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Emissions of Polychlorinated Biphenyls, Polychlorinated Dibenzo-*p*-dioxins, and Polychlorinated Dibenzofurans during 2010 and 2011 in Zurich, Switzerland

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S *Supporting Information*

ABSTRACT: Persistent organic pollutants (POPs) are ubiquitous contaminants of environmental and human health relevance, but their emissions into the environment are still poorly known. In this study, concentrations of selected POPs were measured in ambient air in Zurich, Switzerland, and interpreted with a multimedia mass balance model. The aim of the combination of measurements and modeling was to back-calculate atmospheric emission rates of POPs. Measurements were performed in summer 2010 and winter 2011 and target analytes included polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). Estimated emissions were higher in summer than in winter. Emission estimates for Zurich can be extrapolated to annual averages for Switzerland of 312 $kg \cdot a^{-1}$ (39 $mg \cdot capita^{-1} \cdot a^{-1}$), 53 $kg \cdot a^{-1}$ (7 $mg \cdot capita^{-1} \cdot a^{-1}$), and 3 $kg \cdot a^{-1}$ (0.4 $mg \cdot capita^{-1} \cdot a^{-1}$, 94 g WHO98-TEQ$\cdot a^{-1}$, 65 g I-TEQ$\cdot a^{-1}$) for the six indicator PCBs (iPCBs), the twelve coplanar dioxin-like PCBs (dlPCBs), and the 17 2,3,7,8-chlorosubstituted PCDD/Fs, respectively. The emission rates of iPCBs are in agreement with existing emission inventories, whereas for PCDD/Fs the emissions are five times higher than the estimates from the Swiss national emission inventory. Emissions of dlPCBs in Switzerland are presented here for the first time. Our study also provides the first seasonally resolved emission rates of POPs, which were determined with our combined measurement and modeling approach. These findings highlight the relevance of ongoing sources of POPs, even decades after regulations aiming to reduce or eliminate sources were established.

■ INTRODUCTION

Persistent organic pollutants (POPs) are environmental contaminants of particular concern due to their resistance to degradation, their tendency to bioaccumulate, their chronic toxic effects, and their potential for long-range atmospheric transport.[1,2] Although POPs are regulated by international agreements, including the Stockholm Convention on POPs[3] and the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP),[4] there are still significant ongoing emissions. Polychlorinated biphenyls (PCBs), which were widely used in the 1950s−1970s as dielectrics in capacitors and transformers and as plasticizers in paints and joint sealants, are still emitted from numerous diffusive sources because of the long use phase of their former applications. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), which are particularly known for their high toxicity, are another example of POPs with continuing emissions, as they are unintentionally formed as byproducts of combustion processes and chemical reactions involving chlorinated precursors.[1]

International conventions regulating POPs require signatory countries to report their emissions of the targeted pollutants. However, in many cases the submitted emission data are poor or incomplete. In the most recent emission inventory compiled under the UNECE Convention on LRTAP, several signatory countries of the POP Protocol did not report their emissions of PCBs,[4] including Switzerland, where around 6000 t of PCBs were imported in total.[5]

Emission inventories of POPs are usually based on estimates derived from a "bottom-up" approach that starts with chemical production, use, and disposal data and combines these data with estimates of emission factors attributed to each of these

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phases of the chemical life cycle. In this work, we use a complementary "top-down" approach to quantify emissions of PCBs and PCDD/Fs based on a combination of field measurements and modeling with the goal to back-calculate atmospheric emissions from concentrations measured in ambient air. We performed trace measurements of PCBs and PCDD/Fs with high temporal resolution in air from the city of Zurich, Switzerland, in two sampling campaigns in summer 2010 and winter 2011 during periods with stable weather conditions lasting for several days. Our study is built on the previous observation that semi-volatile pollutants such as POPs are enriched in stable atmospheric boundary layers over cities that are source areas.[6−13]

We interpreted our field measurements using a model that calculates the trend in air concentrations based on measured time-dependent environmental and meteorological parameters. The aim of the model is to retrospectively quantify emissions of POPs to the atmosphere. All input parameters are predefined in the model with the exception of the emission rate of the target chemicals, which is adjusted and used to scale the modeled ambient air concentrations in such a way that they are close to the field measurements. This approach has been previously employed in summer in Zurich, Switzerland, for PCBs,[9] polybrominated diphenyl ethers,[10] and volatile poly- and perfluorinated alkyl substances,[11] as well as in winter for cyclic volatile methylsiloxanes.[12] Here, we present calculated emission rates for PCBs and PCDD/Fs in both summer and winter, which allows us to investigate the seasonality of emissions and provide more accurate estimates of annual emission rates than those that are derived from single-season measurements. We also revise previous PCB emission estimates made with our approach for Zurich in summer using our new measurements and an updated and improved model parametrization. Finally, we critically evaluate our results and provide a comparison with existing emission data that are based on different approaches. The presented emission rates complement emission inventories of PCBs and PCDD/Fs compiled under international regulations, can serve as an input in future modeling studies, and provide a baseline to evaluate the effectiveness of emission reduction policies for these compounds.

■ MATERIALS AND METHODS

Sampling. The first of two sampling campaigns was carried out in summer 2010 during a period dominated by a high-pressure system, where a stable atmospheric boundary layer formed over the city during the night, preventing convective mixing, whereas during the day effective vertical mixing occurred.[11,14] During four days from August 20−24, 2010, fifteen 4-h samples were taken. A second campaign was performed in winter 2011 during a period with a temperature inversion that resulted in a stable boundary layer lasting for several days at the beginning of the sampling campaign and with day−night fluctuations of the boundary layer at the end of the campaign.[12] During eight days from January 29 to February 6, 2011, sixteen 11-h to 12-h samples were collected. Both sampling campaigns in Zurich, Switzerland, were performed at the sampling station of the Swiss National Air Pollution Monitoring Network (NABEL), located in a large courtyard (approximately 9000 m^2) in the city center (47.38°N, 8.53°E, 409 m above sea level). The median air temperature at the sampling station during the campaign was 22.9 °C (min−max: 16.8−29.7 °C) in summer and −0.9 °C (−3.9−10.8 °C) in winter. High-volume air samplers (flow 500 $L \cdot min^{-1}$) were used to sample particulates on quartz fiber filters and gaseous phase on polyurethane foam plugs. More details about the sampling procedures are given in Müller et al. (2012)[14] and Buser et al. (2013),[12] as well as in the Supporting Information (SI).

