

# Soil Burdens of Persistent Organic Pollutants: Their Levels, Fate, and Risks. Part IV. Quantification of Volatilization Fluxes of Organochlorine Pesticides and Polychlorinated Biphenyls from Contaminated Soil Surfaces

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A volatilization chamber, designed for direct measurements of the soil-air exchange of persistent organic pollutants (POPs) was applied for determination of the volatilization fluxes of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). The volatilization fluxes were determined for 13 model compounds at 3–5 concentration levels, for two soil organic carbon contents, and two wind velocities. The flux values were strongly correlated with physicochemical properties of the compounds. The higher fluxes were measured for soils with lower organic carbon contents, for higher contamination, and higher wind velocities. Experimentally derived values were compared to those predicted by the fugacity model. In general, the fugacity model underestimated the volatilization fluxes, especially for the compounds with higher molecular weights, and soils with higher organic carbon contents. It has been demonstrated that variability of the wind velocities as an important parameter for quantification of the soil-air exchange should be better considered in current models. Presented results draw the attention to often overlooked secondary sources of the atmospheric pollution and point out that their impact can be much greater than indicated by the fugacity models.

## Introduction

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) as persistent, bioaccumulative, and toxic (PBT) substances present a risk to the environment. To reduce their potential to cause environmental and human harm, national and international controls on their production and use (such as the Stockholm Convention (SC) on persistent organic pollutants (POPs) (1)) have been introduced. To develop an effective control mechanism, more information on their sources, distribution, levels, and transport is needed. Signatory countries of the SC are, among others, required to conduct source inventories including inventories of the old

burdens. An impact of such sources on the quality of atmosphere has to be assessed since soil-air exchange is known to be one of the key processes controlling levels of POPs in ambient air. Previous studies (2, 3) have shown that soil can act as a sink for POPs (4) or, in contrast, as a secondary source emitting POPs to atmosphere (4, 5). It means that volatilization is an important mechanism of PCB (6–10) and OCP (11–14) losses from soils. An extent of surface volatilization is influenced by soil concentrations of POPs and their physicochemical properties, the amount and quality of soil organic matter, sand, silt, and clay, as well as by climatic conditions such as wind speed, temperature, precipitation, or air humidity (9, 12, 13, 15–17).

Although secondary sources probably play a major role in global distribution of PCBs and legacy pesticides, model inventories of atmospheric emissions are often based on the emission factors derived from direct measurements of the primary sources (18) while emissions from the secondary sources are not included. As a result, atmospheric concentrations predicted by distribution models may be significantly underestimated. This is a case of the EMEP MSC-East model (19, 20), which is based on emissions from the main categories of industrial sources and does not take into account revolatilization from soils and water bodies. A field validation of this transport model with monitoring data from the EMEP background station in Kosetice, Czech Republic (21, 22), indicated underestimation of calculated concentration levels for all environmental compartments (20).

A soil-air equilibrium status has been investigated recently for various soil categories using an extensive database of coupled soil and time integrated air samples (23). Soil was found to be a source of pollution to air for lower molecular weight PCBs and OCPs especially during the summer but at heavily contaminated industrial sites the fugacity fractions indicated a strong net soil-air transfer for all seasons. This approach, however, only provided a net direction of the soil-air exchange and confirmed significant soil-air flows. A quantification of these flows is obviously needed to estimate an extent of such burden (23).

To perform emission inventories of secondary sources, soil volatilization fluxes have to be quantified and combined with available soil contamination data (24). Because of difficulties with direct measurements of volatilization fluxes, they were often simply calculated using a combination of monitoring data and environmental fate models (4, 25).

Systematic experimental data suitable for verification or improvement of current models is, however, still lacking. Field measurements of volatilization fluxes have been attempted for both PCBs (9, 10) and pesticides (11, 14) using several approaches. Either the vertical POP vapor gradient was assessed by measuring the air concentrations at several heights above the soil surface and relating this gradient to the volatilization flux using various theoretical techniques or the flux chamber was placed over the soil surface. The experimental conditions, of course, could not be fully controlled in such experiments, and they rarely covered a wider range of parameters. Therefore, laboratory measurements of volatilization fluxes have been carried out more often. The experimental apparatus consisted of the volatilization chamber with contaminated soil (4, 8, 12, 15, 26) across which precleaned air was drawn. While it is easier to control conditions of such experiments, the real environment is never really simulated accurately (12, 16).

To fill existing gaps, direct measurements of PCB and OCP volatilization fluxes have been carried out in well controlled laboratory conditions so that a range of factors

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affecting volatilization (soil organic matter content, soil structure, temperature, wind speed, properties of chemicals, and their concentrations) could be assessed.

