉₈ TEQ) fg m^{-3} (Fig. 3A, Table S6).

Total WHO₉₈ TEQ levels were dominated by the PCDD/F contribution, in particular in winter months (Figs. 2 and 3, Tables S3–S6, SM). Total PCDD/F TEQ was dominated by 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD accounting for the $37 \pm 4\%$ and

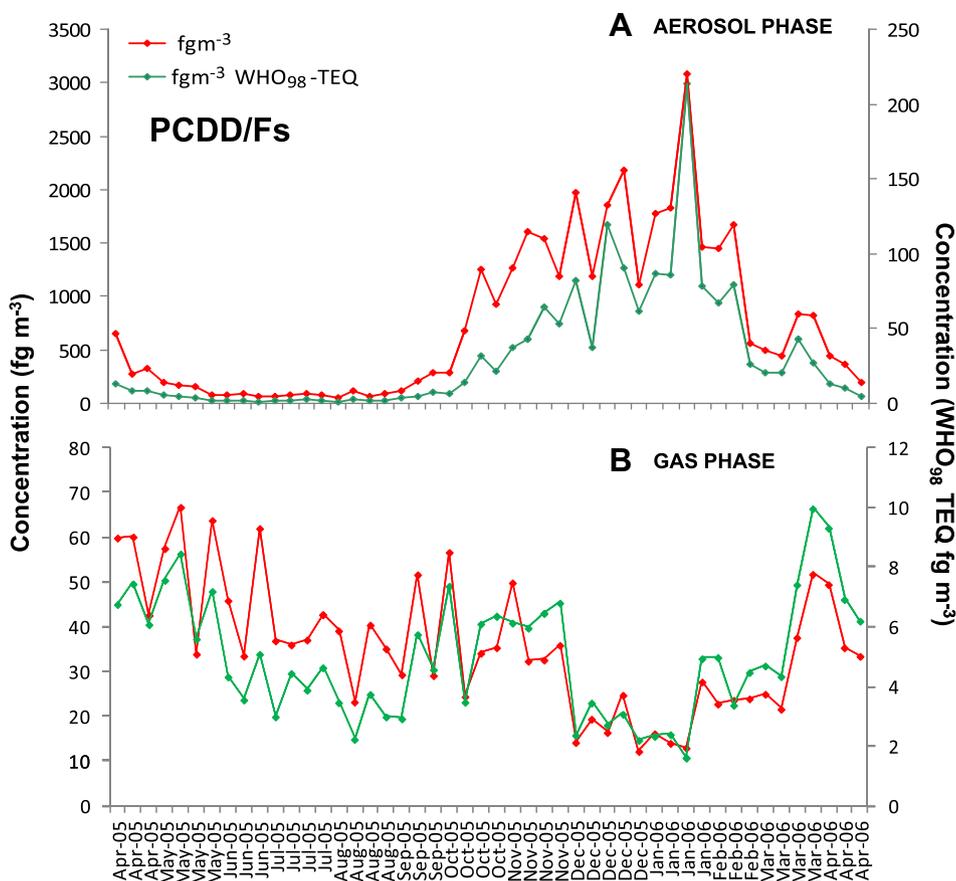


Fig. 2. Atmospheric boundary layer concentrations of aerosol and gas phase PCDD/Fs monitored in 2005–2006 in sub-alpine northern Italy.

14 ± 4%, respectively (Fig. S2A), whereas PCB-126 (72 ± 7%) and PCB-118 (13 ± 6) dominated the total DL-PCB TEQ (Fig. S2B). PCDD/F levels in sub-alpine northern Italy are within the range of those reported for rural or semi-rural areas around the world (Lohmann and Jones, 1998; Abad et al., 2004; Shih et al., 2006; Cleverly et al., 2007; Choi et al., 2008; Venier et al., 2009), whereas DL-PCB levels are within the range of those reported for residential or moderate urban/industrial areas (Choi et al., 2008; Martínez et al., 2010; Castro-Jiménez et al., 2011).

