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An Assessment of Air–Soil Exchange of Polychlorinated Biphenyls and Organochlorine Pesticides Across Central and Southern Europe

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Estimating the net flux direction of polychlorinated biphenyls and organochlorine pesticides is important for understanding the role of soil as a sink or source of these chemicals to the atmosphere. In this study, the soil–air equilibrium status was investigated for various soil categories in Central and Southern Europe using an extensive database of coupled soil and time-integrated air samples. Samples were collected from 47 sites over a period of 5 months to assess both site-specific as well as seasonal variations in fugacity fractions, calculated as a potential measure of soil–air exchange. Sampling sites were carefully selected to represent a variety of background, rural, urban, and industrial areas. Special attention was given to sites in the former Yugoslavia, a country affected by recent conflicts, where soils were found to be highly contaminated with polychlorinated biphenyls (PCBs). Industrial soils from the Czech Republic, heavily polluted as a result of previous pesticide production, were also included in the survey. Soil was found to be a sink for highly chlorinated PCBs and for dichlorodiphenyltrichloroethane (DDT); for dichlorodiphenyldichloroethylene (DDE), the status was closer to equilibrium, with a tendency for net deposition during winter and net volatilization during summer. For lower-molecular-weight PCB congeners, as well as for α -HCH, soil tends to be a source of pollution to the air, especially, but not exclusively, during summer. Fugacity fractions were found to decrease during the colder seasons, especially for the more volatile compounds, although in both the war-damaged areas and the heavily contaminated industrial sites, seasonal variability was very low, with fugacity fractions close to 1, indicating strong net soil-to-air transfer for all seasons. The original assumption that residents of the Western Balkans are still exposed to higher levels of PCBs due to the recent wars was confirmed. In general, the soil–air transfer of PCBs and organochlorine pesticides was found to be site-specific and dependent on the physicochemical properties of the contaminant in question, the soil properties, the historical contamination record and a site's vicinity to sources, and the local meteorological conditions.

Introduction

Assigning current levels of persistent compounds such as polychlorinated biphenyls (PCBs) or organochlorine pesticides (OCPs) to sources is not trivial since these compounds have been banned in Europe and there are no fresh inputs of PCBs or OCPs into the environment. However, they are still emitted from various secondary sources such as contaminated soils, sediments, buildings, or equipment (1). These semivolatile compounds are continuously cycling between the atmosphere and the terrestrial environment over long periods of time as they move toward equilibrium between environmental compartments or phases (2–5). Understanding the processes responsible for transport across phase boundaries becomes even more important than quantifying transport within a phase, since processes like soil–air exchange influence the levels and fate of semivolatile organic chemicals in terrestrial ecosystems, as well as control the risks posed to humans by the presence of these chemicals in the atmosphere. This fact is reflected by the number of studies devoted to the experimental and theoretical quantification of interphase transfer, including air–water, water–sediment, air–terrestrial, and various biological interphases (6).

There are generally two approaches to the characterization of soil–air equilibrium: the use of partition coefficients and the use of fugacity and Z values. Fugacity has the advantage of giving a clear statement of the relative equilibrium status (3, 6). A common way for estimating this status is to measure both the gaseous concentration in the atmospheric boundary layer and the corresponding soil concentration. Fugacity values can then be calculated for the compound in question using the concentrations in the two compartments and the fugacity capacities. Equal fugacity values in two compartments characterize the equilibrium (2, 7–12).

Backe et al. (8) measured PCBs in the air and precipitation to estimate a transfer of chemicals between the soil and air compartments. Cousins et al. (2) have described a field experiment where soil–air exchange was measured for a number of PCBs, PAHs, and polychlorinated dibenzodioxins and furans (PCDD/Fs). Meijer et al. (11) and Bidleman and Leone (12) have applied the fugacity fraction (defined as a ratio of soil fugacity to the sum of soil and air fugacities) as an indication of the net direction of air–soil exchange. Fugacity calculations in both cases indicated general non-equilibrium between the soil and air (12).

In this study, a similar approach to assessing soil–air equilibrium was adopted to investigate the potential for soils in the Western Balkan region to be a source of PCBs and OCPs to the atmosphere. The Western Balkans were selected because there is a general lack of information regarding the levels and fate of persistent organic pollutants (POPs). Further interest in this region stems from the recent conflict, which saw a large number of destroyed military and industrial facilities which resulted in the escape of various chemicals. The few investigations that have focused on POP contamination of the soil and aquatic environment have indicated serious pollution problems in the vicinity of war-damaged facilities in Croatia and Serbia (13–15), with regional contamination confirmed by pollution monitoring in neighboring countries after the wars (16–18). The only systematic data, however, have been generated within the framework of the EU's APOPSBAL project, aimed at evaluating the extent to which the residents of former Yugoslavia (YU) are exposed to elevated POP levels as a consequence of the Balkan conflict.