## Materials and Methods

**Model Compounds.** Six PCB congeners and seven pesticides covering a range of physicochemical properties (Supporting Information, Table S1) were selected for a purpose of this study. Standard solution of PCB congeners in iso-octane ( $10 \mu\text{g mL}^{-1}$ , Dr. Ehrenstorfer GmbH, Germany), Aroclor 1254 mixture ( $1000 \mu\text{g mL}^{-1}$  in methanol, Dr. Ehrenstorfer GmbH, Germany), and pesticide mix standard solution in hexane/toluene (1:1) ( $2000 \mu\text{g mL}^{-1}$ , Dr. Ehrenstorfer GmbH, Germany) were used for the soil contamination.

**Soil Treatment.** POP volatilization from two different soil types was investigated: sandy loam soil (Luvisol) with an organic matter (OM) content of 1.8% (arable soil) and loamy sand soil (Cambisol) with an OM content of 5.2% (grass land). Soil samples were air-dried and sieved through a 2-mm mesh sieve. The physicochemical properties (Supporting Information, Table S2), as well as background concentrations, of all model compounds were determined for both soils.

Each soil sample (100 g) was mixed with hexane (100 mL) containing an appropriate amount of PCB or OCP standards in a round-bottom flask. The samples were agitated at a shaker for 12 h (9) and air-dried for 3 days allowing complete evaporation of hexane. Resulting concentrations of the individual compounds were between  $0.02 \text{ ng g}^{-1}$  and  $1 \mu\text{g g}^{-1}$  (dry weigh) (Supporting Information, Tables S3A and B).

**Volatilization Chamber.** The experimental setup is shown in Figure S1, Supporting Information. A glass volatilization chamber (width, 395 mm; depth, 250 mm; height, 350 mm) was connected to an air sampling device that draws air across a soil surface. The low and high volume air pumps (sampling rates 4.5 and  $570 \text{ L min}^{-1}$ , respectively) simulated two wind velocities. A clamping device was applied to fasten a glass lid; silicone and a friction tape sealed it airtight (15, 27, 28).

Approximately 1 cm of treated soil was exposed to steady flow of precleaned air for the interval of 4 days. This sampling period was selected based on the results of a pilot study indicating stabilization of volatilization fluxes after 2–3 days. All experiments were conducted at laboratory temperature ( $20\text{--}27 \text{ }^\circ\text{C}$  with a mean of  $24.7 \text{ }^\circ\text{C}$ ). Atmospheric humidity was measured using a relative humidity probe with a thermometer (51–82% with a mean of 66.5%). A polyurethane foam (PUF) filter was used at the chamber inlet to remove any background contamination of incoming air. Another PUF plug was deployed at the outlet to sequester evaporated compounds. It was replaced every 24 h (four air samples per each experiment).

**Extraction and Analysis.** The soil and PUF samples were extracted with dichloromethane in a Büchi System B-811 automatic extractor. Surrogate recovery standards (PCB 30 and PCB 185) were spiked on each sample prior to extraction. PCB 121 was used as an internal standard. The volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation was achieved on a sulfuric acid modified silica gel column. Samples were analyzed using a GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph.

**Quality Assurance/Quality Control.** Recoveries were determined by spiking all samples with the surrogate standards prior to extraction. They were higher than 71% for all samples, and recovery factors were not applied to any of data. Laboratory blanks were always lower than 1% of the amount found in samples.

A chamber blank was obtained as a flux from an empty volatilization chamber in 24 h. At the same time, background levels of PCBs and pesticides in the laboratory were determined and the adsorption efficiency of the PUF plug was

calculated. Sorbent adsorption efficiency  $\varepsilon$  was defined for each compound as a ratio between the inlet–outlet air concentration variance, and the inlet concentration (Supporting Information, Table S4).

$$\varepsilon = (m_1 - m_2)/m_1 \quad (1)$$

**Experimental Volatilization Fluxes.** For each air sample, a total mass ( $\Delta m$ , ng) of all sequestered compounds was determined. Volatilization loss ( $N$ ,  $\text{ng m}^{-2}$ ) was calculated as a ratio of the total mass ( $\Delta m$ , ng) and the soil surface area ( $A_c$ ,  $\text{m}^2$ ).

$$N = \Delta m/A_c \quad (2)$$

Volatilization flux ( $N_{(t)}$ ,  $\text{ng m}^{-2} \text{ h}^{-1}$ ) was defined as a ratio of the volatilization loss and duration of each experiment.

$$N_{(t)} = \Delta m/\Delta t A_c \quad (3)$$

**Predicted Volatilization Fluxes.** Mackay's fugacity model (5) was employed for calculations. Fugacity is a parameter frequently used for description of a thermodynamic equilibrium between two phases. Fugacity capacity ( $Z$ ,  $\text{mol m}^{-3} \text{ Pa}^{-1}$ ) is defined as the affinity of a compound to environmental media. For air, it can be obtained from the ideal gas law

$$Z_a = 1/RT \quad (4)$$

where  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is absolute temperature (K).

Fugacity capacities of neighboring compartments are related through the partitioning coefficients

$$Z_1 = 1/(RTK_{aw}) \text{ for water} \quad (5)$$

where  $K_{aw}$  is the air–water partitioning coefficient, and

$$Z_s = K_{sw}Z_1 \text{ for the solid phase} \quad (6)$$

where  $K_{sw}$  is the soil–water partitioning coefficient.