$\sum_{2,3,7,8}$ -PCDD/F and \sum DL-PCBs aerosol phase concentrations were higher from October 2005 to February/March 2006. Concentrations peaked in the coldest months of winter, in particular in January 2006 when the highest concentrations were measured (Figs. 2 and 3A). These concentration peaks reflect the unusually high PM_{2.5} values (up to 120 $\mu\text{g m}^{-3}$) registered at the EMEP Ispra station during the period 17–24 January, corresponding with the third integrated sample of the month (Table S1, SM). The seasonal trend was especially marked for dioxins. The aerosol-bound DL-PCBs, although not dominating total (gas + aerosol) atmospheric levels, exhibited a very similar trend to the aerosol-bound PCDD/Fs. Higher PCDD/F concentrations in winter are reported elsewhere and have been attributed to a lower atmospheric mixing height (less favoring dispersion of local emissions) and the increase of household wood burning for heating in the cold period (Lohmann and Jones, 1998; Lee et al., 1999; Coutinho et al., 2007). Horizontal and vertical dispersion of pollutants emitted in northern Italy are hindered by low wind speeds (daily mean values around 1 ms^{-1}) and frequent inversion layers near ground with fog episodes in the cold season (Rodríguez et al., 2005). Moreover,

yearly wood consumption of 1.57 million tons for residential heating has been estimated for the region of Lombardy (Pastorello et al., 2011).

PCDD/F and DL-PCB gas phase concentrations also exhibited a seasonal trend. However, dioxin-like pollutant gas phase concentrations were in general higher in warmer months (spring/summer), and lower in the coldest months (Dec–Feb 2005) (Figs. 2 and 3B). Higher PCB gas phase concentrations in the warmer season have been largely attributed to the increase of PCB volatilization rates (temperature dependent) from environmental reservoirs such as, formerly exposed soils, water, vegetation, etc. (Manchester-Neesving and Andren, 1989; Hillery et al., 1997; Simcik et al., 1997; 1999; Cousins and Jones, 1998; Wania et al., 1998). Indeed, this effect has also been observed at the same site and time period for non-DL-PCBs (Castro-Jiménez et al., 2009). PCDD/F gas phase concentrations are infrequently measured due to the fact that ambient levels are dominated by the aerosol-bound fraction as a sum of congeners (see discussion above). We have estimated that the $\sum_{2,3,7,8}$ -PCDD/F percent in the gas phase can vary from 0.5% (winter) to 39% (summer) of the total concentration in the studied area. This share of gas phase fraction to the total atmospheric concentration may be higher for low MW PCDD/Fs, in particular for 2378-TCDD and 2378-TCDF (the most toxic ones), reaching in average up to 49 ± 20% and 60 ± 26% of the total $\sum_{2,3,7,8}$ -PCDD/F atmospheric concentrations, respectively (Fig. S3, SM). However, the seasonality of dioxin gas phase concentrations, very similar to gas phase PCBs, better reflects the temperature dependence of the gas-particle partitioning of the PCDD/Fs present in the atmosphere. The gas-particle partition coefficient (K_p) was calculated as follows:

