EMISSION SOURCE STRENGTH OF POLYCHLORINATED BIPHENYLS IN ZURICH: A COMBINATION OF LONG-TERM MEASUREMENTS AND MODELING

Diefenbacher P[1,2]*, Bogdal C[1], Gerecke A C[2], Schmid P[2], Scheringer M[1], Hungerbuehler K[1]

[1]Swiss Federal Institute of Technology Zurich (ETH Zurich), Vladimir-Prelog-Weg 1, CH-8093 Zürich, Switzerland; [2]Swiss Federal Laboratories for Materials Testing and Research (Empa), Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

Introduction

Polychlorinated biphenyls (PCBs) were widely used as dielectrics in electrical devices and as plasticizers in a variety of materials. Due to their persistence, global distribution and environmental toxicity, PCB usage was banned in most industrialized countries by the late 1970s. Nevertheless, due to the long use phase of their former applications, PCBs are still present in the environment. Especially in urban areas, large PCB stocks still exist and a substantial reduction of emissions in the nearer future is not foreseeable[1].

Several international conventions pursue the goal to identify and quantify PCB emissions, such as the UNECE Convention on LRTAP. As a result of the poor knowledge about effective emissions, several signatory countries, including Switzerland, did report that national emission inventories are unknown.

To overcome this knowledge gap, several studies were performed in the city of Zurich, Switzerland[2]. By combining field measurement during stable weather conditions with a multimedia mass balance model, the short-term variability of PCB air concentrations could be explained. Based on the observation that contaminants get enriched under a stable atmospheric boundary layer, total emissions of the city were estimated.

A drawback of these studies is that they are based on short-term measurements during a specific stable weather situation. As these measurements indicated that PCB air concentrations show a strong seasonal variability, it is unclear whether resulting emissions are suitable to extrapolate total annual emissions. In this work, a long-term dynamic multimedia model was developed. The goal of this model was to reproduces the diurnal and seasonal variability of PCB air concentrations. To account for ambient conditions, meteorological parameters such as temperature, wind speed and boundary layer height were collected hourly. The combination of continuing air measurement during three years at one location within Zurich and this long-term model allowed us to validate the developed model. Furthermore, we were able to determine the annual source strength of urban PCB emissions.

Materials and methods

Air sampling: Passive air samplers equipped with polyurethane foam (PUF) disks were deployed from March 2011 to December 2013 in the city center of Zurich, Switzerland, (Kasernenhof, E 8°31'49'', N 47°22'39''). Thereby the PUF disk were housed in stainless steel housings[3] and equipped with an anemometer to measure wind speed. The samples were collected after 6 weeks and replaced with pre-cleaned PUF disks.

Before Soxhlet extraction, PUF samples were spiked with isotope-labeled internal standards. The extracts were cleaned by column chromatography on acidic silica gel and separated into two fractions using deactivated Florisil. Quantification of analytes (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180) was performed using a gas chromatograph coupled to a high resolution mass spectrometer (GC-HRMS). PCB-70 was used as a recovery standard. Field blanks, method blanks and sample replicates were used for quality assurance. To determine the daily air sampling rate (SR), an active high volume air sampler was installed next to the passive air sampler. Calculated sampling rates were in the range of 3.2 - 5.5 m^3 air per day for all PCB congeners. According to literature[3], an average of 4 m^3 was used for all congeners to enable comparison with existing data.

Modeling: The model represents the densely populated area of the city of Zurich (100 km^2, approx. 400'000 inhabitants) and consists of different environmental compartments. Besides soil, vegetation, water and sediment, it includes three atmospheric sub-compartments[2,4]. Using meteorological parameters, the heights of these

atmospheric layers were adjusted diurnally. Mass exchanges between compartments are described by mass transfer coefficients (m/h). To determine advective air transport, wind speed was taken as the average from four nearby stations. Further important environmental parameters are: deposition of particles in air and water, diffusive air-water, air-soil and air-vegetation exchanges, and losses into the deep sediment and the free atmosphere. Reactions with OH radicals in air were determined by a time-dependent forcing function. The emission rate of the PCBs in the city was modeled as a temperature-dependent volatilization flux from a hypothetical pool of pure chemical and was used to fit the model to the measurement data by visual inspection.