$K_{sw}$  can be obtained from the organic carbon content in soil (29) according to

$$K_{oc} = 0.411K_{ow} (\text{L kg}^{-1}) \quad (7)$$

$$K_{sw} = K_{oc} f_{oc} \rho_s / 1000 \quad (8)$$

where  $f_{oc}$  is a fraction of organic matter in soil and  $\rho_s$  is a density of soil ( $\text{kg m}^{-3}$ ).

To calculate a fugacity capacity of bulk soil, the products of liquid, solid, and vapor capacities and their respective volume fractions in soil were summed

$$Z_{sb} = Z_1 f_w + Z_a f_a + Z_s f_s \quad (9)$$

Furthermore, a transfer coefficient  $D$  ( $\text{mol h}^{-1} \text{ Pa}^{-1} \text{ m}^{-2}$ ) representing a molar flux between the soil and air compartments was defined based on the three resistance model

$$D_{sa} = 1/(1/D_{sab} + 1/(D_{saa} + D_{sal})) \quad (10)$$

where  $D_{sab}$ ,  $D_{saa}$ , and  $D_{sal}$  are contributing  $D$  transfer coefficients.

$$D_{sab} = K_{sa}Z_a \quad (11)$$

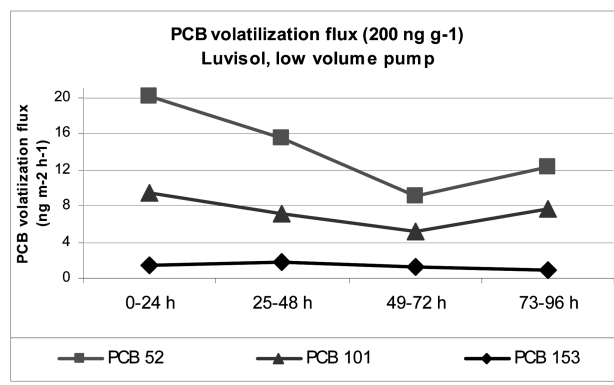
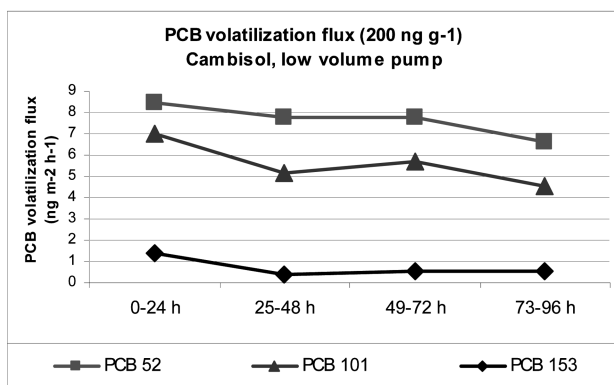
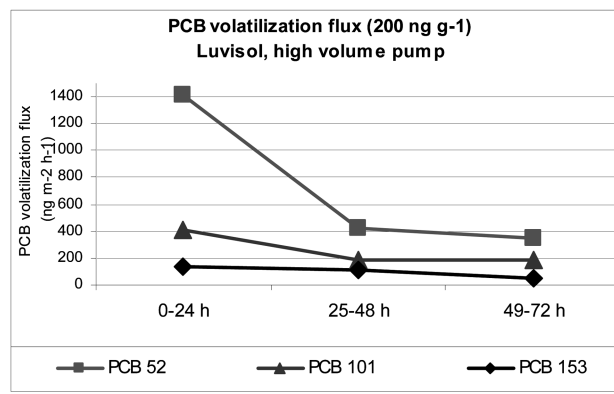
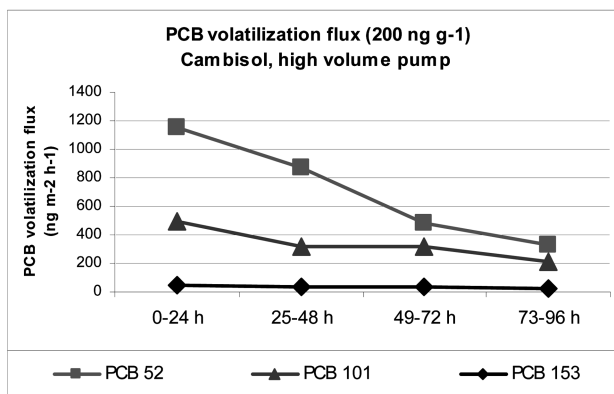
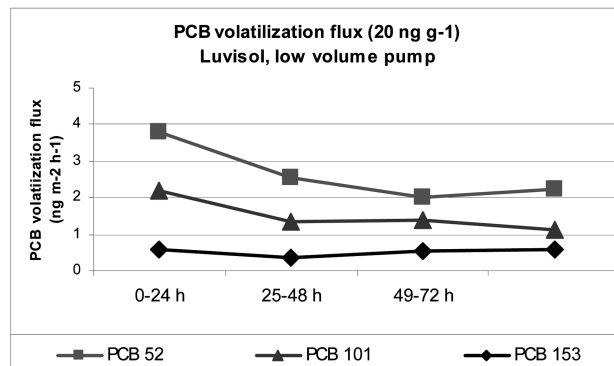
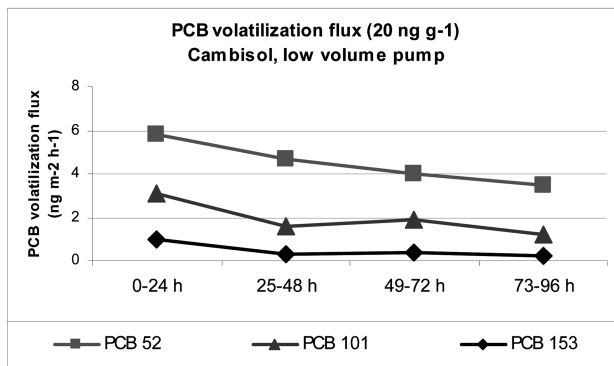
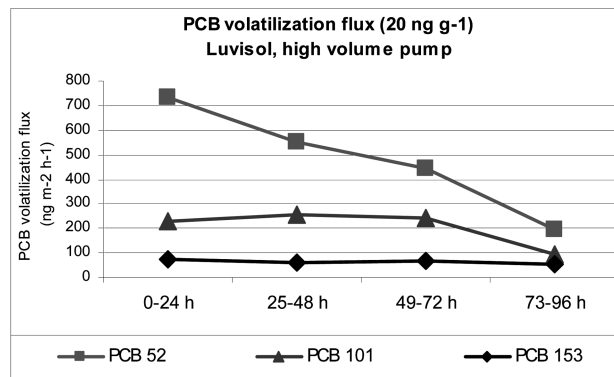
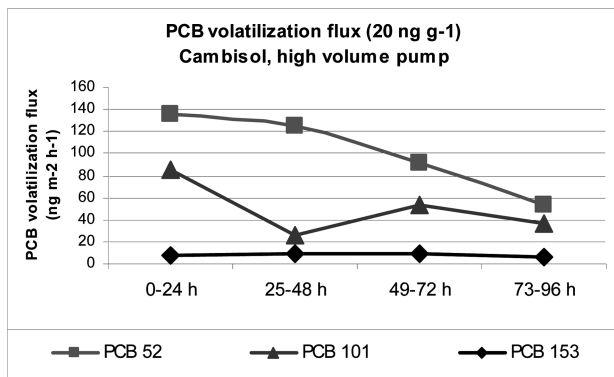
represents the air boundary layer