Sample Analysis. For each target analyte, the corresponding ^{13}C-labeled analogue was spiked into the samples as an internal standard. After Soxhlet extraction, the extracts were cleaned over several liquid chromatography columns, containing each silica gel, Florisil, alumina, and activated carbon as stationary phases. Analysis was performed by gas chromatography coupled to high-resolution mass spectrometry. Target analytes included the six indicator PCB congeners (PCB-28, 52, 101, 138, 153, and 180) thereafter referred to as iPCBs, the twelve coplanar dioxin-like PCBs (PCB-77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189) denoted dlPCBs, and the seventeen 2,3,7,8-chlorosubstituted PCDD/Fs denoted PCDD/Fs. The analytical procedure, PCB congener numbering, and calculation of PCDD/F toxic equivalents (TEQ) are further specified in the SI.

Analytical Quality Assurance. Regular field and procedural blank samples, fortified field samples, and replicates were analyzed (see SI).

Modeling. The mass balance model is a derivative of the Berkeley-Trent (BETR) contaminant fate modeling framework[15] that has been further developed in previous studies.[8−12,16,17] The model tracks the mass balance of a chemical in a regional environment composed of the compartments atmosphere, soil, vegetation, water, and sediment. The model region includes the area of the city center of Zurich (100 km^2, approximately 400,000 inhabitants). The atmosphere is described using three layers: the stable boundary layer (0−100 m and 0−300 m in summer and winter, respectively), the residual layer (100−1500 m and 300−1000 m in summer and winter, respectively), and the free troposphere (1500−5000 m and 1000−5000 m in summer and winter, respectively). Mass transfer coefficients (in $m \cdot h^{-1}$) are used to describe the air exchange between these layers. Environmental processes in the model include the following: mixing between atmospheric layers; advective inflow and outflow with air; dry particle deposition to water, soil, and vegetation; bidirectional air−water, air−soil, and air−vegetation diffusion; settling of suspended particles in water. In addition, biodegradation in soil, water, vegetation, and sediment and reaction with OH radicals in air are implemented in the model. The temperature-dependent physicochemical properties and degradation half-lives of the target compounds, the environmental parameters describing the city of Zurich, the time-dependent meteorological parameters including atmospheric boundary layer height, temperature, wind speed, and OH radical concentrations, as well as the kinetic parameters describing interphase transport processes of chemicals are derived from empirical studies. Thus, these input parameters are predefined in the model, i.e., these are not adjustable parameters. The concentrations of chemicals entering the model with inflowing air in the three atmospheric layers were defined based at European background air data, as well as own measurements on an urban background site around Zurich (SI).

The only adjustable parameter in the model is the emission rate of the target chemicals into the lower air compartment. The emissions of chemicals in the city were modeled as a temperature-dependent volatilization flux from a hypothetical

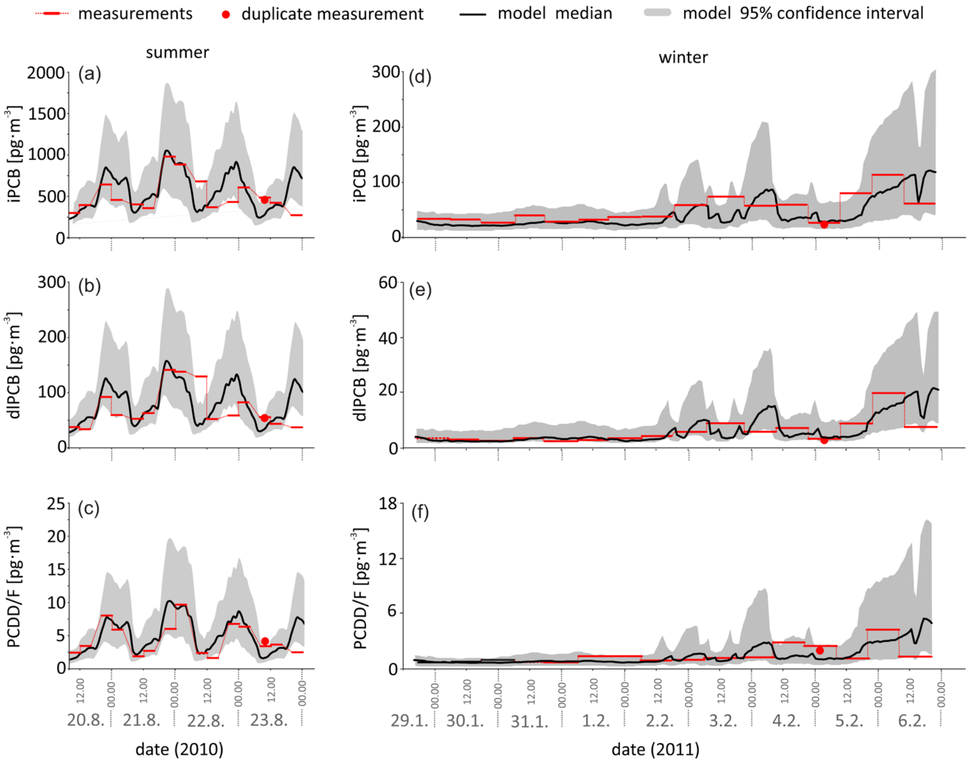

Figure 1. Measured and modeled concentrations of iPCB (a, d), dlPCB (b, e), and PCDD/F (c, f) measured in summer (a−c) and winter (d−f) in the city center of Zurich, Switzerland. The red line, black line, and gray area indicate the measured concentrations, the modeled concentrations, and the 95% confidence interval of the modeled concentrations, respectively. The red dot in each panel (23.8.2010 in summer and 5.2.2011 in winter) shows the result of a duplicate analysis of the corresponding air sample included in the red line. On the *x*-axis, the long tick marks indicate midnight.