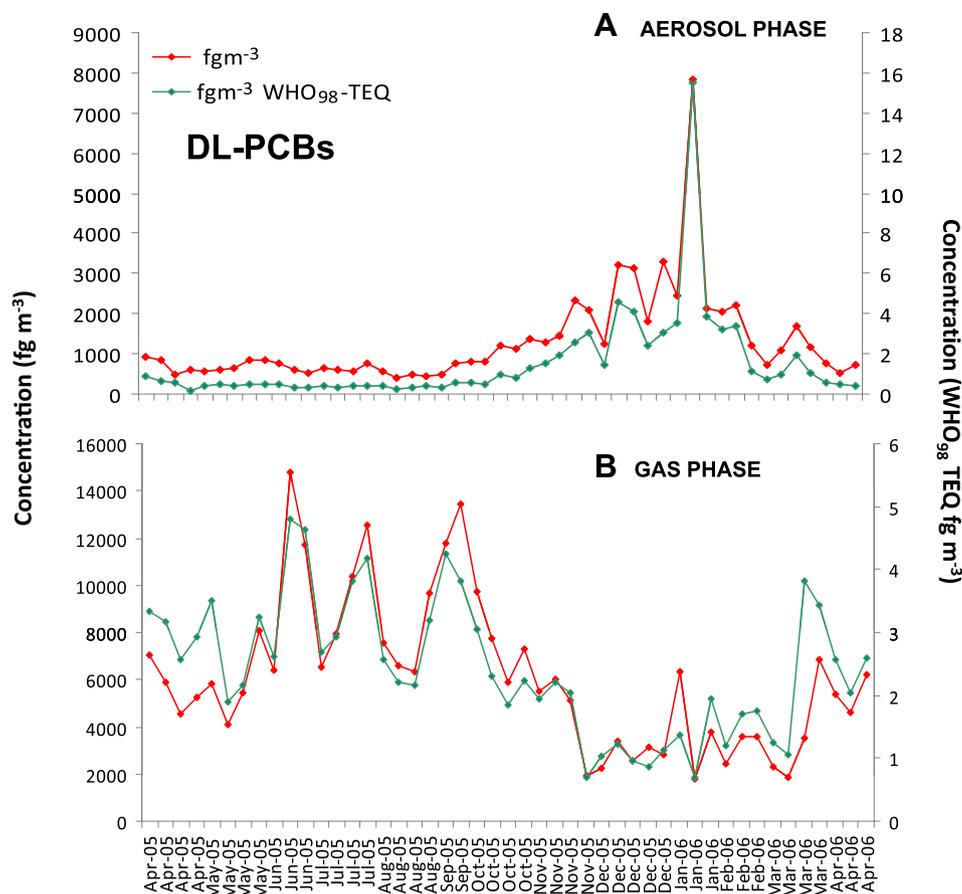


Fig. 3. Atmospheric boundary layer concentrations of aerosol and gas phase DL-PCBs monitored in 2005–2006 in sub-alpine northern Italy.

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

where, F and A are the contaminant concentrations in the particular and gas phases, respectively (fg m^{-3}), and TSP is the total suspended particulate matter concentration ($\mu\text{g m}^{-3}$). TSP values were not available for the sampling period, therefore PM_{10} annual average concentrations for 2005 ($41.2 \mu\text{g m}^{-3}$) and 2006 ($32.8 \mu\text{g m}^{-3}$) measured at the station were used instead (PM_{10} represents $\sim 75\%$ of the TSP in the sampling site) (Castro-Jiménez et al., 2009). When plotting $\ln Kp$ vs $1/T$ a significant correlation was obtained for all PCDD/F congeners (Table 1). This was also true for DL-PCBs (Table S7, SM). However, the much higher gaseous fraction of PCBs than PCDD/Fs makes gas-particle partitioning unable to explain seasonality in the case of PCBs. In summary, both the aerosol and gas phase concentrations of PCDD/Fs and PCBs exhibit a very similar seasonality. Aerosol-bound dioxin-like pollutants are influenced by seasonal sources and specific meteorological conditions hindering pollutant dispersion. However, temperature is the main driver of gas phase concentrations of dioxin-like pollutants and can explain its seasonality. In the case of PCBs, temperature exerts a dominant effect by controlling the volatilization rates, while in the case of PCDD/F it does by controlling the gas-particle partitioning. Indeed, the variations in the gas-particle partitioning due to changes in ambient temperature could explain between the ~ 50 – 90% of the dioxin gas phase annual variability. However, potential re-volatilization of PCDD/Fs from environmental reservoirs could be also feasible even if this process appears not to be predominant. Indeed, PCDD/F volatilization from other environmental compartments such as water (Castro-Jiménez et al., 2010; Friedman et al., 2012) and soils (Schuhmacher et al., 2006; Aberg et al., 2010) have been already

reported. It was not possible to assess this process with the present data set and further research is needed in this regard. This behavior may have implications for environmental exposure to dioxins, in particular in the hot season when an increase of the gas phase fraction of the most toxic congeners is likely to occur.