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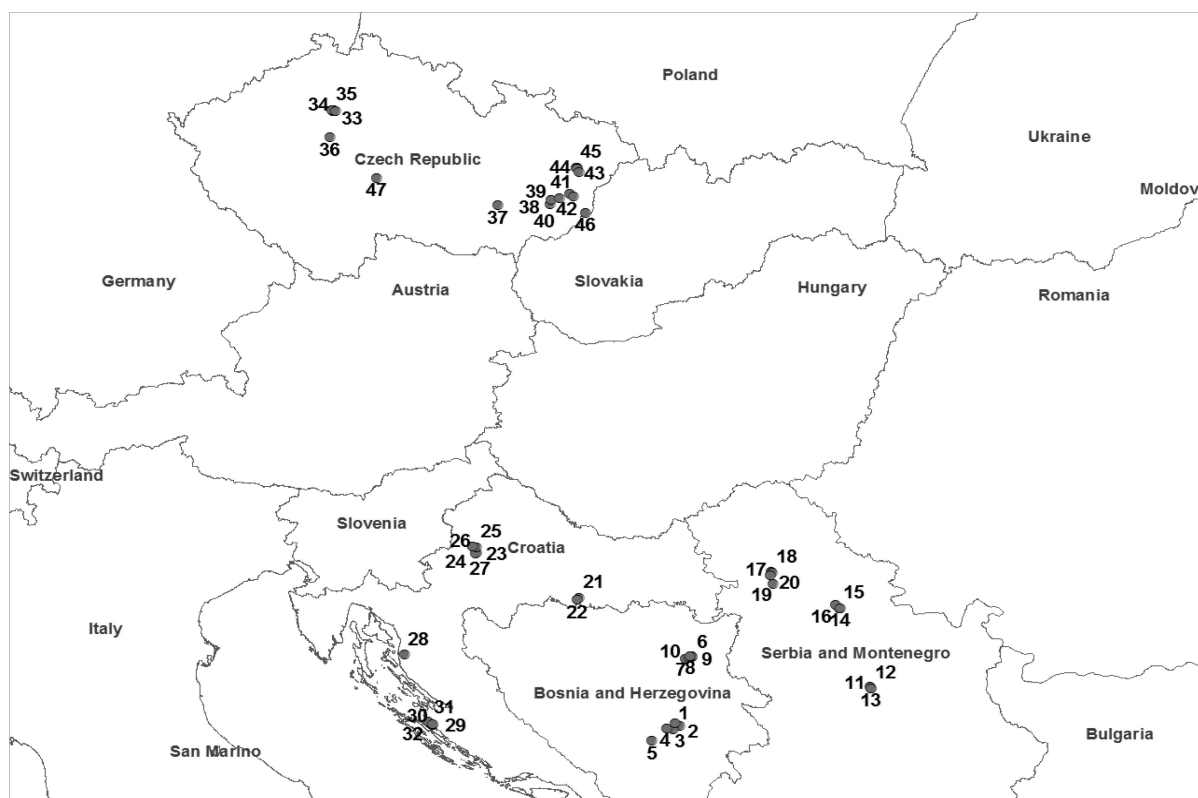


FIGURE 1. The map of all sampling sites in Central and Southern Europe.

As a part of the APOPSBAL project, a high-volume ambient air sampling was performed in Croatia, Serbia, Bosnia and Herzegovina, and levels of PCBs and OCPs were determined (19–21). Significant PCB contamination of damaged facilities as well as of some storage and waste disposal sites was confirmed (PCB concentrations ranged between 67 pg m^{-3} and 40 ng m^{-3} for a sum of seven indicator congeners) (22). A total of 32 well categorized sites with known levels of pollution along with the historical record of contamination were selected from the APOPSBAL sites for this soil–air exchange study. In addition, 15 sites in the Czech Republic (CR) were sampled, as a region not affected by the war, but heavily impacted by intensive industry. A coupled analysis of the soil samples and time-integrated passive air samples allowed an assessment of the site-to-site and seasonal variability in soil–air transfer.

