Does the Soil-Air-Plant Pathway Contribute to the PCB Contamination of Apples from Allotment Gardens?

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Introduction

The presence of persistent organic pollutants (POPs) like PCBs in plants poses a risk to humans and animals as it determines an exposure through the terrestrial food chain [1,2]. A number of studies have shown that the transfer from the atmosphere is the dominant pathway for an uptake of POPs by aboveground parts of plants [3-5], in which dry gaseous as well as wet and dry particulate deposition are involved. The relative contribution of the different pathways to the overall deposition depends strongly on the physical-chemical properties of the compounds, but also on microclimatic conditions and characteristics of the plant, which both contribute to diffusive resistance at the its surface [6]. In contrast, root uptake and translocation in the shoot is probably much less important for these highly hydrophobic compounds, although there are contradicting results in the literature [5,7-9].

While the air-plant distribution of POPs received increasing attention, the importance of the soil-air-plant pathway has rarely been studied [10-12]. It is not known whether the volatilisation of POPs from contaminated soils and subsequent deposition to plants may be a significant source compared to "background" deposition in the field, as well as a deposition of contaminated soil dust raised by wind or rain splash [7,11]. Particularly the latter pathway can hardly be assessed under exposure chamber conditions; instead a field study is required despite the increased overall complexity, which renders process identification more difficult.

The objective of our study was to assess whether the local soil contamination (soil-air-plant pathway) could contribute to the PCB contamination of apples (*Malus domestica* Borkh.) at an allotment garden site additionally to background deposition (air-plant pathway).

Methods and Materials

Site. The study site was contaminated with PCBs by deposition of industrial sludges in the 1950s and 1960s prior to conversion to allotment gardens, which are still in use today. We selected 13 allotments from an area of 300 x 300 m on that site, which covered a wide range of soil PCB loads (cf. Table 1).

Sampling. The deposition measurement was designed to distinguish between gaseous and particle-bound PCB deposition from background and allotment sources. Therefore, we installed passive samplers at 25, 80, and 160 cm above the bare soil surface on a pole to collect simultaneously gaseous and particulate PCB deposition for 16 weeks on every allotment. With increasing height above the soil surface, the influence of the underlying soil should diminish compared to the background deposition, which we consider as the by far dominant source at 160 cm.

To collect gaseous deposition, we used polyurethane foam plugs (PUF; 10x2.5x2.5 cm), which were exposed in aluminium foil-coated polyethylene shelters (12.5 cm height, 12 cm diameter). A gas exchange with the surrounding air was only possible by a bottom opening of 9 cm diameter, which was covered with a 0.4 mm steel mesh. We are aware that the used passive samplers do not allow for a direct determination of gaseous air concentrations or the determination of gaseous PCB deposition to the apple surface, as the deposition depends on the exposure time and the diffusive resistance at the apple surface besides the air concentration [12,13]. However, these samplers are meaningful for a simultaneous and standardised monitoring of gaseous deposition over a certain period of time at different heights on all allotments. The sampling rate should not be affected by air turbulence, as Wania et al. (2003) [12] showed for a passive sampler of similar shape and size that no direct air flow occurred through the shelter and thus the POP uptake was diffusion controlled.

Wet and dry particulate deposition was collected on glass fibre filters (GFF; 100 mm diameter) exposed in pots, which were covered by a 1 mm polyethylene mesh to prevent leaves or insects from falling in. Similar to the PUF plugs, these samplers allow not for a direct determination of particulate deposition to the apples, but for a comparison of different heights on all allotments simultaneously.

Two or three apples (170-550 g fresh weight) of different varieties were harvested at maturity from each allotment, in general between 120 and 180 cm height above the soil surface. Immediately after sampling the apples were rinsed with demineralised water to remove particle-bound PCBs from the surface, followed by hexane to remove the wax layer and associated PCBs. Both rinsing solutions were collected in glass bottles and stored in a fridge until analysis. The apples were wrapped in aluminium foil and stored in a freezer. Immediately before extraction, the apples were peeled; fruit and peel were extracted separately. Soil samples were taken from each allotment by mixing 10 subsamples taken from 0-10 cm depth.