3.2. Congener patterns

PCDD/F and DL-PCB congener patterns are presented in Fig. S4 (SM). The pattern of 2,3,7,8-PCDD/Fs was dominated by the

Table 1
Temperature dependence of the gas–aerosol partition coefficient (Kp) for PCDD/Fs along the 1-year sampling period ($\ln Kp = m(1/T) + \text{const}$).

Dioxin congener	Slope (m) \pm SE ^a	Intercept \pm SE ^a	n	r^2	P
2378-TCDD	5907 \pm 952	3.24 \pm 3.35	47	0.46	<0.001
12378-PeCDD	12882 \pm 960	-20.45 \pm 3.38	47	0.80	<0.001
123478-HxCDD	17218 \pm 862	-34.57 \pm 3.03	47	0.90	<0.001
123678-HxCDD	17910 \pm 884	-36.97 \pm 3.11	47	0.90	<0.001
123789-HxCDD	17977 \pm 969	-36.96 \pm 3.41	47	0.88	<0.001
1234678-HpCDD	17115 \pm 829	-32.90 \pm 2.92	47	0.90	<0.001
OCDD	11515 \pm 838	-12.41 \pm 2.95	47	0.81	<0.001
2378-TCDF	9759 \pm 850	-10.82 \pm 2.99	47	0.75	<0.001
12378-PeCDF	13933 \pm 998	-24.79 \pm 3.51	47	0.81	<0.001
23478-PeCDF	15261 \pm 918	-28.92 \pm 3.23	47	0.86	<0.001
123478-HxCDF	18128 \pm 871	-38.26 \pm 3.06	47	0.91	<0.001
123678-HxCDF	18732 \pm 915	-40.31 \pm 3.22	47	0.90	<0.001
234678-HxCDF	16290 \pm 731	-31.38 \pm 2.57	47	0.92	<0.001
123789-HxCDF	17968 \pm 1000	-37.11 \pm 3.52	47	0.88	<0.001
1234678-HpCDF	19192 \pm 851	-40.82 \pm 2.99	47	0.92	<0.001
1234789-HpCDF	15501 \pm 1200	-27.25 \pm 4.22	47	0.79	<0.001
OCDF	11533 \pm 842	-12.89 \pm 2.96	47	0.81	<0.001

^a Standard Error.

higher chlorinated congeners, OCDD and 1234678-HpCDD accounting for the $43 \pm 7\%$ and $15 \pm 2\%$ of the $\sum 2,3,7,8$ -PCDD/Fs. TCDFs, PeCDFs and OCDD dominated the homologue series pattern accounting for the $22 \pm 5\%$, $14 \pm 2\%$ and $15 \pm 5\%$ of the $\sum \text{Cl}_{4-8}$ PCDD/Fs, respectively. The DL-PCB pattern was dominated by CB-118 ($65 \pm 3\%$) and CB-105 ($20 \pm 1\%$). These patterns agree with those from this site obtained earlier (Castro-Jiménez et al., 2008) and with those reported in the atmosphere around the Great Lakes, US (Venier et al., 2009).

3.3. Atmospheric deposition

3.3.1. Dry deposition

PCDD/Fs and DL-PCB dry deposition fluxes during April 2005–2006 were estimated according to Eq. (1) and are shown in Fig. 4. Atmospheric dry deposition of $\sum \text{DL-PCB}$, ranging from 140 to $1940 \text{ pg m}^{-2} \text{ d}^{-1}$, was higher than dry deposition of $\sum 2,3,7,8$ -PCDD/Fs (16 – $1065 \text{ pg m}^{-2} \text{ d}^{-1}$). Dry deposition fluxes for individual DL-PCBs and 2,3,7,8-PCDD/Fs congeners are presented in Table S8 (SM). Deposition fluxes for both contaminant's families exhibited the same annual pattern, with higher fluxes in the cold season peaking in the month of January 2006. Due to the assumptions in the dry deposition estimations these fluxes follow the seasonality of contaminant aerosol phase concentrations.