pool of pure-phase chemicals. The surface area of this pool was adjusted to determine the chemical emission source strength; for each target chemical, the adjustment was made in such a way that the median of the modeled concentrations in air is equal to the median of the measured concentrations. Further details, including all model parameters, are available in Wang et al. (2012)[11] for the summer conditions and Buser et al. (2013)[12] for the winter conditions. The model parameters specific to this study, including the physicochemical properties and transformation rate constants of PCBs and PCDD/Fs, are presented in the SI.

Model Uncertainty. To assess the uncertainty of the model output due to the uncertainty and variability in model input parameters, a Monte Carlo analysis was performed, assuming all input variables to be independent with their uncertainty and variability described by log-normal distributions. For the Monte Carlo analysis, 1500 discrete runs for each chemical were performed to estimate the range of modeled concentrations and derived emissions resulting from the estimated distribution of input parameters.[18] The techniques used in the uncertainty analysis are described in detail in Wang et al. (2012)[11] for the summer model and Buser et al. (2013)[12] for the winter model.

RESULTS

Measured Concentrations in Ambient Air. Analyte levels determined in duplicate analysis of a field sample, including duplication of the complete analytical procedure, were typically within 20% of each other, and these differences are small compared to variability between samples (see red dots in Figure 1 and SI Tables S7−S8). In summer (Figure 1a−1c), measured concentrations are highest for iPCB (median, min−max: 430, 270−980 pg·m^{-3}), followed by dlPCB (59, 34−140 pg·m^{-3}) and PCDD/F (3.5, 1.6−9.7 pg·m^{-3}). In terms of toxicity equivalents, the median dlPCB concentration is 45 fg WHO98-TEQ·m^{-3} (min−max: 24−160 fg WHO98-TEQ·m^{-3}) and the median PCDD/F concentration is 62 fg WHO98-TEQ·m^{-3} (32−190 fg WHO98-TEQ·m^{-3}) or 44 fg I-TEQ·m^{-3} (25−130 fg I-TEQ·m^{-3}). Concentrations in winter (Figure 1d−1f) are lower for all chemicals but are also highest for iPCB (38, 26−110 pg·m^{-3}) followed by dlPCB (4.2, 2.7−20 pg·m^{-3}) and PCDD/F (0.61, 0.38−2.1 pg·m^{-3}). In terms of toxicity equivalents, the median dlPCB concentration in winter is 2.7 fg WHO98-TEQ·m^{-3} (1.2−7.9 fg WHO98-TEQ·m^{-3}) and the median PCDD/F concentration is 35 fg WHO98-TEQ·m^{-3} (11−100 fg WHO98-TEQ·m^{-3}) or 23 fg I-TEQ·m^{-3} (6.8−61 fg I-TEQ·m^{-3}). The measured concentrations of individual congeners are shown in the SI (Figures S1−S6). For both sampling campaigns the most prominent congeners are PCB-28 and PCB-52 among iPCBs and PCB-118 among dlPCBs. For PCDD/Fs the pattern is slightly different between summer and winter. In summer samples OCDD and OCDF are the dominating congeners, whereas in winter 1,2,3,4,6,7,8-HpCDD is similarly important among PCDD/Fs.

During the two sampling campaigns, distinct temporal patterns are observed. In summer, for all compound classes concentrations show a day−night pattern in the city center with minima occurring during the day and maxima observed during the night. The night-to-day ratio is, on average, a factor of 3. In winter, no day−night pattern is observed for most of the campaign, but all compounds follow a similar trend with concentrations being low during the first five days of the sampling campaign (January 29 to February 2, 2011), followed by slowly increasing concentrations from the sixth to the eighth day (February 3–5, 2011), and maxima on the last night (second last sample on February 5–6, 2011). The peak concentrations at the end of the winter sampling campaign are higher by a factor of 3 compared to the concentrations at the beginning of the campaign.

Modeled Concentrations in Ambient Air. The model results for the median concentrations of iPCBs, dlPCBs, and PCDD/Fs in the boundary layer air compartment are shown in Figure 1 (black lines) with 95% confidence intervals (2.5-to-97.5-percentile range, gray area). The trend of the modeled concentrations is similar to the measurements. For the summer campaign, the model parametrized for summer conditions with the prevailing boundary layer dynamics reproduces the day—night cycle observed in the measurements during the first two sampling days, whereas the model disagrees with the measurements on the last day. For the winter campaign, the model predicts ambient air concentrations that are lowest at the beginning, have an intermediate maximum on the sixth day (February 3–4, 2011), and peak on the last night (February 5–6, 2011). Compared to the summer campaign, in winter the modeled peak concentrations are less consistent with the measurements.

Derived Emissions. Emission rates for Zurich derived from our model calculations for summer and winter are shown in Table 1, together with *per-capita* emissions in Zurich. Emissions of individual congeners are presented in Table 2 for PCBs and Table 3 for PCDD/Fs. Annual emissions in Switzerland are estimated based on two assumptions: (i) emissions remain constant for the summer and the winter half-year; (ii) emissions are directly proportional to the population in Switzerland. The estimates for annual Swiss emissions of iPCBs, dlPCBs, and PCDD/Fs are listed in Table 1.

