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ATMOSPHERIC DEPOSITION OF SEMIVOLATILE ORGANIC COMPOUNDS TO TWO FOREST CANOPIES

MICHAEL HORSTMANN and MICHAEL S. MCLACHLAN*
Ecological Chemistry and Geochemistry, University of Bayreuth, 95440 Bayreuth, Germany

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Abstract—The deposition of polycyclic aromatic hydrocarbons, hexachlorobenzene and polychlorinated biphenyls, dibenzo-*p*-dioxins and dibenzofurans to a coniferous and a deciduous forest canopy was measured by simultaneously sampling bulk deposition below the canopies and in an adjacent clearing for one year. In addition, ambient air was sampled continuously, with separate analysis of the gaseous and particle-bound phases. The deposition of almost all compounds was higher under the forest canopies than in the clearing. The excess deposition to the forest sites was attributable to equilibrium partitioning between the atmosphere and the canopy vegetation, kinetically limited gaseous deposition, or particle-bound deposition. Which of these deposition processes dominated for a given compound was shown to depend on the octanol–air partition coefficient of the chemical and its gas/particle partitioning. Deposition velocities–to our knowledge the first for SOCs to forests–were calculated by dividing the excess deposition by the air concentrations. The gaseous deposition velocities were 0.78 cm s^{-1} to the coniferous canopy (annual weighted average) and 3.6 cm s^{-1} to the deciduous canopy (6 month summer average). These values are high compared to deposition velocities to forest canopies that have been measured for inorganic gases, reflecting the fact that lipophilic organic chemicals are taken up by the leaf/needle cuticle and not just via the stomata. The dry particle bound deposition velocities for particle diffusion and impaction were 0.05 and 0.73 cm s^{-1} for the coniferous and deciduous canopies, respectively. These values are considerably lower than the gaseous deposition velocities, underlining the importance of gaseous deposition for the accumulation of semivolatile organic compounds in forest ecosystems. © 1998 Elsevier Science Ltd. All rights reserved.

Key word index: Atmospheric deposition, forests, SOCs, PCDD/F, PCB, PAH.

INTRODUCTION

It is becoming apparent that forests play an important role in the environmental fate of many semivolatile organic compounds. Matzner (1984) showed bulk deposition of polycyclic aromatic hydrocarbons (PAHs) to be elevated under forest canopies. Simonich and Hites (1994) estimated that 44% of the PAHs emitted in the northeastern United States are deposited to forests. Hagenmaier and Krauß (1993) reported that forest soils contain two-thirds of all polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) present in the environment in southwestern Germany, and we have presented strong evidence linking the higher concentrations found in forest soils to elevated atmospheric deposition to the forest canopy (Horstmann and McLachlan, 1996; Horstmann *et al*., 1997).

Atmospheric contaminants can be transferred to forest canopies through either wet or dry deposition. Wet deposition, with the exception of orographic fog, can be expected to be similar to forested and non-forested land. Hence, the elevated deposition to forests must arise from dry deposition. It has been shown that dry deposition of SOCs to ryegrass can be divided into three categories according to the volatility of the compound (McLachlan *et al*., 1995). More volatile SOCs are deposited primarily through gaseous diffusion and achieve a partitioning equilibrium between the air and the leaf. SOCs of intermediate volatility are also subject mainly to dry gaseous deposition. However, due to the very large capacity of ryegrass to take up these compounds they remain far from a partitioning equilibrium, and the deposition is determined by the rate of transport from the atmosphere to the surface of the grass (the air side resistance). The third category is made up of relatively involatile SOCs where gaseous deposition is superseded in importance by dry-particle-bound deposition. Dry-particle-bound deposition can in turn be sub-divided into three processes (Sehmel, 1980): particle sedimentation, which is similar to forested and non-forested land, and particle impaction and diffusion, which can be expected to be higher to forests (Jonas and Heinemann, 1985). Mathematically, the deposition to the canopy N (mol m^{-2}) as a result of equilibrium partitioning can be expressed as the

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*Author to whom correspondence should be addressed.