Results and discussion

Measured air concentrations: Figure 1 shows PCB air concentrations and mean air temperatures in the city center of Zurich. The measurements cover the years 2011 to 2013 with deployment periods of six weeks. Air temperature varies between an average of 0.9 °C in December 2011 and 20.5 °C in July 2013. The PCB air concentrations show a consistent seasonal trend with highest concentrations in July 2012 (240 pg/m^3) and lowest concentrations in February 2012 (57 pg/m^3).

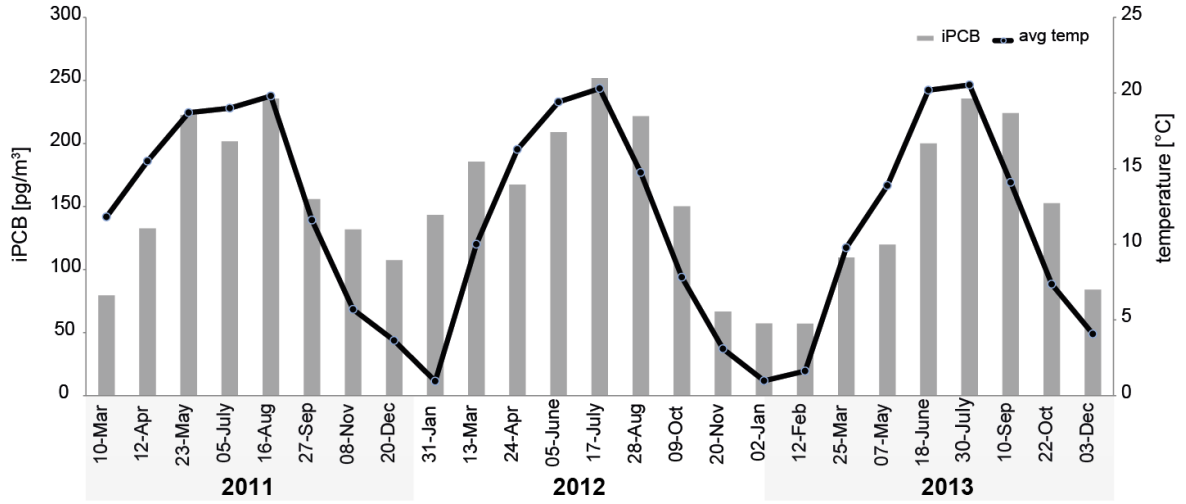

Figure 1: Measured air concentrations of PCBs from March 2011 to December 2013 in the city center of Zurich, Switzerland. The gray bars represent average air concentrations as sum of the six indicator PCBs; the black line indicates the average air temperature for each sampling period.

Summer air concentrations were approximately 3-5 times higher than concentrations during winter months. This seasonal behavior can be explained by vapor pressure, leading to increased vaporization of PCBs at higher temperatures. The strong effect of temperature on air concentration indicates the existence of local PCB reservoirs which can act as sources to the atmosphere[5]. Nevertheless, the temperature effect on vapor pressure cannot fully explain this seasonal variability, as it would lead to much higher differences between winter and summer. Therefore, a long-term mass balance model was used to reproduce the seasonality.