$$D_{saa} = K_{sap}Z_a \quad (12)$$

represents the soil–air phase diffusion, and

$$D_{sal} = K_{swp}Z_1 \quad (13)$$

is the soil–water phase diffusion.



**FIGURE 1.** Volatilization fluxes ( $\text{ng m}^{-2} \text{h}^{-1}$ ) of selected PCBs at two concentrations ( $20 \text{ ng g}^{-1}$ , upper 4 graphs;  $200 \text{ ng g}^{-1}$ , lower 4 graphs) from the soil with higher (Cambisol, left column) and lower (Luvisol, right column) organic carbon content using a high volume (rows 1 and 3) and low volume (rows 2 and 4) air sampler.

$K_{sa}$  is the soil-air boundary layer mass transfer coefficient (MTC),  $K_{sap}$  is the soil-air phase diffusion MTC, and  $K_{swp}$  is the soil-water phase diffusion MTC. General mass transfer coefficients (air boundary layer

$MTC = 5 \text{ m h}^{-1}$ , soil-air phase boundary layer  $MTC = 0.02 \text{ m h}^{-1}$ , soil-water phase boundary layer  $MTC = 0.00001 \text{ m h}^{-1}$ ) were applied for a purpose of this study (5).

**TABLE 1. Volatilization Fluxes of Selected Polychlorinated Biphenyls and Organochlorine Pesticides Estimated from the 4-Day Experiment**