PCB analysis. The soil samples were extracted by pressurized liquid extraction (hexane:acetone 2:1), the glass fibre filters and polyurethane foam plugs by shaking extraction (hexane:acetone 2:1 and hexane, respectively).The fruit samples were mashed, 10 % (v) of methanol was added and the extraction was carried out two times with hexane on a rotary shaker. The hexane phase was separated. The aqueous rinsing solutions were liquid-liquid-extracted twice with hexane. All extracts were evaporated to approximately 1 ml and purified by column chromatography using sulphuric acid-modified silica gel [14]. We analysed the following PCBs (IUPAC numbers) using ^{13}C-labelled internal standards and gas chromatography-electron ionisation mass spectrometry: No. 1, 8+5, 18, 28+31, 20, 52, 44, 66, 95, 101, 87, 110, 118, 105, 151, 149, 153, 141, 138+158, 187, 183, 174, 180, 170, 199, 194+205, 206, and 209. Congeners linked by ‘+’ could not be separated chromatographically.

Calculations and statistics. The presented PCB concentrations in different fractions of the apples are based on the fresh weight of the whole apple. For statistical calculations, the different allotments were treated as independent replicates. We identified significant differences of congener patterns between different groups of samples (soils, deposition, apple, etc.) using a t-test for dependent samples ("paired differences" test). All reported linear correlation coefficients refer to log-transformed data, as log-transformation was necessary to obtain normally distributed concentration and deposition datasets. The significance level was set at $P < 0.05$.

Results and Discussion

Deposition of PCBs. The Σ32 PCB concentrations in the PUF plugs were highest at 25 cm and lowest at 160 cm height above the soil surface at 9 of the studied 13 allotments (Table 1). In 25 and 80 cm, the Σ32 PCB concentrations increased significantly with an increasing Σ32 PCB concentration in soil ($r = 0.73$ and 0.74, respectively). The Σ32 PCB concentrations in the PUF plugs at 160 cm showed no significant relationship with the Σ32 PCB concentration in soil ($r = -0.40$). The Σ32 PCB concentrations at 160 cm height, which are probably almost exclusively derived from background deposition, show a considerable variation among the allotments (on average 199 ± standard deviation 114 µg kg^{-1}). The particulate deposition of the Σ32 PCB was highest at 25 cm at 12 of the 13 allotments and lowest at 160 cm at 8 of 13 allotments (Table 1). The particulate deposition of the Σ32 PCB showed weaker correlations with the Σ32 PCB concentrations in soil (160 cm: $r = 0.56$, 80 cm: $r = 0.02$; 25 cm: $r = 0.52$) and a high variation at 160 cm (on average 106 ± standard deviation 113 µg m^{-2}) as well. The gaseous and particulate deposition of individual PCB congeners followed in general the outlined trends of the Σ32 PCB.

The congener profile (i.e. composition of the PCB mixture) of the particulate deposition was almost identical at 25, 80, and 160 cm height. The dominant congeners were 110, 118, 138+158, and 153 (Figure 1). Although this congener profile was in general similar to that of the soils, we detected in the particulate deposition significantly higher percentages of PCB 105, 118, 138+158, and 153, but lower percentages of PCB 44, 52, 95, and 101 (shown in Figure 1 for the deposition in 25 cm height).

Table 1: Concentration of the Σ32 PCB in soils, and particulate and gaseous deposition of the Σ32 PCB at different heights above the soil surface within 16 weeks sampling time.