Experimental Section

Sampling Sites. A map of the sampling sites is provided in Figure 1, and a complete list of sites including their GIS coordinates can be found in the Supporting Information (SI; Table S1). This set includes four categories of sites: (i) background; (ii) rural, urban, and residential; (iii) industrial; and (iv) heavily contaminated. In the first category, Ivansedlo, Fruska Gora, and Zavizan are representatives of background mountain sites to compare to PCB-contaminated sites in Bosnia, Serbia, and Croatia. The remaining three sites (Libuš, Pláňava, and Košetice) represented urban and rural backgrounds and an EMEP monitoring station in CR. In the group of heavily contaminated sites (iv), there were two sites at the Zastava factory in Kragujevac (YU) which suffered PCB spills. While contaminated soils are still expected to be responsible for the majority of PCB air pollution at this site, operational PCB-filled transformers poses another source of contamination. A similar situation was apparent at the Tuzla fire station, which serves as a storage site for discarded electrical equipment. On the other hand, there were no PCB transformers at the Zadar transformer station, and contaminated

soil was considered to be the only PCB source to the atmosphere at this site. An additional two sites, Spolana Archive and Gate (CR), were considered as pollution “hot spots” due to contamination records related to the production of OCPs and poor waste management. The group of industrial areas (iii) contains 14 sites affected by various types of industries (refinery, chemistry, cement, machinery, or car manufacturing). The largest group (ii), offers a variety of 21 rural, urban, and residential sites in YU and CR, with various levels of contamination and proximity to sources, with some sites located in the vicinity of the above-mentioned “hot spots”.

Air and Soil Sampling. Passive air samplers were employed at 32 sampling sites in YU and at 15 sites in CR for five consecutive periods of 28 days between July and December of 2005. Polyurethane foam disks (PUFs; 15 cm diameter, 1.5-cm-thick, density 0.030 g cm^{-3} , type N 3038; Gumotex Breclav, Czech Republic) housed in protective stainless steel chambers were employed as passive air samplers in this study (23, 24). The soil samples (top 10 cm) were collected at each site at the beginning of the sampling campaign. Sampling and analytical procedures including quality assurance/quality control measures were described earlier (1, 25) (see also the Experimental Section in the SI for details).

Air Concentrations. The air concentrations (ng m^{-3}) were calculated from PUF concentrations (ng PUF^{-1}) by application of a conversion factor, derived from laboratory calibration experiments (where the average sampling rate was 100 m^3 per 28 days) (24). We are aware that air concentration data are underestimated for those compounds with a significant particle-bound fraction because passive samplers have a limited ability to collect particles. However, the predominance of gaseous PCBs in the atmosphere is well-known. On average, particle-bound PCBs account for less than 5% of the total amount of PCBs in the atmosphere (26).

TABLE 1. Summary of Air and Soil Concentrations (ng m⁻³ and ng g⁻¹, Respectively) for the Various Site Categories

		<i>C_A</i> (ng m ⁻³)				<i>C_S</i> (ng g ⁻¹)			
		min	max	mean	med	min	max	mean	med
PCBs ^a	background sites (<i>n</i> = 6)	0.04	0.016	0.11	0.12	1.3	2.3	1.8	1.8
	residential, rural, urban sites (<i>n</i> = 21)	0.04	0.73	0.20	0.16	1.8	20.1	6.8	5.9
	industrial sites (<i>n</i> = 14)	0.08	1.35	0.29	0.22	0.7	68.4	27.2	23.3
	heavily contaminated sites (<i>n</i> = 6)	0.08	90.6	7.56	0.64	42.5	3085	839	563
OCPs ^b	background sites (<i>n</i> = 6)	0.10	0.59	0.22	0.15	1.2	3.2	2.4	2.9
	residential, rural, urban sites (<i>n</i> = 21)	0.07	0.90	0.23	0.18	0.5	59.3	12.5	7.9
	industrial sites (<i>n</i> = 14)	0.07	0.95	0.29	0.26	0.2	95.5	18.1	6.1
	heavily contaminated sites (<i>n</i> = 6)	0.10	54.9	1.88	0.43	3.9	5243	870	54.5

^a Sum of seven congeners. ^b Sum of *p,p'*-DDT; DDE; DDD; and α -, β -, γ -HCH.

Fugacity Calculations. In this work, the fugacities of a compound in the soil (f_s) and air (f_a) were calculated according to Harner et al. (27):

$$f_s = C_s RT / 0.41 \Phi_{OM} K_{OA} \quad (1)$$

$$f_a = C_a RT \quad (2)$$

where C is the concentration in the medium (mol m⁻³), R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (K), Φ_{OM} is the fraction of the organic matter in the soil (1.7 times the organic carbon fraction), and K_{OA} is the octanol–air partitioning coefficient of the compound. The factor 0.411 improves the correlation between the soil–air partitioning coefficient and K_{OA} (12, 28, 29). K_{OA} can be obtained from the relation:

$$K_{OA} = K_{OW} / K_{AW} \quad (3)$$

$$K_{AW} = H / 100 RT \quad (4)$$

$$R = R' 100 \quad (5)$$

where K_{OW} is the octanol–water partitioning coefficient, K_{AW} is the air–water partitioning coefficient, H is Henry's law constant (Pa m³ mol⁻¹), and R' is the gas constant (0.08205 l atm K⁻¹ mol⁻¹). A temperature correction of H was obtained using the integrated van't Hoff equation (cf., e.g., Cousins and Jones 7, 8):

$$\ln(H_1/H_2) = -\Delta H_{AW} (1/T_1 - 1/T_2) / R \quad (6)$$

where H_1 and H_2 are Henry's law constants at two temperatures, T_1 and T_2 are temperatures (K), and ΔH_{AW} is the enthalpy of vaporization (J mol⁻¹).

The fugacity fraction (f_i) is calculated as the fugacity in soil divided by the sum of fugacities in soil and air and gives an indication of the net direction of air–soil exchange (27).

$$f_i = f_s / (f_s + f_a) \quad (7)$$

The fugacity fractions near 0.5 indicate equilibrium; fractions >0.5 indicate net volatilization from the soil into air, whereas values <0.5 indicate net deposition from air to soil (see also SI for more details). However, due to uncertainties and the propagation of errors in the calculation using eq 7, fugacity fractions between 0.3 and 0.7 were not considered to differ significantly from equilibrium (11, 27).

Results and Discussion

Soil and Air Concentrations. An overview of the soil and air concentrations of PCBs and OCPs found in four categories of sampling sites is provided in Table 1. Detailed information on the soil and air concentrations measured at the individual sites is presented in Table S2, SI.

In the soil samples (uppermost soil layer), PCB concentrations ranged between 1 ng g⁻¹ and 3 μ g g⁻¹ for a sum of seven indicator congeners, with the highest values found in

the Zastava factory in Kragujevac, Gorica, and Tuzla fire station. Similarly, the highest PCB air concentration of 90 ng m⁻³ was observed in Zastava.

OCP concentrations in the Balkan soils were below 1 ng g⁻¹ for HCHs, and between 1 and 60 ng g⁻¹ for the dichlorodiphenyltrichloroethanes (DDTs). Corresponding maximum concentrations in the soils from CR (Spolana factory) were much higher: 0.4 μ g g⁻¹ for α -HCH, 4.3 μ g g⁻¹ for β -HCH, 0.1 μ g g⁻¹ for γ -HCH, 1.8 μ g g⁻¹ for DDT, and 1.4 μ g g⁻¹ for dichlorodiphenyldichloroethylene (DDE). Ambient air concentrations as high as 55 ng m⁻³ for the sum of HCHs and 1 ng m⁻³ for the sum of DDTs were determined at this most contaminated site from CR.

Fugacity Fractions. Fugacity fractions (f_i) of six PCB congeners and six OCPs were calculated for three seasons at all sampling sites: a full list of f_i values is provided in the SI (see Tables S3 and S4). For the individual compounds, the fugacity fractions varied widely between 0 and 1 except for γ -HCH, which showed very low values (below 0.1) at all sites. In general, PCBs displayed a decrease in f_i values with the degree of chlorination, whereby median values were 0.64–0.76 for the less-chlorinated PCBs, while PCB 180 had a low value of 0.24. This is accounted for by an increasing fugacity capacity, Z_o , from low-chlorinated to high-chlorinated PCBs (in line with variation of K_{OW} and K_{OA}).

From the range of fugacity fractions for the various compounds shown in the SI, Figure S1, it can be concluded that soil is a sink for highly chlorinated PCBs (PCB 180), for DDT, and for γ -HCH. For DDE, the status is closer to equilibrium, with a tendency toward net air-to-soil transfer (depositional behavior) during winter and net volatilization during summer. For most of the PCB congeners, as well as for α -HCH, soil tends to be a source of these chemicals to the air especially, but not exclusively, during summer. This is in a good agreement with previously published studies (11, 12). For most substances, these findings are explained by their physicochemical properties: notably, low vapor pressures and a high K_{OA} corresponding to low f_i values and *vice versa*. For example, PCB-180 and *p,p'*-DDT (displaying f_i values of 0.35 and 0.48 at the Praha urban background site, for instance) have low vapor pressures of 0.13 and 0.034 mPa, at 298 K, respectively (30, 31), and high values of K_{OA} at 10^{10.9} and 10^{10.1}, respectively (32), whereas PCB 28 and α -HCH had f_i values of 0.88 and 0.98 at the same site but have relatively high vapor pressures (23 and 8.4 mPa at 298 K, respectively) (30, 31) and lower values of K_{OA} (10^{8.2} and 10^{7.8}, respectively) (32). On the other hand, γ -HCH, which has a high vapor pressure and moderate K_{OA} (6.6 mPa and 10^{8.1}, respectively), was less easy to predict, as these physicochemical properties would suggest that this chemical undergoes net volatilization from soil, whereas the f_i values were all <0.5, indicating net deposition. We speculate that fugacity from soil might have been overcompensated for by depositional processes: wet deposition of γ -HCH is particularly effective due to its