product of the gaseous concentration C_G (mol m^{-3}) in the atmosphere, a vegetation/air partition coefficient (K_{PA} on a volume/volume basis) and the volume density of vegetation in the canopy V (m^3 m^{-2}), while the deposition in the last two categories can be written as the time integral of the product of a deposition velocity v (m s^{-1}) and the gaseous (C_G) or particle-bound (C_P) concentrations, respectively.

$$\text{Gaseous, equilibrium } N_{GE} = VK_{PA}\, C_G \tag{1}$$

$$\text{Gaseous, non-equilibrium; } N_{GN} = \int v_G C_G\, dt \tag{2}$$

$$\text{Particle bound; } N_P = \int v_P C_P\, dt. \tag{3}$$

It should be noted that there are transitions between these three categories. Compounds falling between categories 1 and 2 do not achieve a partitioning equilibrium and yet the vegetation concentration becomes so high that it significantly reduces the diffusive gradient from the atmosphere to the vegetation. This can be described using a modified form of equation (2) (McLachlan *et al.*, 1995). Similarly, for compounds falling between categories 2 and 3 both gaseous deposition and particle-bound deposition play a significant role. Nevertheless, the three simple cases described in equations (1)–(3) provide a useful basis for interpreting deposition of SOCs.

Assuming that the results for ryegrass can be extrapolated to forests, the deposition velocities are the key parameters determining the deposition of many SOCs to forest canopies. They are highly variable, both in time and with location in the canopy. While estimates of the true deposition velocity to a given point in the canopy at a given time may be of interest in some cases, long-term integrated average deposition velocities to the whole canopy are required for many applications such as evaluating the influence of forests on the regional and global fate of SOCs.

We are unaware of any experimentally determined deposition velocities of SOCs to forests. In the work presented in this paper, we undertook deposition and ambient air measurements to estimate the deposition velocities of PCDDs, PCDFs, polychlorinated biphenyls (PCBs), hexachlorobenzene and PAHs to a deciduous and to a coniferous forest canopy in southern Germany. Furthermore, through the selection of chemicals covering a broad range of physical–chemical properties, we hoped to establish whether the interpretive framework based on the three deposition regimes described above can also be applied to the deposition of SOCs to forests.

EXPERIMENTAL

Experimental concept

The two canopies studied in this project are located adjacent to each other in a forest 2 km south of the city of Bayreuth. One canopy was an 80–90 yr old spruce (*Picea abies*) stand; the other was an 80 yr old deciduous stand of beech (*Fagus sylvatica*) and oak (*Quercus robur*). Measurements were also conducted in a clearing 150 m from the edge of the forest and 300 m from the forest sampling sites. Previous studies in this area have shown the environmental levels of SOCs to represent Central European background conditions (Umlauf *et al.*, 1994a; McLachlan, 1996).

Simultaneous measurements of the deposition fluxes and the atmospheric concentrations of the study compounds in the gas and particle phases were conducted continuously for 12 months. These were used to calculate the deposition velocities using equations (2) and (3). Since direct measurement of atmospheric deposition to the canopy is difficult, we chose to measure deposition below the canopy. This implies that over a 1 yr period the flux to the canopy is equal to the flux out of the bottom of the canopy. This approach is only valid under the following conditions:

1. The substances are persistent in the canopy. Given the well-documented environmental persistence of these compounds and the long half-lives that have been measured for their clearance from vegetation (Reischl *et al.*, 1989; Umlauf *et al.*, 1991; Bacci *et al.*, 1992), this condition is likely satisfied.
2. The fraction of deposited chemical permanently stored in the canopy is small, or, in other words, most of the chemical deposited to the canopy eventually falls to the ground. A chemical mass balance of several spruce trees in the coniferous canopy indicated that the amount of PCDDs and PCDFs stored in the canopy is approximately 4 times the annual deposition flux, and that about half of the chemical was stored in the needles, which are discarded by the tree after 4–6 yr (Horstmann *et al.*, 1997). Given that the trees were 80–90 yr old, the presence of just 2 yr of deposition in the non-foliar tree parts (mainly bark) indicates that only a small fraction of the total deposition is retained in the canopy over long periods of time. Most of it is deposited to the leaves/needles which eventually fall to the ground. In the case of deciduous trees this occurs within the year. For coniferous trees where the foliage is retained in the canopy for several years condition 3 below becomes an important consideration.
3. The ambient air concentrations have not changed significantly over the last several years. This is important for the spruce canopy, where some of the needles falling to the ground may have been exposed to the atmosphere over a period of 6 yr, whereas the deposition velocity is determined with the current ambient air levels. Ambient air sampling at this site between 1989 and 1996 has produced evidence of declining levels of some of the compounds studied, but the decrease over this time period has been generally less than a factor of two (McLachlan, unpublished data). Hence, this assumption would appear reasonable.
4. All of the chemical present in the canopy comes from atmospheric deposition. This assumption is sound, since there is no known significant natural formation of these compounds, and it has been demonstrated that root uptake/translocation is negligible due to their hydrophobicity (Fries and Marrow, 1981; O'Connor *et al.*, 1991; Hülster and Marschner, 1993; Müller *et al.*, 1993; Fries, 1995).