DISCUSSION

Measured and Modeled Concentrations in Ambient Air. In summer, all target analytes follow a similar day—night cycle of air concentrations that is primarily driven by the boundary layer dynamics prevailing during the sampling campaign. The model provides a mechanistic explanation of this temporal pattern: during the stable high-pressure system in summer, the boundary layer, defined as the part of the atmosphere that comes into contact with the surface within an hour,[19] follows a diel (i.e., day—night) trend. At night, air near the surface has a lower temperature than the air above (temperature inversion), preventing convective mixing. After sunrise, solar radiation heats the ground and, thus, heats the air adjacent to the surface. This heating produces convectional movement of air parcels and leads to the disappearance of the stable boundary layer and vertical mixing of contaminants enriched under the boundary layer with the less-contaminated upper air (dilution).

In winter, the temporal trend is also similar for all compound classes and confirms the expected accumulation of air pollutants below the capping inversion. Winter inversions are common in Zurich when warmer and less dense air moves over cooler air masses and the energy provided from the sun is too low to enable convective mixing. The cooler air masses are trapped in the valley, and the result is colder air near the surface and warmer air at higher altitudes, i.e., inversion of the normal vertical temperature gradient. This stratification of the air masses prevents vertical mixing. In Zurich these temperature inversions can easily be observed by the formation of fog. For air pollutants emitted from the city, including POPs, the

Table 1. Atmospheric Emissions Determined in This Study for Zurich and Switzerland[d]

	summer		winter		combination summer and winter	
	emissions for Zurich in summer 2010	emissions *per-capita* in summer 2010[a]	emissions for Zurich in winter 2011	emissions *per-capita* in winter 2011[a]	emissions *per-capita* in 2010/2011[b]	annual emissions for Switzerland in 2010/2011[c]
iPCBs	71 (41–127) g·d^{-1}	176 (103–318) μg·capita^{-1}·d^{-1}	15 (8.1–28) g·d^{-1}	38 (20–70) μg·capita^{-1}·d^{-1}	107 (61–193) μg·capita^{-1}·d^{-1}	312 (178–564) kg·a^{-1}
dlPCBs	11 (5.8–21) g·d^{-1}	28 (15–53) μg·capita^{-1}·d^{-1}	3.1 (1.6–6.5) g·d^{-1}	7.8 (4.0–16) μg·capita^{-1}·d^{-1}	18 (10–35) μg·capita^{-1}·d^{-1}	53 (29–102) kg·a^{-1}
	7.7 (3.9–14) mg WHO98-TEQ·d^{-1}	19 (10–35) ng WHO98-TEQ·capita^{-1}·d^{-1}	1.3 (0.7–2.8) mg WHO98-TEQ·d^{-1}	3.3 (1.8–7.0) ng WHO98-TEQ·capita^{-1}·d^{-1}	11 (5.7–22) ng WHO98-TEQ·capita^{-1}·d^{-1}	32 (17–64) g WHO98-TEQ·a^{-1}
PCDD/Fs	0.6 (0.3–1.0) g·d^{-1}	1.5 (0.75–2.5) μg·capita^{-1}·d^{-1}	0.2 (0.1–0.6) g·d^{-1}	0.50 (0.25–1.5) μg·capita^{-1}·d^{-1}	1.0 (0.54–2.2) μg·capita^{-1}·d^{-1}	2.9 (1.6–6.4) kg·a^{-1}
	12 (6.5–21) mg WHO98-TEQ·d^{-1}	30 (16–53) ng WHO98-TEQ·capita^{-1}·d^{-1}	13 (7–33) mg WHO98-TEQ·d^{-1}	33 (18–83) ng WHO98-TEQ·capita^{-1}·d^{-1}	31 (16–68) ng WHO98-TEQ·capita^{-1}·d^{-1}	91 (47–199) g WHO98-TEQ·a^{-1}
	8.3 (4.6–15) mg I-TEQ ·d^{-1}	21 (12–38) ng I-TEQ·capita^{-1}·d^{-1}	9.0 (4.5–23) mg I-TEQ ·d^{-1}	23 (11–58) ng I-TEQ·capita^{-1}·d^{-1}	22 (11–47) ng I-TEQ·capita^{-1}·d^{-1}	64 (32–137) g I-TEQ·a^{-1}

[a] Based on a population of *ca.* 400,000 inhabitants in Zurich in 2010/2011. [b] Based on the assumption that emissions are equal to summer emissions for half of the year and equal to winter emissions for the other half of the year. [c] Based on a population of *ca.* 8 million inhabitants in Switzerland in 2010/2011. [d] The provided values are as follows: median (2.5-percentile–97.5-percentile).

Table 2. Calculated *Per-Capita* Emissions of Individual PCB Congeners Determined in This Study in Zurich, Switzerland (Summer and Winter) and Comparison to Available Literature[d]