Allotment	Soil	Particulate deposition (PCB mass on GFF)			Gaseous deposition (PCB concentration in PUF plug)		
		25 cm	80 cm	160 cm	25 cm	80 cm	160 cm
	mg kg^{-1}	µg m^{-2}			µg (kg PUF)$^{-1}$		
1	634.6	1739	40	259	4236	1796	12
2	78.8	1197	542	128	782	649	340
3	46.9	134	51	34	156	180	153
4	34.5	43	29	28	160	115	125
5	30.4	70	19	21	217	176	149
6	28.4	1833	45	379	1471	517	324
7	28.2	1274	146	209	299	184	140
8	18.6	1177	116	130	584	528	346
9	15.3	1233	374	60	809	270	372
10	8.6	94	103	51	260	177	219
11	7.6	246	55	19	151	181	117
12	2.4	126	73	39	170	166	203
13	1.1	51	45	20	87	96	86

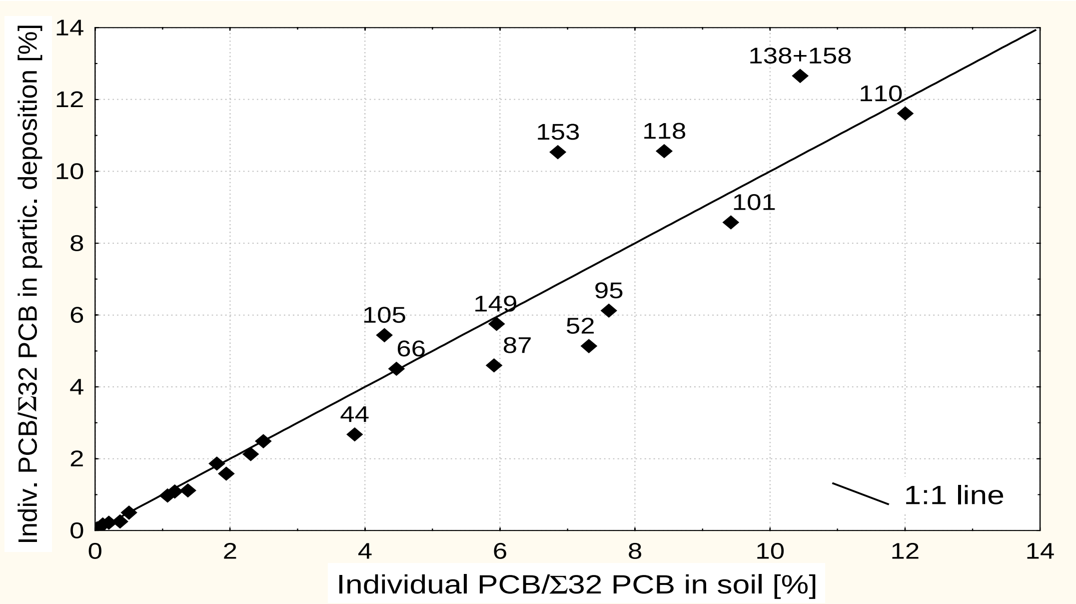

Figure 1: Relationship between the congener patterns of PCBs in soil samples and particulate deposition in 25 cm height above the soil surface (means of 13 allotment gardens).

The vertical deposition gradients as well as the differences among the allotments demonstrate that the local soil of a particular allotment was probably a source for gaseous and particulate PCB deposition at 25 and also 80 cm height above the soil surface. However, the low correlation coefficients suggest that adjacent areas with different PCB concentrations in soil also contributed to the PCB deposition at one particular allotment, which was not accounted for by our not spatially resolved experimental design. Both, gaseous and particulate deposition show a strong variation at 160 cm, making a sound calculation of the contribution of background sources hardly possible.

A comparison of the congener pattern does not give any indications, as these are almost identical in all particulate deposition samplers. The differences in congener profiles between soil and particulate deposition could therefore suggest that soil is not a source of the PCB deposition. However, this seems unlikely, since the vertical gradients and high deposition rates, particularly at 25 cm, could not be explained from background deposition alone, which should be in the range of several µg m^{-2} for the studied 4-month period [15,16]. A possible reason might be that the bulk soil sampled from 0-10 cm depth represents poorly the soil fraction susceptible to wind erosion, which is located at the surface and includes predominantly silt-sized particles.