		volatilization flux (ng m <sup>-2</sup> h <sup>-1</sup> )					
		Cambisol			Luvisol		
		predicted	experimental		predicted	experimental	
low vol	high vol		low vol	high vol			
soil concentration (ng g <sup>-1</sup> )							
PCB28	0.02			0.008	0.001		0.01
	0.24	0.004	0.02	0.07	0.01	0.08	0.16
	2.42	0.04	0.44	0.25	0.11	0.17	1.04
	10	0.16		0.82	0.47		0.83
	100	1.61		1.12	4.66		0.92
PCB52	0.24	0.002		0.05	0.01		0.07
	2.37	0.02	0.05	0.49	0.06	0.02	0.05
	10	0.09		0.71	0.26		0.94
	23.74	0.21	0.11		0.61	0.13	1.12
PCB101	100	0.88		0.78	2.55		3.66
	0.28	0.001		0.04	0.003		0.03
	2.84	0.01	0.022	0.26	0.03	0.01	0.26
	10	0.03		0.47	0.10		0.48
PCB138	28.38	0.09	0.08		0.27	0.08	0.74
	100	0.33		0.71	0.96		2.08
	0.68	0.01		0.05	0.02		0.06
	6.83	0.08	0.04	0.04	0.22	0.06	0.10
PCB153	10	0.11		0.153	0.33		0.17
	68.27	0.77	0.07	0.15	2.23	0.13	0.26
	100	1.13		0.67	3.26		0.70
	0.24	0		0.02	0		0.03
PCB180	2.39	0	0.01	0.12	0.001	0.004	
	10	0.002		0.27	0.005		0.40
	23.86	0.004	0.01	0.39	0.01	0.01	0.48
	100	0.02		0.79	0.05		1.11
$\alpha$ -HCH	0.04			0.002	0		0.002
	0.39		0.003	0.001	0	0.002	0.03
	3.91	0.001	0.02	0.03	0.002	0.002	0.01
	10	0.002		0.14	0.005		0.08
$\gamma$ -HCH	100	0.02		2.12	0.05		2.13
	10	0.93	0.13	0.95	2.67	0.62	3.70
	100	9.25	0.85	1.78	26.71	0.73	16.20
$p,p'$ -DDE	1000	92.5	38.59		267.1	12.24	
	10	0.84	0.14	0.68	2.42	0.53	2.87
	100	8.36	0.62	1.34	24.16	0.39	9.54
$p,p'$ -DDD	1000	83.6	11.11		241.6	72.95	
	10	0.04	0.05	0.17	0.11	0.18	0.49
	100	0.39	0.27	0.20	1.13	0.43	0.62
$p,p'$ -DDT	1000	3.9	1.84		11.3	0.45	
	10	0.004	0.05	0.12	0.01	0.10	0.17
	100	0.04	0.30	0.29	0.13	0.13	0.70
	1000	0.45	0.37		1.29	0.33	

Fugacity of a compound in soil can be calculated from the soil concentration

$$f_s = C/Z_{sb} \quad (14)$$

Thus, a volatilization flux ( $N$ , mol h<sup>-1</sup> m<sup>-2</sup>) can be calculated according to

$$N = D_{sa} f_s \quad (15)$$

assuming zero air concentration.

## Results and Discussion

**POP Levels in Soils.** Soil monitoring data from the Czech Republic as a model country revealed PCB concentrations as high as 300 ng g<sup>-1</sup> for the sum of 7 indicator congeners (8.5 ng g<sup>-1</sup> for PCB 52, 27 ng g<sup>-1</sup> for PCB 101, 78 ng g<sup>-1</sup> for PCB 138, 95 ng g<sup>-1</sup> for PCB 153, 125 ng g<sup>-1</sup> for PCB 180) (18). The median level in agricultural soils was 2.5 ng g<sup>-1</sup> for the sum of 7 congeners. Maximal measured soil concentrations of OCPs were 2.4 ng g<sup>-1</sup> for  $\alpha$ -HCH, 1.2 ng g<sup>-1</sup> for  $\beta$ -HCH, and 2.1 ng g<sup>-1</sup> for  $\gamma$ -HCH (although  $\alpha$ -HCH levels as high as

400  $\mu$ g g<sup>-1</sup> were measured at some hot spots), 3279 ng g<sup>-1</sup> for  $p,p'$ -DDE, 411 ng g<sup>-1</sup> for  $p,p'$ -DDD, and 2429 ng g<sup>-1</sup> for  $p,p'$ -DDT. The median concentration in agricultural soils was 3.2 ng g<sup>-1</sup> for  $p,p'$ -DDE, 0.5 ng g<sup>-1</sup> for  $p,p'$ -DDD, and 3.8 ng g<sup>-1</sup> for  $p,p'$ -DDT (18). On the basis of this range, the experimental soil concentrations were selected for the model compounds (Supporting Information, Tables S3A and B).

**Experimental Volatilization Fluxes.** Two parallel sets of experiments were carried out for selected POPs, each at three concentration levels ranging over 3 orders of magnitude. Each experiment was repeated for two soil types (Luvisol, Cambisol), and two simulated wind speeds (0.01 m s<sup>-1</sup>, 1 m s<sup>-1</sup>). A total amount of each compound volatilized from soil has been determined every 24 h for four consecutive days. Soil samples were analyzed at the end of each experiment. A summary is provided in Supporting Information (Tables S5–S17, Figure S2).