	"top-down" studies based on combinations of field data and modeling				"bottom-up" studies based on emission inventories and substance flow analyses	
	Zurich, Switzerland summer, 2010[e] this study [μg·capita^{-1}·d^{-1}][a] median (p2.5−p97.5)	Zurich, Switzerland winter, 2011[e] this study [μg·capita^{-1}·d^{-1}][a] median (p2.5 − p97.5)	Zurich, Switzerland summer, 2007[e] Gasic et al., 2009[9] [μg·capita^{-1}·d^{-1}] median (p2.5 − p97.5)	Toronto, Canada spring, 2008[e] Csiszar et al., 2013[32] [μg·capita^{-1}·d^{-1}] mean (mean−SD−mean+SD)	Germany 2001−2013[e] Weber, 2013[38] [μg·capita^{-1}·d^{-1}] min−max	Switzerland 2011[e] Breivik et al., 2007[33] [μg·capita^{-1}·d^{-1}] default (min−max)
PCB-28	54 (30−101)	10 (5.7−21)	2010 (1120−3620)	8.8 (0.5−20)		2.1 (0.04−39)
PCB-52	52 (28−95)	17 (6.8−25)	1200 (660−2150)	4.7 (0.5−8.8)		1.1 (0.02−18)
PCB-101	29 (18−48)	5.7 (3.3−11)	434 (241−781)	2.7 (0.5−4.7)		0.6 (<0.01−10)
PCB-138	16 (9.4−29)	2.6 (1.6−4.9)	109 (61−196)	n.a.		0.4 (<0.01−11)
PCB-153	21 (12−37)	2.3 (1.4−3.8)	173 (96-311)	2.7 (0.5−6.0)		0.5 (<0.01−15)
PCB-180	4.9 (2.9−9.0)	0.84 (0.52−1.6)	14 (7.8−25)	2.2 (0.5−4.9)		0.2 (<0.01−4.3)
iPCBs	177 (103−318)	37 (21−69)	3960 (2200−7120)	21 (2.7−45)[b]	50−82[c]	4.9 (<0.1−98)
PCB-77	5.8 (3.0−11)	0.70 (0.40−1.2)				
PCB-81	1.1 (0.62−2.2)	0.30 (0.16−0.58)				
PCB-105	4.1 (2.3−7.6)	1.4 (0.60−4.0)				
PCB-114	0.41 (0.24−0.75)	0.14 (0.07−0.39)				
PCB-118	14 (8.0−26)	4.1 (2.3−8.0)				
PCB-123	0.61 (0.35−1.1)	0.14 (0.08−0.29)				
PCB-126	0.14 (0.08−0.25)	0.02 (0.01−0.03)				
PCB-156	0.79 (0.46−1.4)	0.57 (0.27−1.5)				
PCB-157	0.18 (0.10−0.34)	0.05 (0.03−0.08)				
PCB-167	0.60 (0.33−1.1)	0.08 (0.05−0.20)				
PCB-169	0.19 (0.09−0.37)	0.08 (0.05−0.21)				
PCB-189	0.11 (0.06−0.21)	0.03 (0.01−0.08)				
dlPCBs	28 (16−53)	7.6 (4.0−17)				

[a] Based on a population of *ca.* 400,000 inhabitants in Zurich in 2010/2011. [b] Sum of PCB congeners 28, 52, 101, 153, and 180. [c] Based on a population of 80 million inhabitants in Germany and based on the assumption that emissions of iPCBs are five times lower[41] than the sum of all PCB congeners (the authors report an emission factor of 0.06% per year from the remaining German PCB inventory representing 12,000−19,000 t, resulting in *per-capita* emissions of all PCB congeners of 250−410 μg·capita^{-1}·d^{-1}). [d] p2.5: 2.5-percentile of modeled emission distribution; p97.5: 97.5-percentile of modeled emission distribution; SD: standard deviation; n.a.: not analyzed. [e] Season, year.

temperature inversion results in an accumulation of pollutants in the stable boundary layer. During our winter campaign, the capping inversion was initially at high altitude but continuously went down to lower altitudes during the eight-day sampling period. Throughout the first five days, the inversion remained stable, whereas during the last three days the solar heating became stronger and the inversion partly followed a day−night pattern with weakening or dissolution of the boundary layer during the day.

The concentrations of iPCBs and dlPCBs measured in Zurich are higher by almost an order of magnitude in summer than in winter. Compared to previous measurements of iPCBs performed in Zurich in summer 2007,[9] the concentrations are lower by a factor of 3. However, compared to measurements performed over different seasons in 2005−2006 in the rural region of Lake Thun, Switzerland (min−max: 2−66 pg·m^{-3}),[20] to a single measurement in summer 2006 at a rural site in Payerne, Switzerland (39 pg·m^{-3}), and at the high Alpine research station Jungfraujoch (22 pg·m^{-3}), Switzerland,[21] or to remote background air analyzed in fall 2005 over the North Atlantic Ocean (mean ± standard deviation: 50 ± 52 pg·m^{-3}),[22] concentrations are higher in Zurich by at least a factor of 2, indicating that the highly urbanized area of Zurich still is a source of PCBs to ambient air. Concentrations of dlPCBs in Zurich are also higher than previously reported: in the major cities in North Rhine-Westphalia, Germany (min−max: 7−9 fg WHO05-TEQ·m^{-3})[23] and at urban sites in Rome, Italy (min−max: 1−7 fg WHO98-TEQ·m^{-3}),[24] dlPCB concentrations were lower than in Zurich.

PCDD/Fs concentrations in Zurich are slightly lower in winter than in summer but in a very similar range in terms of toxicity equivalents (min−max: 32−190 and 11−100 fg WHO98-TEQ·m^{-3} in summer and winter, respectively). Previous studies have reported concentrations of PCDD/Fs in the same range as measured in Zurich. Levels in Zurich are higher than the concentrations in major cities in North Rhine-Westphalia, Germany (min−max: 20−27 fg I-TEQ·m^{-3}, 17−24 fg WHO05-TEQ·m^{-3})[23] and in major cities in the UK (min−max: 1−60 fg WHO98-TEQ·m^{-3}).[25] Levels in Zurich are, however, lower than measured at urban and rural sites in Catalonia, Spain (min−max: 5−1196 fg I-TEQ·m^{-3}),[26] at urban and industrial sites of the Malopolska region, Poland (min−max: 40−3200 fg WHO98-TEQ·m^{-3}, 37−2900 fg I-TEQ·m^{-3}),[27] and in urban sites in Rome, Italy (min−max: 5−734 fg WHO98-TEQ·m^{-3}).[24]

For both sampling campaigns, the modeled temporal trends of all substances are consistent with the measurements. It is important to point out that the time trend of the modeled concentrations of air pollutants results from the parametrization of the model, including the prescribed meteorological and environmental input data, as well as the physicochemical properties and degradation rate constants of the chemicals. In other words, the modeled time trend does not result from fitting the model to the measurements. The similar trend of the model and the measurements indicates that in our model relevant environmental processes governing the fate of POPs in the city environment are captured. However, there are also several factors that influence the measured concentrations but

Table 3. Calculated *Per-Capita* Emissions of Individual PCDD/F Congeners Determined in This Study in Zurich, Switzerland (Summer and Winter)[a]