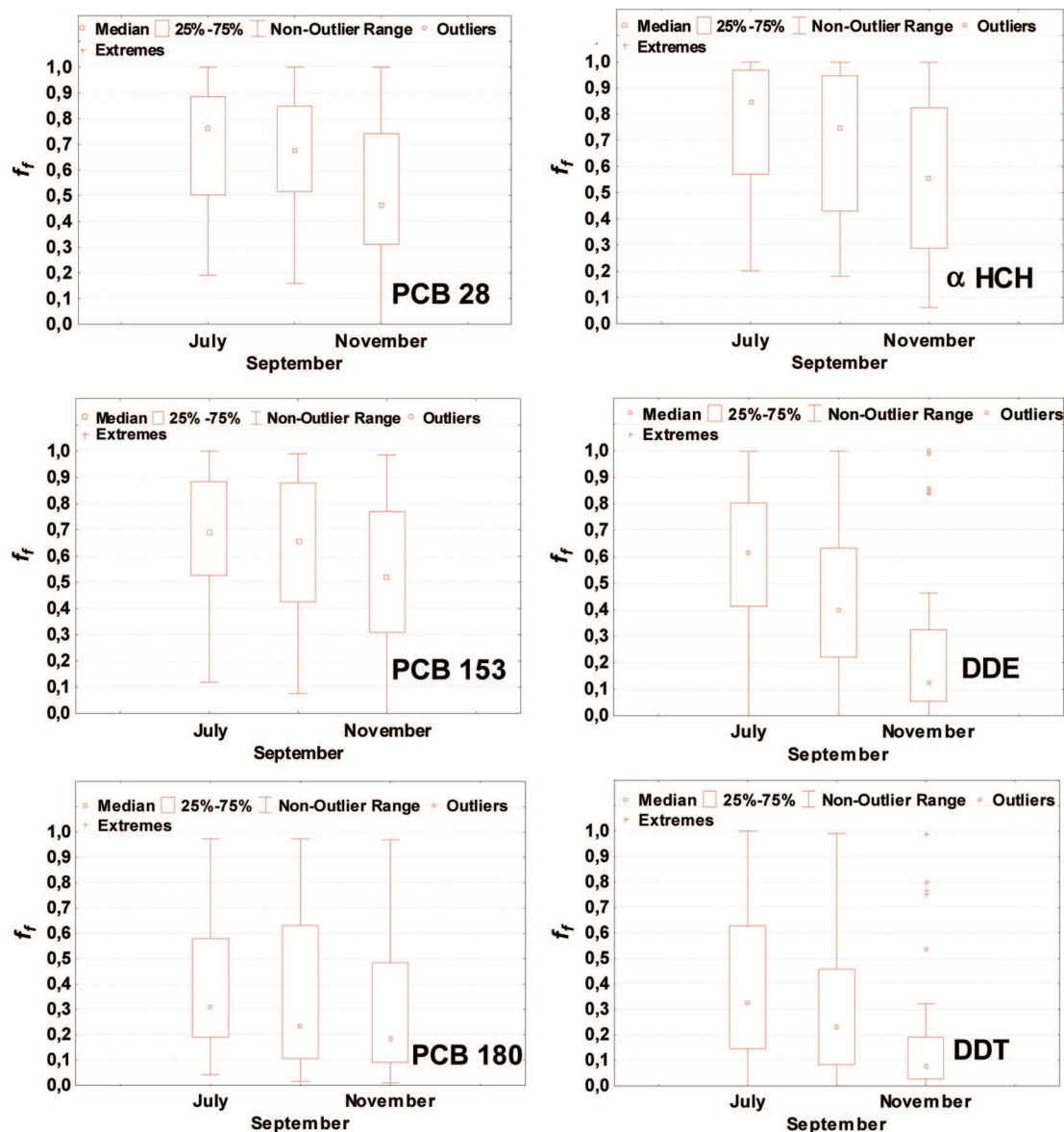


FIGURE 2. Seasonal variability of the fugacity fractions, $f_i = f_s/(f_s + f_a)$, of selected PCBs and OCPs as measured at 47 sampling sites between July and December, 2005.

significant water solubility (7.4 mg L^{-1} , while it is only 2.0 mg L^{-1} for α -HCH). For this reason, retention in the aqueous phase within humid soils will be enhanced.