Parameterization of the long-term model: Previous short-term studies showed a strong day-night cycle of air concentrations during stable weather conditions, caused by boundary layer dynamics. During the day convective mixing is driven by ascending air from the heated ground. At night, air layers near the surface cool down much faster leading to a temperature inversion, which prohibits convective mixing. Descending boundary layers during night lead to an enrichment of contaminants in the lower air and prevent dilution with the less-contaminated upper air. Therefore, air concentrations usually increase during night. During a typical summer day, energy provided by the sun is sufficient to re-enable convective mixing. In winter the solar energy is much lower and therefore cooler air masses can be trapped near the soil, preventing vertical mixing. Such winter inversions are

quite common in Zurich and can lead to elevated air concentrations of contaminants over longer time periods. Our model considers varying mixing heights throughout the year by determining individual daily mixing heights from meteorological data. Another crucial factor is the PCB concentration in air entering the model through advection. These concentrations are based on own measurements at background sites around Zurich.

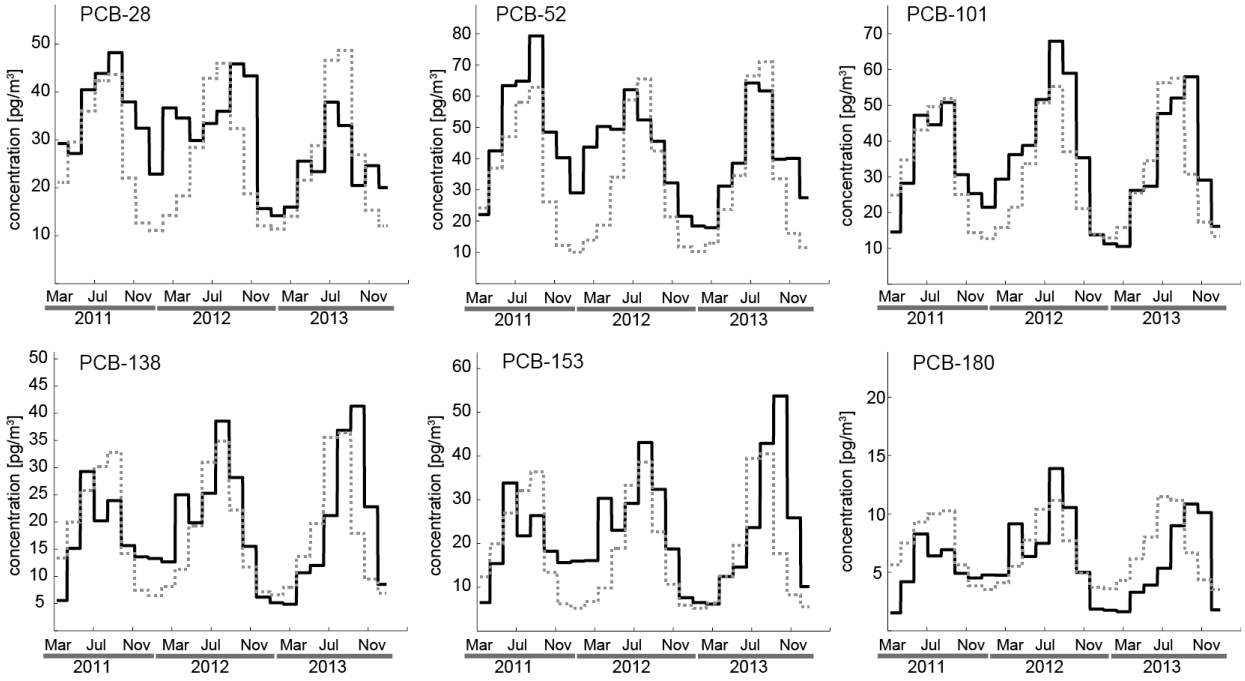

Figure 2: Measured and modeled air concentrations of PCB congeners at Zurich from March 2011 to December 2013. The solid line (-) represents the measured average air concentration over 6 weeks. The dotted line (···) shows the model results averaged over identical time periods.