	Zurich, Switzerland summer 2010 [μg·capita^{-1}·d^{-1}] median (p2.5–p97.5)	Zurich, Switzerland winter 2011 [μg·capita^{-1}·d^{-1}] median (p2.5–p97.5)
2,3,7,8-TCDD	0.008 (0.005–0.016)	0.008 (0.005–0.016)
1,2,3,7,8-PeCDD	0.008 (0.005–0.017)	0.005 (0.002–0.011)
1,2,3,4,7,8-HxCDD	0.008 (0.005–0.013)	0.011 (0.005–0.031)
1,2,3,6,7,8-HxCDD	0.012 (0.007–0.023)	0.008 (0.004–0.020)
1,2,3,7,8,9-HxCDD	0.012 (0.007–0.022)	0.010 (0.006–0.026)
1,2,3,4,6,7,8-HpCDD	0.036 (0.022–0.064)	0.104 (0.058–0.207)
OCDD	0.589 (0.343–1.097)	0.224 (0.107–0.627)
2,3,7,8-TCDF	0.020 (0.011–0.041)	0.053 (0.021–0.164)
1,2,3,7,8-PeCDF	0.008 (0.005–0.017)	0.012 (0.007–0.033)
2,3,4,7,8-PeCDF	0.005 (0.003–0.009)	0.012 (0.007–0.023)
1,2,3,4,7,8-HxCDF	0.019 (0.009–0.040)	0.013 (0.007–0.037)
1,2,3,6,7,8-HxCDF	0.007 (0.004–0.013)	0.007 (0.005–0.013)
1,2,3,7,8,9-HxCDF	0.007 (0.005–0.015)	0.008 (0.004–0.020)
2,3,4,6,7,8-HxCDF	0.007 (0.004–0.012)	0.005 (0.002–0.012)
1,2,3,4,6,7,8-HpCDF	0.088 (0.046–0.172)	0.032 (0.016–0.078)
1,2,3,4,7,8,9-HpCDF	0.032 (0.017–0.064)	0.036 (0.013–0.107)
OCDF	0.522 (0.284–0.989)	0.064 (0.035–0.151)
PCDD/Fs [μg·capita^{-1}·d^{-1}]	1.5 (0.75–2.5)	0.50 (0.25–1.5)
PCDD/Fs [ng WHO98-TEQ·capita^{-1}·d^{-1}]	30 (16–53)	33 (18–83)
PCDD/Fs [ng I-TEQ·capita^{-1}·d^{-1}]	21 (12–38)	23 (11–58)

[a] p2.5: 2.5-percentile of modeled emission distribution. p97.5: 97.5-percentile of modeled emission distribution

are not represented in the model. In summer, a difference between field measurements and model can be observed at the end of the sampling period (August 23, 2010): the model predicts a continuation of the day–night cycle, whereas the measurements do not show an increase in concentrations. Besides the uncertainty in the measurements, this discrepancy is probably due to changing weather conditions. On the last day of the campaign, a thundery front approached Zurich and it began to rain. These turbulent conditions resulted in a break-up of the stable boundary layer and of the regular concentration cycling that was not captured by the model. Although advective inflow/outflow is considered in the model, the available wind speed data from several measurement stations are not necessarily representative of the whole city. In winter, advection may also be a reason for the divergence between measured and modeled concentrations on some days, particularly in the middle (February 3–4, 2011) and at the end of the sampling campaign (February 5–6, 2011). Wind speed was higher in winter than in summer, resulting in less stable conditions that are not captured by the model.

Derived Emissions. The calculated emission rates are higher in summer than in winter by a factor of 4.7, 3.7, and 2.3 for iPCBs, dlPCBs, and PCDD/Fs, respectively. Especially for PCBs, the summer-to-winter ratio shows that emissions are temperature-dependent. PCBs are likely emitted to a large extent from volatilization from outdoor applications directly affected by ambient air temperatures, such as PCB-containing joint sealants or paints in buildings constructed in the 1950–1970s when usage of PCBs peaked.[28] Considering the average temperature difference of 23.8 °C between the two sampling campaigns, the temperature effect on the vapor pressure of PCBs is a factor of 17 (based on an enthalpy of vaporization of 80,000 J·mol^{-1}; see calculation in the SI). The lower PCB summer-to-winter ratio of 4–5 may, therefore, indicate that not all PCBs emissions derive from sources that are subject to the full seasonal temperature change. Thus, emissions from indoors with little seasonal temperature variation followed by room ventilation may also contribute to PCB contamination in ambient air.

PCDD/Fs have a smaller difference between summer and winter emissions. This finding might be best explained by the combustion-related sources of PCDD/Fs that are active throughout the whole year. Whereas open burning (e.g., garden fires) may be more frequent in summer than in winter, heating may be an additional source of PCDD/Fs in winter.[29,30] In the SI (Figure S7) PCDD/F congener patterns of summer and winter air are compared with typical PCDD/F patterns presented in the literature. Possibly, combustion processes are slightly more important in winter than in summer, as indicated by marker congeners, such as 1,2,3,4,6,7,8-HpCDD. Interestingly, the OCDF contribution is significantly increased in winter. The reason for this pattern is still unclear; however, sewage sludge monitoring performed in Switzerland also revealed an increasing abundance of OCDF during the last years.[31] Possibly, the contribution of waste incineration (leading mainly to OCDD) decreased due to efficient exhaust gas filtering techniques installed in Switzerland during the last decades, resulting in other PCDD/F sources such as illegal waste burning gaining in relevance (see below).