A mass-balance was calculated for each experiment as a ratio of the individual POP amounts trapped in four consecutive PUF filters plus the amount found in soil, and

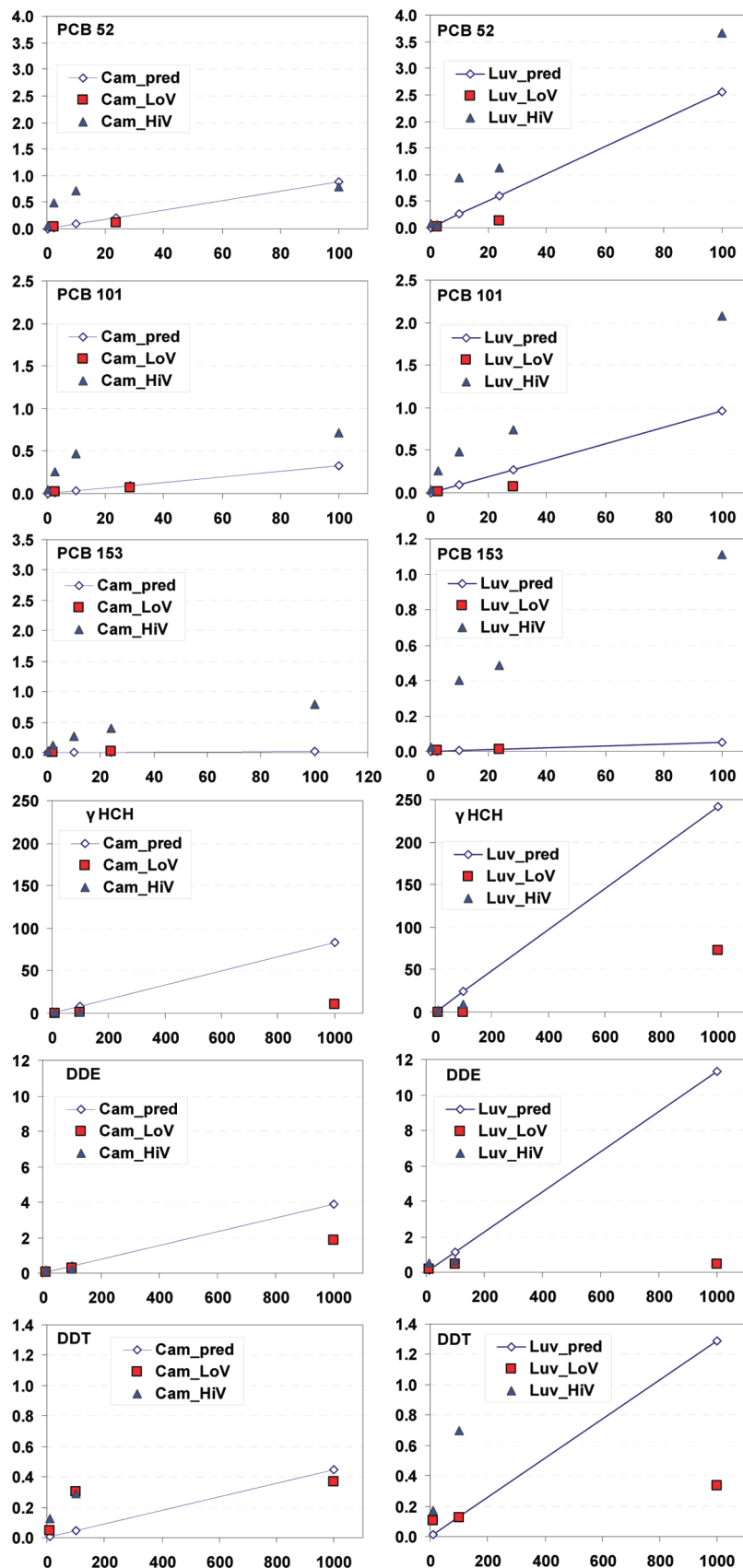
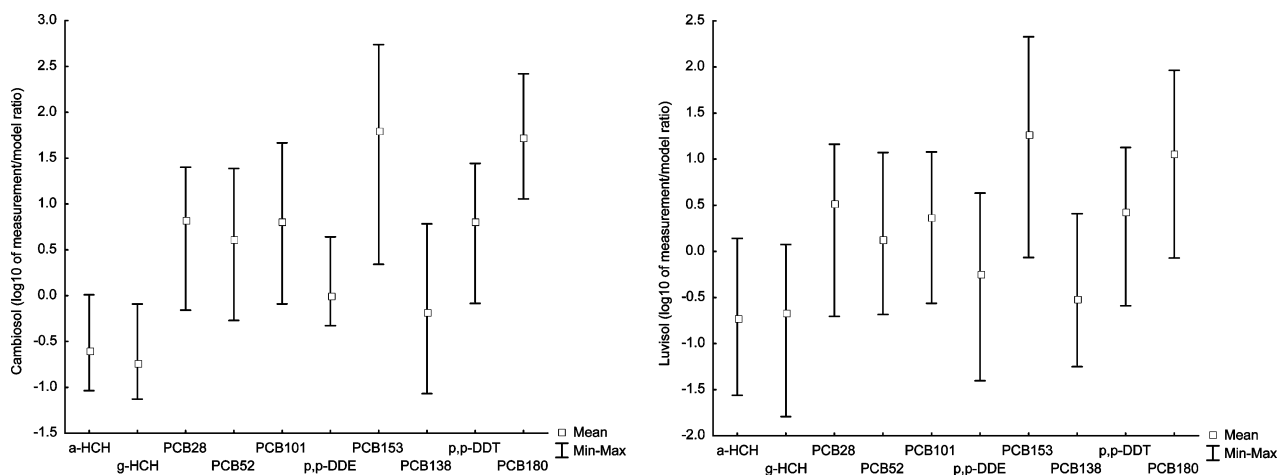