Validation of the model: Figure 2 compares measured PCB air concentrations with results from the long-term mass balance model. Since modelled air concentrations have an hourly resolution, results were averaged over the relative sampling periods. Emission source strength into the lower atmosphere is the only adjustable parameter in this model. Therefore, it was used to fit the model output to measurements. Importantly, this fitting procedure only shifts absolute concentrations and does not affect the seasonal trend.
Measured and modeled air concentrations show a very good agreement over the whole sampling time. Only in winter 2011/2012 our model underestimated the air concentrations. The adaptability of this long-term model on PCB congeners with a broad range of physicochemical properties supports the assumption that the most relevant environmental parameters were integrated into the model and provides confidence in model outputs.

Determination of source strength: Previous studies determined PCB emission during short time periods, resulting in 4-5 times higher emission during summer[2]. For the first time, this long-term model quantifies daily emissions throughout the year and therefore allows a well-founded estimation of annual emissions. Table 1 shows model results for individual PCB congeners. To compare them with literature values, daily emissions were averaged and normalized to the population in the study area. Additionally, the minimum and maximum values of daily emissions are listed to demonstrate the substantial differences between a winter day with an average temperature of -10 °C and a summer day with +28 °C. Compared to recent emission estimates for Zurich, our results for single PCB congeners were always between summer and winter emissions. For PCB-28, 52, 101, and 180, annual mean emissions were closer to the winter values, whereas emissions of PCB-138 and 153 corresponded more to the data from the summer campaign.

Table 1: Calculated emissions of individual PCB congeners and comparison to available literature. Per capita Emissions are based on a population of 400'000 inhabitants in the city of Zurich.

	this study	literature			
	Zurich, Switzerland [µg·capita^{-1}·d^{-1}] 2011-2013 annual mean (daily min-daily max)	**Zurich, Switzerland[2] [µg·capita^{-1}·d^{-1}] summer 2010 median (range)**	**Zurich, Switzerland[2] [µg·capita^{-1}·d^{-1}] winter 2011 median (range)**	**Switzerland[6] "bottom-up" [µg·capita^{-1}·d^{-1}] 2011 default (min-max)**	**Toronto, Canada[7] [µg·capita^{-1}·d^{-1}] spring 2008 mean (mean-SD-mean+SD)**
PCB-28	12 (0.5-63.3)	54 (30-101)	10 (5.7-21)	2.1 (0.04-39)	8.8 (0.5-20)
PCB-52	21 (0.7-117.4)	52 (28-95)	17 (6.8-25)	1.1 (0.02-18)	4.7 (0.5-8.8)
PCB-101	14.1 (0.4-82.3)	29 (18-48)	5.7 (3.3-11)	0.6 (<0.01-10)	2.7 (0.5-4.7)
PCB-138	10.2 (0.3-62.8)	16 (9.4-29)	2.6 (1.6-4.9)	0.4 (<0.01-11)	n.a.
PCB-153	12.1 (0.2-84.4)	21 (12-37)	2.3 (1.4-3.8)	0.5 (<0.01-15)	2.7 (0.5-6.0)
PCB-180	2.1 (0.04-14.7)	4.9 (2.9-9)	0.84 (0.52-1.6)	0.2 (<0.01-4.3)	2.2 (0.5-4.9)
Sum PCBs	71.6 (2.1-424.9)	177 (103-318)	37 (21-69)	4.9 (<0.1-98)	21 (2.7-45)

Compared to the data derived from emission inventories, our data were quite close to the maximum values. This supports the assumption of Breivik and coworkers that the maximum emission scenario is the most appropriate[6]. Our data can be compared to a study in Toronto, Canada[7], based on a similar approach. Emissions derived for Toronto in spring 2008 were quite similar for PCB-180 and up to a factor 5 lower for other congeners.

Conclusion

The combination of measurements and modeling proved to be a powerful tool to assess emission rates of chemicals that are diffusely emitted from poorly-characterized sources. For the first time, our study back calculates atmospheric emissions on the basis of long-term measurements. This has the advantage that seasonal variability is included and the uncertainty of predicted annual emissions is lower. Our study clearly confirms the continuing emission of PCBs in urban areas[1]. Beside PCBs, an application to other semi-volatile organic compounds is planned.

Acknowledgements

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