3.3.2. Wet deposition

Wet deposition fluxes of $\sum \text{DL-PCBs}$ and $\sum 2,3,7,8$ -PCDD/Fs, estimated applying Eqs. (2)–(4), are shown in Fig. 5 (Table S9 in SM compiles the fluxes of individual congeners). Estimated fluxes varied from 2 to $4660 \text{ pg m}^{-2} \text{ d}^{-1}$ for $\sum \text{DL-PCBs}$ and from 0.2 to $3540 \text{ pg m}^{-2} \text{ d}^{-1}$ for $\sum 2,3,7,8$ -PCDD/Fs. Similar values were observed for PCDD/F and DL-PCB in the coldest period (mid-October 2005 to March 2006), whereas in the warmer months (April–September 2005) the DL-PCB fluxes were in general higher than those of PCDD/Fs. Indeed, the average PCDD/Fs to DL-PCB ratio of wet fluxes during the cold period (0.74 ± 0.23) was significantly different (*t*-test, $p < 0.001$) than the corresponding ratio (0.26 ± 0.18) for the warm period. The wet deposition of particles (washed out by rain) was the dominant process accounting for the 98% and $\sim 100\%$ of the wet deposition for $\sum 2,3,7,8$ -PCDD/F and $\sum \text{DL-PCB}$, respectively being the wet deposition of gas phase negligible for both chemical classes. The seasonal fluxes reflect the variations of the aerosol-bound contaminants and the precipitation

pattern (rainy in spring and autumn). The contaminant loads in all precipitation events occurring in the colder months were higher than in the warmer months for comparable precipitation rates, especially for PCDD/Fs (up to ~ 30 fold-times higher) (see for example fluxes from 1st sample of August 2005 and 2nd samples of February 2006, Fig. 5, Table S9). The higher pollutant loads in winter reflect the higher aerosol share occurring in the cold season respect to the warm season, especially pronounced for PCDD/Fs (Fig. S5, SM). These results are in agreement with modeling estimations made for the atmospheric deposition of PCDD/Fs in North America (Zhang et al., 2009).

3.3.3. Total atmospheric inputs

Total atmospheric (dry + wet) depositional fluxes of dioxin-like pollutants (2,3,7,8-PCDD/Fs + DL-PCBs) in sub-alpine northern Italy vary from 0.2 to $\sim 9.5 \text{ ng m}^{-2} \text{ d}^{-1}$. While dry deposition fluxes are higher for DL-PCBs during the whole year (Fig. 4), wet deposition of DL-PCBs are greater than fluxes of PCDD/Fs only for the warm period as indicated above (Fig. 5). The dominant input to regional terrestrial and aquatic ecosystems is wet deposition. Table 2 shows the agreement of the present estimations with experimentally measured atmospheric bulk deposition fluxes. Estimated fluxes are within the range of atmospheric bulk deposition measurements performed in March 2005 in the same site ($\sim 8 \text{ ng m}^{-2} \text{ d}^{-1}$ for $\sum 2,3,7,8$ -PCDD/Fs + DL-PCBs) (Vives et al., 2007). The comparison with atmospheric bulk deposition measurements from other areas world-wide highlights the high variability of the PCDD/F atmospheric deposition fluxes in the study area (Table 2). Thus, the lower range of PCDD/F estimated fluxes (wet + dry) in northern Italy ($0.02 \text{ ng m}^{-2} \text{ d}^{-1}$) is comparable with the bulk deposition of PCDD/Fs measured in various north European background sites in the last decade (Hovmand et al., 2007; McLachlan and Sellström, 2009; Bergknut et al., 2011). However, the higher end estimation of $3 \text{ ng m}^{-2} \text{ d}^{-1}$ better compares with reported bulk deposition measurements in urban areas (Hallsall et al., 1997; Ogura et al., 2001). This fact is not surprising since the sampling site is characterized as rural/semi-rural area with a relative urban influence (mostly from Milan, 60 km to the south-east).