FIGURE 2. Comparison of the experimental values of volatilization fluxes (red and blue points) of selected PCBs and OCPs to the values predicted from the fugacity model (blue line) ( $y$ -axes,  $\text{ng m}^{-2} \text{h}^{-1}$ ). Model soils with higher (left) and lower (right) organic carbon content and range of soil concentrations of POPs ( $x$ -axes,  $\text{ng g}^{-1}$ ) were compared. The red squares represent the fluxes derived from the experiments using a low volume air sampler, while the blue triangles show the fluxes from the high volume experiments. It should be noted that the individual data points do not represent a single values but the set of experiments where each flux was derived from four independent measurements.



**FIGURE 3.** Logarithmic ratio of measured and modeled volatilization fluxes of selected compounds from Cambisol (left) and Luvisol (right). Compounds on the x-axes are ordered according to their  $K_{OA}$  values. Each graph shows the mean value and min–max range of this ratio. Experimental data from both low and high air velocity conditions and over the full range of soil concentrations were included.

the amount of compound applied in the beginning. The median mass balance was 74% for PCBs, and 70% for OCPs (details provided in Supporting Information, Tables S5–S17).

A volatilization loss ( $N$ ) was calculated for every day of each experiment according to eq 2, and volatilization flux ( $N_{(t)}$ ) was calculated according to eq 3. An order of magnitude increase of the soil concentration (Figure 1) resulted in the flux grow up to 1 order of magnitude. As demonstrated in Figure 1 (upper row), the volatilization flux from Luvisol was almost half-order of magnitude higher than the one from Cambisol using lower soil concentration of PCBs and a high volume pump. A difference between two soils was much smaller when PCB concentration increased by a factor of 10 (Figure 1, third row). An influence of the air flow can be also seen in Figure 1: Increasing the air flow caused an increase in the volatilization flux from Cambisol about half-order of magnitude. A similar effect was observed for Luvisol. Similar set of data for OCPs is presented in Supporting Information, Figure S2.

**Temperature-Normalized Long-Term Fluxes.** Since temperature is a crucial parameter for quantification of volatilization fluxes and laboratory temperature fluctuated between 20 and 27 °C in course of the experiments, the primary fluxes obtained from the individual experiments were normalized to 20 °C using equation

$$k = N_{T_{\text{exp}}} / N_{T_{20^{\circ}\text{C}}} \quad (16)$$

where  $N_{T_{\text{exp}}}$ ,  $N_{T_{20^{\circ}\text{C}}}$  are the volatilization fluxes under experimental a standard temperatures derived from the fugacity model, and  $k$  is a correction factor.

A significant decrease of volatilization fluxes has been observed in the first days of each experiment probably as an effect of the soil spiking. Pollutants adsorbed to the outermost surfaces were released faster as they were not incorporated in the soil matrix. A similar decrease in volatilization fluxes has been observed in earlier experiments on volatilization of Aroclor 1242 (30) and pesticides (31). All fluxes have stabilized within 2–3 days and nonlinear regression was applied to quantify a constant value of the flux for each compound. All experimental fluxes from the same experiment were fitted to selected  $y = ax^b$  model, where  $y$  value represented the estimated constant flux of the individual compound for given experimental setup (32).

A summary of estimated fluxes is presented in Table 1. It can be seen that fluxes of  $\alpha$ -HCH and  $\gamma$ -HCH were close to the ones of lighter PCBs (PCB 52), while DDT and its metabolites showed fluxes similar to higher PCBs (PCB 153).

The values of the individual volatilization fluxes were correlated with the physicochemical properties of compounds ( $K_{OA}$ ,  $K_{OC}$ , vapor pressure, molecular weight) using the Pearson and Spearman methods. Cambisol and Luvisol soils were assessed separately as the fluxes from two soils with different organic carbon contents varied significantly. Correlations of the fluxes with selected properties were significant ( $p < 0.05$ ) for both, Cambisol and Luvisol soils. Strongest correlations were found for  $K_{OA}$  (0.976) and vapor pressure (0.939) on Cambisol and for  $K_{OA}$  (0.930) and  $K_{OC}$  (0.924) on Luvisol. On the contrary, no significant correlations were found for the soil concentrations higher than 100 ng  $g^{-1}$ .