Variability of the fugacity fractions was higher for the lower-chlorinated PCB congeners. At the Košetice background site, f_i ranged between 0.30 and 0.53 for PCB 52, but only 0.02–0.11 for PCB 180. Similarly, at Pancevo City Hall, values ranged from 0.10 to 0.31 for PCB 28 but only 0.02–0.08 for PCB 180. Differences in mobility of the PCB congeners provide a possible explanation for this observation. Due to their higher volatility and low retention in soil (lower Z_o), the less-chlorinated PCB congeners are probably more mobile and subject to soil-to-air transfer, resulting in their widespread dispersal to soils in rural and background areas. The temporal variability displayed in the air concentrations of the lower-chlorinated PCBs (in turn determined by varying spatial and temporal patterns of emissions and atmospheric transport) is reflected in elevated but varying values of f_i . Consistent with this explanation, this effect (i.e., the difference in f_i variability between the lower- and higher-chlorinated congeners) was not pronounced at the heavily contaminated sites, where for example f_i values ranged from 0.75 to 0.99 for PCB 52 and 0.79–0.89 for PCB 180 in the Spolana factory,

and similarly 0.93–0.98 for PCB 28 and 0.77–0.90 for PCB 180 in Pancevo, Petrochimika. A special case is the polluted site of the Zadar transformer station, where the soil was—unlike the other sites—contaminated with Pyralene oil with a high content of PCB 28 but less PCB 180 when the station was damaged. This is reflected in the very high f_i values for PCB 28 (0.86–0.90), with relatively low values for PCB 180 ($f_i = 0.18$ –0.27).

For OCPs, the median values of fugacity fractions were higher in CR than in YU. α -HCH, for instance, had a median of 0.45 in YU and 0.93 in CR. Similarly, DDE and DDT median f_i values were 0.32 and 0.14, respectively, in YU, but 0.62 and 0.33, respectively, in CR. This corresponds to higher soil contamination in CR. For example, both DDE and DDT had soil concentrations ranging from 0.3 to 41.3 and 0.1 to 53.2 ng g^{-1} (median 1.8 and 1.3 ng g^{-1}), respectively, while at YU, concentrations ranged from 1.0 to 1135.7 and 0.7 to 1906.9 ng g^{-1} (median 7.0 and 4.3 ng g^{-1}).

Effect of Soil Properties. Strong correlations between the fugacity fractions for the various compounds and soil organic carbon were not evident across the whole data set. A weak correlation was observed for the most volatile compounds, that is, α -HCH (see SI, Figure S2), PCB 28, and PCB 52, with