Transfer of PCBs to apples. The total Σ32 PCB concentrations in apples (sum of the Σ32 PCB in superficial particles, wax layer, peel, and fruit flesh) ranged from 3.2 to 32 µg (kg fresh weight)$^{-1}$, which was higher than the 0.5-6.6 µg kg^{-1} (sum of 18 congeners) reported for apples sampled in Britain[17]. The Σ32 PCB concentration in superficial particles contributed in general only to 0.1-10% of the total Σ32 PCB concentration, 9-74% were located in the wax layer, 14-86% in the peel, and 1.5-10% in the fruit flesh. Thus, peeling before consumption removes 90 to 98% of the PCB burden, while the effect of washing alone is limited. These results confirm previous findings of Lovett et al. (1997)[17]. The Σ32 PCB concentrations in wax layer and peel increased with increasing Σ32 PCB concentrations in soil (r = 0.50 and 0.51, respectively), but the correlations were not significant. The gaseous deposition of the Σ32 PCB in 80 cm height showed a significant correlation with their concentration in the wax layers (r = 0.61, respectively; Figure 2), but not the gaseous deposition in 160 cm or the particulate deposition. The concentration from superficial particles was not correlated to the Σ32 PCB soil concentration or particulate deposition. The reason might be that these PCBs are subject to a highly variable balance between deposition and resuspension by rain rather than a continuous accumulation like those in the wax layer.

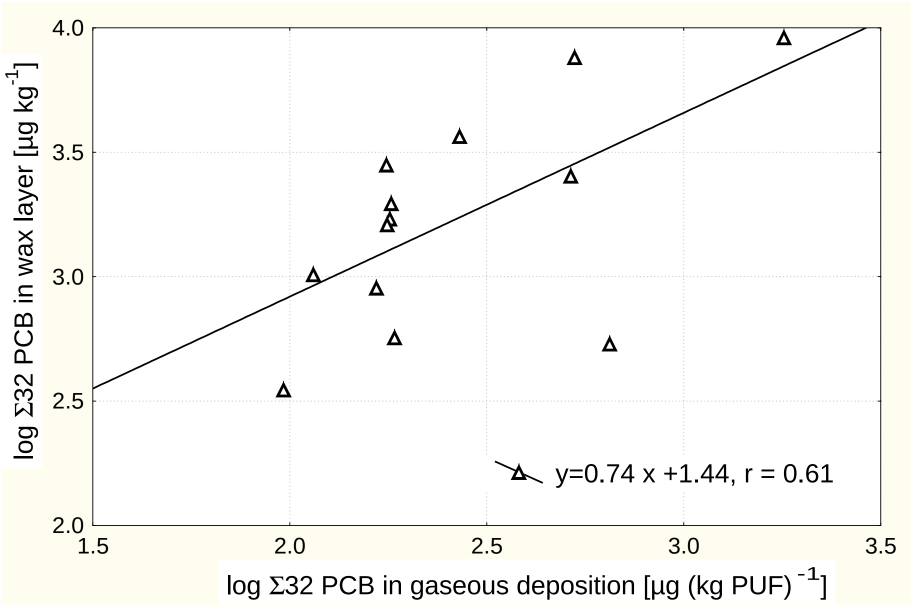

Figure 2: Relationship between the Σ32 PCB in gaseous deposition to the passive samplers at 80 cm and the Σ32 PCB concentration in wax layers of the apples (n = 13).

The results show that the local soil contamination has an impact on particulate and gaseous deposition of PCBs at 25 and 80 cm height above the soil surface at allotment garden sites. On the other hand, the relationships between the soil concentration or deposition of PCBs and their concentration in apples were rather weak, allowing no sound estimation to which extent local soil contamination contributed to the PCB contamination of apples growing at 120-180 cm height. It is however likely that fruits growing closer to the surface might be affected stronger by PCB deposition originating from local soil contamination.

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