**Comparison with Currently Available Experimental Data.** Such complexity of the laboratory experiments is a unique feature of presented project since majority of previous studies was limited to few compounds (most frequently PCBs), one concentration, and a rigid set of the environmental conditions. In addition, technical mixtures (Aroclor, for instance) were used rather than the individual compounds, and applied concentrations were often far from the environmentally relevant values. Chiarenzelli (8), for instance, worked in his laboratory experiments with very high Aroclor concentrations (close to 100  $\mu\text{g}$  per gram in all cases) applied on sand. Mills and Bennet (33) covered a range of soil concentrations by combination of the field and laboratory experiments. Most concentrations were, however, also too high to be compared to our data.

In contrast, the soil concentrations in the field measurements of Backe et al. (10) were very low (mostly below 1 ng  $g^{-1}$ ), and the experiments were focused on volatilization fluxes of the individual PCBs from soils with various organic carbon contents (3–40%). Estimated volatilization fluxes corresponded very well to our results for lower concentration ranges.

Cousins et al. (15) compared results of the laboratory experiments to predicted values of PCB fluxes. A difference between measured and modeled fluxes was often 1–2 orders of magnitude for PCB 52 and 101. Interestingly, the experimental values were often lower than predicted ones.

**Model Predictions.** Expected emission rates were calculated using the Mackay's fugacity model according to eq 15 and compared to experimental data for the low and high air flows in Figure 2. As the soil-air boundary layer MTC was set for the wind speed of 4 m  $h^{-1}$ , predicted fluxes were expected to be higher than both experimental values. In reality, predicted fluxes demonstrated better agreement with

those measured under the low flow conditions, while the high flow experiments resulted in much higher emission rates. Lower than predicted fluxes were measured only for HCHs as the most volatile among selected compounds. It can be argued that a break-through effect lowered the yield of evaporated volatile chemicals during the laboratory simulations but a good mass-balance of these experiments speaks against this hypothesis. The explanation can probably be found in Figure 1 showing that evaporation of very volatile compounds was much more affected by higher wind velocities. Increasing the air flow by 2 orders of magnitude caused a 2–5 fold increase of the flux for heavier compounds in Cambisol and a 2–8 fold increase in Luvisol. For very volatile PCBs, however, this difference was 20 times for Cambisol and 100 times for Luvisol. A gap between the low and high wind velocity fluxes was wider for soils with lower organic carbon contents.

A ratio of measured and modeled volatilization fluxes is presented in Figure 3, where every bar represents 6–8 independent experiments (four flux measurements each). The lowest values of the ratio originate from the experiments under the low wind velocity, and the highest values from the high wind velocity conditions. Cambisol and Luvisol soils are shown separately. For  $\alpha$ - and  $\gamma$ -HCH, the model predicted higher concentrations, probably because it presumes the higher wind velocities than those simulated in the laboratory experiments. A good agreement between the experimental and modeled values was observed for the medium molecular weight compounds as DDE. Most of the PCB fluxes, especially those of highly chlorinated congeners, were underestimated. It is apparent that predicted flux values of these compounds corresponded more to the windless conditions for Cambisol and to the low wind velocities (below  $1 \text{ m s}^{-1}$ ) for Luvisol.

There are, of course, uncertainties connected to the laboratory measurements. Using treated soil rather than intact, untreated soil structure collected in the field was less environmentally realistic (but improved homogeneity of results). In addition, volatilization in the field is further limited by vegetation cover. Simulated wind speeds could reduce the effective thickness of the boundary layer above soil in a volatilization chamber. Precleaning of air could result in somewhat enhanced fluxes. All of these artifacts, however, burden all experiments with the same bias and cannot diminish a value of such consistent data. Another source of uncertainty is a fugacity model. MTC coefficients depend on many factors including a soil structure and composition, and optimization of these coefficients for specific conditions of the experiments was not possible.

Results of the study drew attention to secondary sources of the atmospheric pollution which are very often overlooked. They pointed out that impact of such sources can be orders of magnitude greater than indicated by the fugacity models. It has been shown that volatilization fluxes of organochlorines were strongly correlated to their physicochemical properties, especially to the  $K_{OA}$  value. They were also controlled by the soil properties and initial soil concentrations of these compounds. Presented results indicated that variability of the wind velocities is one of important influential parameters deserving further attention. Including the secondary sources of organochlorines to emission inventories, and improvement of current distribution models has to be recommended. Volatilization fluxes generated in frames of this study can be combined with available soil monitoring data to assess an impact of contaminated soil on the air quality. That would be a valuable contribution to ongoing POP inventories organized in compliance with reporting commitments of the Stockholm Convention.

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## Supporting Information Available

List of the model compounds and their properties (Table S1), detailed soils characteristics (Table S2), ranges of PCB (Table S3A), and OCP (Table S3B) soil concentrations in volatilization experiments, a chamber blank analysis (Table S4), overview of total volatilized mass, soil concentration, and mass balance for all compounds in all experiments (Tables S5–S17), and figures presenting the experimental setup (Figure S1) and volatilization fluxes of selected OCPs (Figure S2). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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