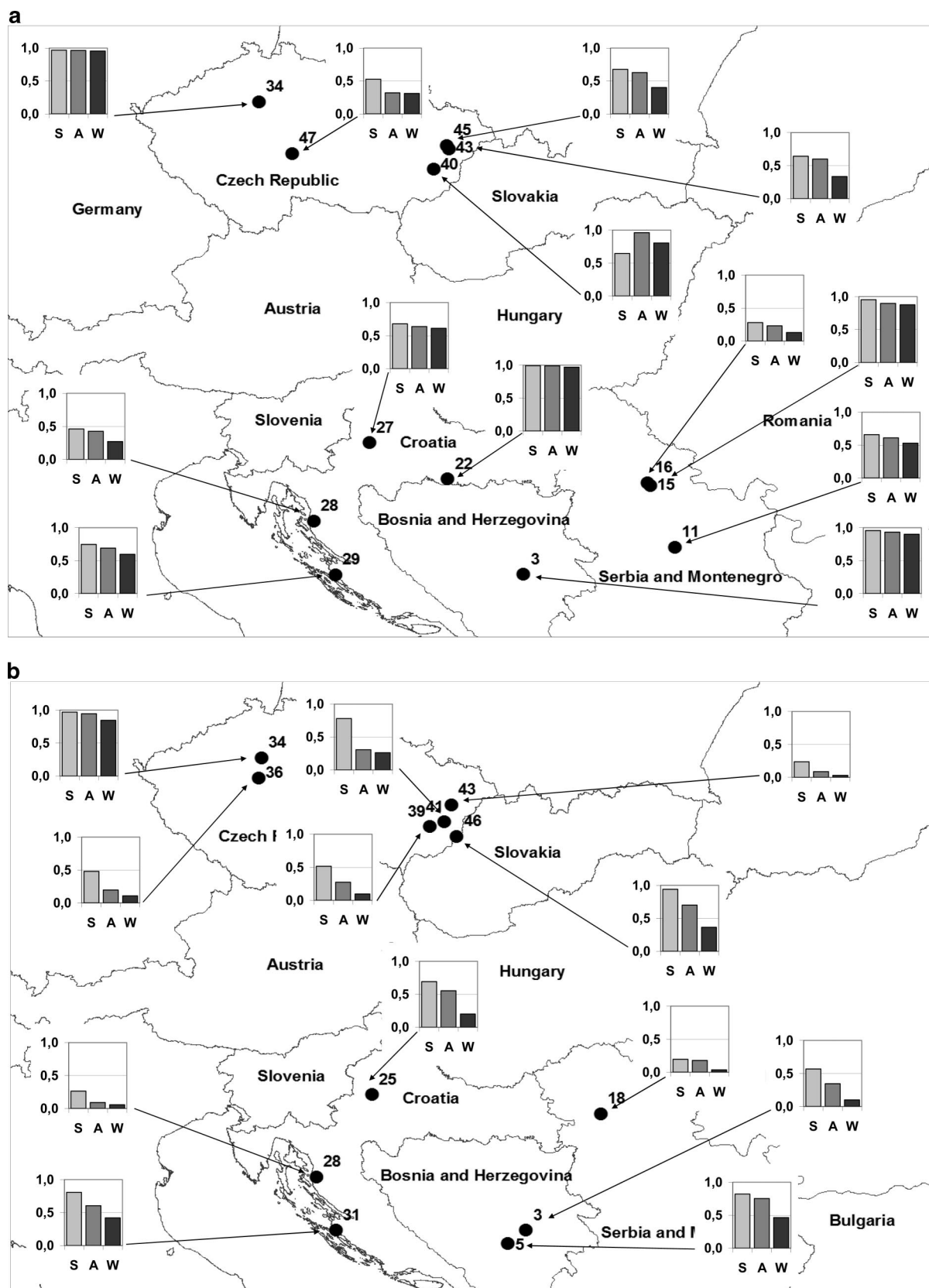


FIGURE 3. (a) Site-specific and seasonal variability of the fugacity fractions, f_i , of PCB 153. Three bars at each sampling site represent f_i determined in July (summer), September (autumn), and November (winter). (b) Site-specific and seasonal variability of the fugacity fractions, f_i , of DDE. Three bars at each sampling site represent f_i determined in July (summer), September (autumn), and November (winter).

the exception of γ -HCH. The correlation did not appear to be influenced by season and hence temperature. These findings suggest that the organic carbon content can only

control air–soil equilibrium if retention in soils is limited by significant variations in physicochemical properties such as vapor pressure or K_{OA} . It means that, for low-volatile

compounds and substances with a high K_{OA} , coupled to high soil concentrations, the air–soil equilibrium cannot be achieved unless strong sources maintain very high atmospheric concentrations (which may be the case at the Zastava factory site where high levels of PCBs are maintained by evaporation from the PCB-filled transformer). A stronger correlation was achieved when soils were analyzed separately for the background sites and heavily contaminated sites (see SI, Table S5).

Seasonality of Soil–Air Equilibrium Status. From July to December, a decreasing trend in the levels of PCBs and OCPs in the atmosphere was observed. As this corresponded to the decrease of average daily temperatures as well as to the reduced average daytime atmospheric mixing depth, we conclude that during the warm season enhanced evaporation from soil to air overcompensated for more efficient dilution of the contaminants emitted from surfaces. A seasonal trend of corresponding fugacity fractions (reduction in median f_i values toward the colder season) for selected PCBs and OCPs (more pronounced for more volatile compounds, such as PCB 28 and α -HCH) can be observed in Figure 2.

Effect of Historical Records of Contamination. In Figure 2, the overall seasonal variability of f_i values is shown. This variability, however, differs from site to site, as presented in the sampling sites in Figure 3a and b, for example (highlighted in Table S2, see SI).

For PCB 153, very low fugacity fractions were observed at the background sites (Kosetice observatory, no. 47: f_i = 0.3–0.5, Zavizan, no. 28) where soil serves as a depositional sink (Figure 3a). Zavizan observatory, for instance, was selected as a background site to the Zadar transformer station (no. 29). Although most of the soil from the immediate vicinity of the damaged transformer had been removed, enhanced PCB evaporation was still apparent during the warm season. While in Zadar the fugacity fractions varied between 0.60 in winter and 0.75 in summer, the corresponding values for Zavizan stayed between 0.25 and 0.45. At this site, the soil is relatively uncontaminated, with PCBs present due to deposition from air advected over contaminated sites like Zadar and other facilities in the area damaged during the war.