Table 2 provides a comparison between our estimates of Swiss emissions of PCB congeners with emission assessments found in other top-down studies,[9,32] as well as derived from a bottom-up global emission inventory.[33] In summer 2007, emissions of iPCBs[9] were determined based on the same approach of measurements combined with modeling. The *per-capita* emissions of iPCBs determined for Zurich in summer 2007 are higher than in our study in summer 2010 by approximately a factor of 20, which can be attributed to different factors. First, concentrations of iPCBs in ambient air were on average 2.6 times higher in the previous study compared to the current investigations, which resulted in higher emission rates for 2007. Therefore, the decrease in the measured levels of iPCBs in air between the two studies may be partly attributable to a reduction of PCB sources within these three years; however, it could also reflect the different sampling locations used in the studies. Measurements of PCBs in Toronto, Canada,[34] Philadelphia, US,[35] and Birmingham, UK,[36] revealed spatial variability of ambient air concentrations of up to an order of magnitude, but these measurements were performed with passive air samplers that are less accurate than active air samplers, and these metropolitan areas are 10–100 times larger than the city center of Zurich, thus including a considerably larger variability of population density and diversity of human activities. In the latter studies, the sampling sites were also intentionally selected to cover different urbanization types. In our study performed in Zurich in 2007,[9] samples were taken on the roof of a building in central Zurich, which is only 1300 m away from the NABEL courtyard where we sampled air in 2010 and 2011.

An additional and probably more important factor is that the surface area of the model region is different in the two studies. In the previous study an area of 1000 km^2 was modeled, which is eleven times larger than the city of Zurich (92 km^2) and which included the urban agglomeration as well as rural areas around Zurich.[9] The population within this area (approximately 1 million inhabitants) is, thus, less dense (1000 inhabitants·km^{-2}) than in the current study where the total surface area of the model region was set to 100 km^2, covering only the most densely populated area (4000 inhabitants·km^{-2}) of the city of Zurich (approximately 400,000 inhabitants). We believe that the large model area used in the 2007 study was not well-represented by a single sampling site in the city center, and thus the study probably overestimated the total emissions from the city of Zurich for iPCBs by a factor of 4 (ratio of population densities: 4000/1000). Finally, for the calculation of *per-capita* emissions Gasic et al. (2009)[9] related their total emission rate obtained for the large area of 1000 km^2 to the population of the city of Zurich of 400,000 inhabitants (instead of the actual population of 1 million inhabitants in the 1000 km^2 model area). This caused an additional factor of 2.5 by which the *per-capita* emissions reported in the 2007 study are too high. Altogether the difference in iPCB *per-capita* emissions in the previous study[9] due to the different model area considered, the lower population used in the calculations, as well as the higher concentrations observed in air samples is likely a factor of 26 (= 2.5 · 4 · 2.6), which corresponds well with the factor of 20 observed between *per-capita* emissions derived in the two studies.

A top-down study was performed in Toronto, Canada, based on air measurement combined with a spatially resolved model and exploiting also an inventory of PCBs.[32] *Per-capita* emissions of iPCBs derived for Toronto in spring 2008 were lower than in our current study in Zurich by a factor of 5. Interestingly, the emissions derived by Csiszar et al. (2013)[32] with the spatially resolved model for Toronto (44–520 μg·capita^{-1}·d^{-1}, sum of 88 PCB congeners) are very close to the emissions estimated by Diamond and co-workers[37] with a single-region model (96–960 μg·capita^{-1}·d^{-1}, sum of 70 PCB congeners) for the same set of measured PCB concentrations. This comparison indicates that the spatial variability of ambient air concentrations is probably of minor relevance in the case of persistent pollutants, such as PCBs, which have atmospheric residence times that are long enough to cause considerable mixing within the domain described by our model.

For iPCBs, Breivik and co-workers (2007)[33] compiled a comprehensive bottom-up emission inventory, reporting emissions of 14 kg·a^{-1} (min–max: <1–279 kg·a^{-1}) or 4.9 μg·capita^{-1}·d^{-1} (0.1–98 μg·capita^{-1}·d^{-1}) for Switzerland in 2011. According to Breivik et al. (2007),[33] the minimum emission values underestimate the real emissions significantly and probably the maximum values are closer to the reality. Our study confirms this assumption, as our median emission estimates for Switzerland (Table 1) are very close to the maximum emission estimates from Breivik et al. (2007).[33] Also *per-capita* emissions derived from recent estimates by Weber (2013)[38] for Germany (50–82 μg·capita^{-1}·d^{-1}), based on an emission inventory performed for selected PCB-containing buildings and extrapolated to a national inventory (total emissions from buildings in Germany estimated at 7000–12000 kg·a^{-1}), are very close to our *per-capita* emissions for Switzerland.

Several countries that are signatories of the POP Protocol of the UNECE Convention on LRTAP do not report PCB emissions, which is unjustified considering the substantial emissions reported in numerous scientific studies.[4] Austria, Denmark, Belgium, Spain, and Switzerland do not mention PCBs in their report submitted to the UNECE Convention on LRTAP, whereas other countries assessing PCBs report emissions ranging from <1 μg·capita^{-1}·d^{-1} (Cyprus, Sweden) up to 279 μg·capita^{-1}·d^{-1} (Serbia) (Table S16, SI). Regarding the very low PCB emission estimates, Sweden for instance mentions the following: “PCB is only estimated for national navigation and national fishing”.[39] In light of the *per-capita* emissions of 10–100 μg·capita^{-1}·d^{-1} back-calculated from Zurich (this study) and Toronto,[32] and derived from the global PCB emission inventory,[33] most national emission estimates submitted to the UNECE Convention on LRTAP have to be viewed with caution and are probably too low. Even though PCBs have been banned in many countries including Switzerland for several decades, our study reaffirms the relevance of ongoing sources today. It is estimated that of the 1.3·10^6 metric tons of historically produced PCBs worldwide about 1–10% have already been emitted to air, and 10–20% are still in use.[33] In addition, from the remaining 50–70% of total PCBs that are assumed to have been disposed of, the majority has been transferred to landfills and may, thus, still be available for future emissions to air or water. Also Weber (2013)[38] reported large remaining stocks of PCBs in buildings in Germany and estimated that only 0.06% of PCBs are emitted annually through volatilization. The stock of PCBs in Switzerland still present in joint sealants of buildings has been estimated to be 50–150 t in 2000.[28] Considering the emissions of a few hundreds of kilograms of PCBs per year for the whole of Switzerland, as derived from our study (Table 1), the existing stock of PCBs in joint sealants alone is theoretically sufficient to supply these emissions for decades to centuries.