Lake Maggiore, the second largest lake in Italy (212.5 km^2) exhibits a historical record of contamination by various inorganic and organic contaminants (Castro-Jiménez et al., 2008 and references therein). Due to human consumption of lake water and fish (both in Italy and Switzerland) and recreational uses of lake water,

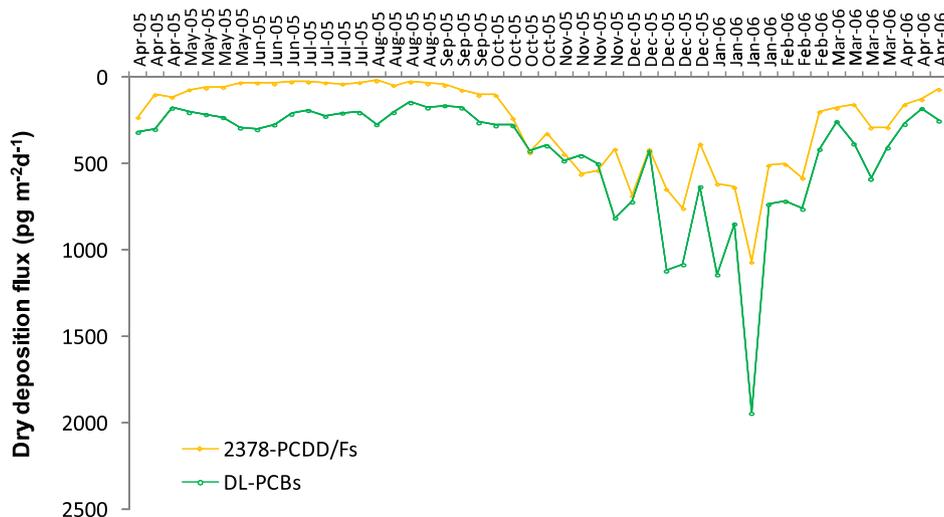


Fig. 4. $\sum 2,3,7,8$ -PCDD/F and $\sum \text{DL-PCB}$ atmospheric dry deposition fluxes ($\text{pg m}^{-2} \text{ d}^{-1}$) in sub-alpine northern Italy (2005–2006).

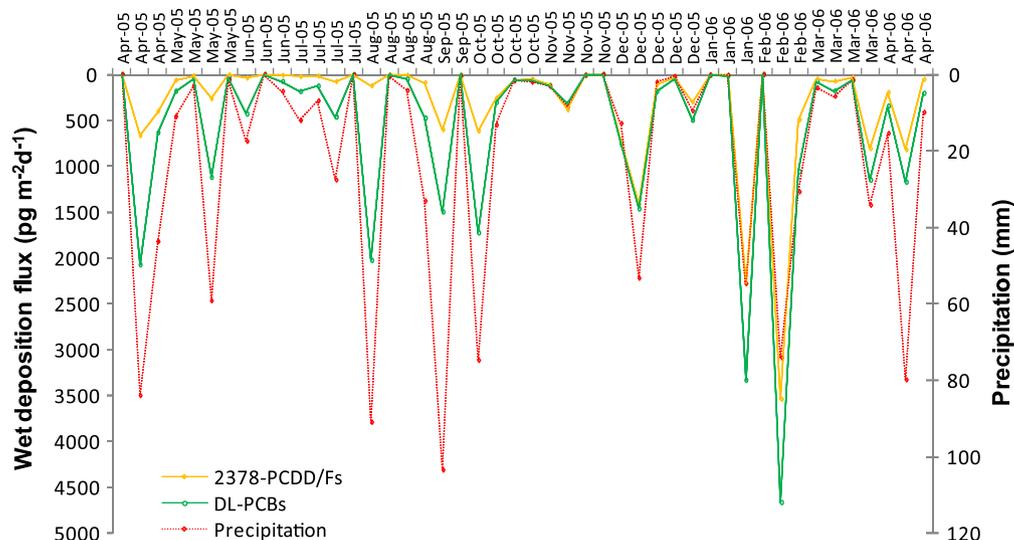


Fig. 5. Σ 2,3,7,8-PCDD/F and Σ DL-PCB atmospheric wet deposition fluxes ($\text{pg m}^{-2} \text{d}^{-1}$) together with precipitation registered during each sampling event in sub-alpine northern Italy (2005–2006).

Table 2
PCDD/Fs and DL-PCB measured and estimated (this study) atmospheric deposition fluxes from the literature in various sites world-wide.