A similar situation can be observed in Pancevo. For example, contaminated soils in Petrochimika (no. 15) act as a source of pollution, causing an increase in the fugacity fraction (0.88–0.95), whereas downtown Pancevo (Cityhall, no. 16) is affected by this locally contaminated air, with soil here acting as a sink (f_i = 0.13–0.28).

As discussed earlier, the fugacity fraction does not decrease significantly in the cold months at heavily contaminated sites (Spolana, no. 34, f_i = 0.95–0.97 throughout July to December). The exception is, however, Zastava factory (no. 11), where the fugacity fraction stayed between 0.52 and 0.66 throughout July to December despite possessing very high PCB soil concentrations. The reason for this is an operational PCB-filled transformer which most likely serves as a strong source of PCBs to the air, particularly during the warmer months.

Our findings suggest that contaminated soils in the war-damaged areas (Kragujevac, Zadar) are still sources of PCBs to the atmosphere. Moreover, many of the PCB-filled capacitors remaining in service (Kragujevac) pose further risks. Taking a preliminary estimation that currently used devices in former Yugoslavia contain 65 tons of PCBs, then this risk cannot be underestimated. Even though operation of some damaged capacitors was already discontinued, there is apparently no systematic solution to this problem, since many of these devices are stored without proper management in place (i.e., Tuzla). The original assumption that residents of the Western Balkans are exposed to higher levels of PCBs due to the recent wars was further confirmed by an ongoing passive air sampling campaign performed at background

sites in the countries of Central, Eastern, and Southern Europe (33). While mean atmospheric concentrations of PCBs (seven indicator congeners) at background sites in Estonia, Latvia, Lithuania, the Czech and Slovak Republics, or Romania varied between 27 and 53 ng m⁻³ in 2006, concentrations reached 117 and 187 ng m⁻³ in Bosnia and Serbia, respectively.

Variability of the f_i values of DDE (Figure 3b) revealed similar trends. In the Spolana factory (no. 34), where the soil was heavily contaminated with DDE (and HCHs), as a consequence of pesticide production and storage in the 1960s and 1970s, f_i values show almost no variation (0.85–0.90), whereas seasonal variation was more apparent at the less-contaminated sites. Summer values were typically 3 times higher than the winter values observed in some urban (Praha, no. 36: f_i = 0.11–0.48; Zagreb, no. 25: f_i = 0.20–0.69) and rural (Pláňava, no. 46: f_i = 0.36–0.94) sites. At these sites, which have been influenced by contamination from regional “hot spots” over recent decades (CR), or at least in recent years (YU), air–soil exchange oscillated around equilibrium, with soils acting more as sinks in winter and as sources in summer. Several sites with very low values of f_i for DDE were evident, particularly the background sites Zavizan (no. 28: f_i = 0.06–0.26) and Novi Sad (no. 18: f_i = 0.04–0.19). We conclude that, for DDTs, the historical record of contamination, longer in CR than in YU, can influence the variation in f_i values.

HCH contamination of the Spolana factory, as a former major HCH producer, is suspected of having of regional significance with regard to HCH emissions. During the years 1961–1965 when only pure lindane was marketed, the ballast congeners were dumped within the factory grounds. Therefore, soils in this area are heavily polluted with α -HCH and β -HCH, while the level of γ -HCH is very low. This is reflected in the fugacity fractions f_i = 0.92–1.00 for α -HCH and f_i = 0.03–0.27 for γ -HCH. This is also the case for all the sample sites in the vicinity of Spolana, with a similar pattern (i.e., high fugacity fractions for α -HCH and low for γ -HCH) found at most sampling sites in CR. The situation is different in YU, where the fugacity fraction of α -HCH is much more variable. In urban areas, such as Sarajevo (f_i = 0.22–0.33) or Kragujevac (f_i = 0.11–0.20), very low values were observed, while in Ivansedlo (a background site), the values ranged between 0.61 and 0.84, and in Pancevo between 0.73 and 0.98.

While only the net direction of the soil–air exchange was addressed in this study, supplementary field and laboratory experiments focused on quantification of the volatilization fluxes from the region are currently in progress. Generated data are being used not only for transport and distribution models but also for the national POPs inventories, organized in compliance with reporting commitments of the member states of the Stockholm Convention.

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Supporting Information Available

Experimental section, GIS coordinates of the sampling sites (Table S1), median soil and air concentrations of PCBs and OCPs at all sampling sites (Table S2), fugacity fractions for selected PCBs (Table S3) and OCPs (Table S4) at all sites, ranges of the fugacity fractions (Figure S1), and correlation between the fugacity fractions and the organic carbon content in the top soils (Figure S2, Table S5). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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