To our knowledge, no emission estimates are available for dlPCBs based on a method similar to our top-down approach and enabling a comparison to our results. If we compare our TEQ emission estimates of dlPCBs in Switzerland with our emission estimates of PCDD/Fs, it appears that both compound classes contribute similarly to TEQ emissions with a slightly higher relevance of PCDD/Fs.

The emissions of PCDD/Fs derived from our study (Table 3) can be compared to emission estimates for Switzerland under the POP Protocol of the UNECE Convention on LRTAP. For 2011, Switzerland reports PCDD/F emissions of 13 g I-TEQ·a^{-1} (min–max: 6.5–26 g I-TEQ·a^{-1}, based on an uncertainty of 50% indicated by the authors), i.e., 4.5 ng I-TEQ·capita^{-1}·d^{-1} (2.2–6.4 ng I-TEQ·capita^{-1}·d^{-1}),[40] which is five times lower than the median emissions we obtain from our calculations and also outside the 95% confidence interval of our calculated emissions. This comparison indicates that the Swiss emission inventory may not capture all relevant sources of PCDD/Fs, or the emission rates of the considered sources may be underestimated. In the 2011 emission inventory,[40] Switzerland attributes PCDD/F emissions mainly to energy production by controlled burning, including municipal and hazardous waste incineration (42%). Illegal waste incineration is considered as the second most important source of PCDD/Fs in Switzerland (28%). Additional sources included in the inventory are small fire damages, including house and motor vehicle fires (18%), industrial processes, including metal foundry and battery recycling (10%), and agriculture (<2%). Zurich has two municipal solid waste incineration plants (MSWI) directly located in the city center (MSWI Josefstrasse and MSWI Hagenholz). Two additional incineration plants (MSWI Dietikon and MSWI Horgen) are located in the region around Zurich, i.e., outside the model region (100 km^2) but only at 11 and 15 km from the city center, respectively. The MSWI plants in the city center release about $5\cdot10^6$ $m^3\cdot d^{-1}$ ($2\cdot 10^5$ $m^3\cdot h^{-1}$) flue gases. Considering emissions of PCDD/Fs with flues gases of a modern MSWI plant under normal operating conditions of 0.01−0.1 ng I-TEQ·m^{-3} (own data, unpublished), the MSWI plants in the city center release 0.05−0.5 mg I-TEQ·d^{-1} (18−180 mg I-TEQ·a^{-1}), i.e., less than 4% of total PCDD/F emissions calculated for Zurich. However, during powering-up and shutting-down of an MSWI plant, emissions can be much higher and flue gas concentrations can reach 100 ng I-TEQ·m^{-3}. Therefore, a single hour of powering-up/shutting-down results in emissions of 20 mg I-TEQ·h^{-1}. Because a powering-up/shutting-down operation lasts a few hours and is performed several times per year, these special procedures result in emissions exceeding by far the continuous emissions under normal conditions. These non-routine emissions are not included in emission inventories and also monitoring of emission compliance of MSWI plants does not consider these emission peaks. This comparison indicates that in the Swiss PCDD/F emission inventory, emissions from controlled waste incineration under normal operating conditions are probably not underestimated, whereas single emission events may need additional attention. Further sources of PCDD/Fs should also be reviewed in the emission inventory. Illegal waste burning in private fireplaces and backyards is very difficult to quantify and control and may represent an underestimated PCDD/F source. During the past decade the number of wood firing facilities has also increased in Zurich, as they represent alternatives for sustainable heating energy. Other European countries might underestimate atmospheric PCDD/F emissions as well. Under the UNECE Convention on LRTAP, the 27 countries in the European Union estimate their PCDD/F emissions in 2010 as 1568 g I-TEQ·a^{-1}, which based on a population of $5\cdot10^8$ inhabitants is equivalent to 8.6 ng I-TEQ·$capita^{-1}\cdot d^{-1}$, i.e., two to three times lower than our emission calculations.[4]

The combination of field measurements and modeling applied in this study proved to be a useful approach to back-calculating atmospheric emissions of semi-volatile pollutants. The top-down approach has the considerable advantage that it is independent of data on chemical production volumes and information on use patterns, which is often confidential or hardly available and subject to large uncertainties. An additional advantage of our method is that a range of compound classes can be targeted at once. Furthermore, our study provides for the first time emission rates for two opposite seasons and shows that the source strength is related to temperature but to a lesser extent than predicted from temperature-dependent volatilization rates. A limitation is, however, that the results are valid for the period and location of the field measurements only and spatial variability within the model region is not captured. Additionally, top-down studies do not provide information about the type of sources emitting the investigated pollutants.

The PCB emissions quantified in our study compare well with available literature data using similar methods or based on bottom-up approaches. These results highlight the relevance of continuous emissions by diffuse sources and call for more attention. Although regulated, the investigated compounds are still emitted at appreciable rates by remaining sources due to the persistent nature of the chemicals and the long lifetime of their applications. For PCDD/Fs, emissions are possibly underestimated by many countries. For PCBs, many countries severely underestimate or neglect their emissions.

The adoption of the Stockholm Convention on POPs in 2001 and its entry-into-force in 2004 was an important step toward an elimination of persistent chemicals such as PCBs. Currently, the Stockholm Convention obliges the Parties to the Convention to discontinue the use of PCB-containing equipment by 2025 and eliminate PCBs using environmentally sound waste management by 2028. Reaching these goals will require a strong commitment from all countries.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Information on sample collection and analysis, model parametrization, measured/modeled concentrations and emission rates of target substances, temperature-dependence of vapor pressure, and emission data reported under the UNECE Convention on LRTAP. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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