Type of flux	Type of data	Reported flux ($\text{ng m}^{-2} \text{d}^{-1}$)	Location	Site description	Study date	Reference
Bulk deposition (PCDD/Fs + DL-PCBs)	Measured	8	Ispra EMEP site (Northern Italy)	Semi-rural area	Mar-05	Vives et al., 2007
Bulk deposition (PCDD/Fs)	Measured	0.01–0.1	Close to Stockholm (Sweden)	Background site	2006–2007	McLachlan and Sellström, 2009
Bulk deposition (PCDD/Fs)	Measured	0.01–0.04	Inlands close to Baltic sea (Sweden)	Background site	2006–2009	Bergknut et al., 2011
Bulk deposition (PCDD/Fs)	Measured	0.07 (mean)	Southern Scandinavia (Denmark)	Background areas	2002–2004	Hovmand et al., 2007
Bulk deposition (PCDD/Fs)	Measured	1.2–3.6	Kanto Region (Japan)	Urban/semi-rural	1996–1997	Ogura et al., 2001
Bulk deposition (DL-PCBs)	Measured	0.2–1.6	Kanto Region (Japan)	Urban/semi-rural	1996–1997	Ogura et al., 2001
Bulk deposition (PCDD/Fs)	Measured	1.0–1.4 (annual mean)	Manchester and Cardiff (UK)	Urban	1991–1992	Halsall et al., 1997
Wet + dry (PCDD/Fs + DL-PCBs)	Estimated	0.2–9.5	Ispra EMEP site (Northern Italy)	Semi-rural area	April 2005–2006	This study
Wet + dry (PCDD/Fs)	Estimated	0.02–3	Ispra EMEP site (Northern Italy)	Semi-rural area	April 2005–2006	This study
Wet + dry (DL-PCBs)	Estimated	0.2–4	Ispra EMEP site (Northern Italy)	Semi-rural area	April 2005–2006	This study

the occurrence of toxic dioxin-like compounds should be taken into account in environmental exposure/risk assessments. A total atmospheric input (2,3,7,8-PCDD/Fs + DL-PCBs) ranging from 14 to 304 g y^{-1} has been estimated for Lake Maggiore based on the calculated daily fluxes and taking into account the total number of days where rainfall was recorded (>0.1 mm) throughout the 1-year sampling period. However, annual precipitation registered in 2005 and 2006 (1000–1200 mm) was in the lower end of average annual precipitation volume recorded in the Lombardy region (1600–4000 mm), which has one of the highest precipitation rates in Europe (European Environmental Agency, 2003). Since atmospheric loads are strongly related to the wet deposition, higher atmospheric inputs can be expected to Lake Maggiore waters and adjacent terrestrial ecosystems (including outdoor crops) if precipitation increases.

4. Conclusions

A comprehensive 1-year data set on aerosol and gas phase atmospheric concentrations and deposition of dioxin-like pollutants has been generated for sub-alpine northern Italy, an area where data on dioxin-like pollutants ambient levels are rare.

Environmental factors driving the total (aerosol + gas phase) atmospheric concentrations throughout the year are different for PCDD/Fs and DL-PCBs. However, when PCDD/F and DL-PCB gas and aerosol phases are examined separately, they follow a very similar seasonality. This finding provides insight on the environmental behavior of the PCDD/F and DL-PCB non-dominant fraction in the atmosphere, which is the gas phase for PCDD/Fs and the aerosol phase for DL-PCBs. Higher environmental concentrations of dioxin-like pollutants is sub-alpine northern Italy and subsequent inputs to Lake Maggiore are expected in the cold season and in rainy days due to a combined effect of the stagnant conditions, household wood burning in the area and higher pollutant burdens in rainfall in winter time. The main atmospheric exposure pathway in winter time will be contaminant particle-bound related and especially relevant for PCDD/Fs. Gas phase contaminants are expected to become more relevant in summer time, in particular the low MW dioxin congeners (i.e. the most toxic ones) and the DL-PCBs.

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Appendix A. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.atmosenv.2012.03.081.

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