Sampling methods

Deposition below the canopies and in the clearing was collected using the German VDI 2119 (Bergerhoff) standard method. This is a bulk deposition sampling method in which glass jars (i.d. = 9 cm) are deployed at a height of 2 m on poles equipped with a ring to prevent bird fouling. The jars are left for one month and then the contents are collected and analysed. This method is described in detail in Horstmann *et al.* (1997). In a detailed validation of a similar glass bulk deposition sampler for PCDDs and PCDFs it was shown that this method collects primarily wet deposition and sedimenting particles, but not dry gaseous deposition or diffusing/impacting particles. Furthermore, sampling was not subject to artifacts due to photodegradation or volatilisation of previously deposited PCDDs or PCDFs

(Horstmann and McLachlan, 1997). The Bergerhoff method was successfully employed in the year preceding this study to measure deposition of PCDDs and PCDFs at the same site (Horstmann and McLachlan, 1996; Horstmann *et al.*, 1997). During these studies no insects or bird fouling were observed in the jars and in no case did the jars overflow.

Ambient air was sampled using a high-volume sampler equipped with a glass fibre filter to capture the airborne particles and an XAD trap for gaseous chemical. It was operated at a flow of 5–6 $m^3 h^{-1}$, and the filter and cartridge were changed on a monthly basis. A detailed description of the sampler and a study showing it to be free of a wide range of sampling artifacts are found in Hippelein *et al.* (1993). It has been successfully employed in a multi-station long term air monitoring program (Hippelein *et al.*, 1996; Kaupp *et al.*, 1996; Dörr *et al.*, 1996).

One high-volume air sampler and 20 Bergerhoff jars were installed at each of the three sites: under the spruce canopy, under the beech/oak canopy, and in the clearing. The sampling program ran for 1 yr, from May 1995 to April 1996. In October and November, laundry baskets were placed in the deciduous forest as a second method of sampling deposition, since it was unclear if the Bergerhoff jars would representatively sample leaf fall. The samples were collected on a monthly basis. The XAD traps and filters from the high-volume sampler were analysed separately. The contents of ten of the Bergerhoff jars were combined for one sample, giving two parallel deposition samples at each site.

Analytical methods

The sampling of the Bergerhoff jars and subsequent extraction of the deposition samples were conducted according to the method in Horstmann *et al.* (1997). The filter and XAD samples were Soxhlet extracted in toluene for 16 h. An internal standard cocktail of labelled isotopes including five 2,3,7,8-substituted PCDD congeners, seven 2,3,7,8-substituted PCDF congeners, hexachlorobenzene, six PCB congeners and 16 PAHs was added to the extraction solvent of all samples. Following the extraction the sample was divided into two parts: 5–10% was used for the PAH analysis, while the remainder was used to determine the PCDDs, PCDFs, PCBs and hexachlorobenzene.

The PCDD/PCDF/PCB fraction was cleaned up on a combined acid silica gel/basic silica gel column and an alox column as described in Horstmann *et al.* (1997), the only modification being that the first fraction from the alox column, which contained the PCBs and hexachlorobenzene, was retained in addition to the third fraction, which contained the PCDDs and PCDFs. The PCB fraction was concentrated to 1 ml for analysis, the PCDD/PCDF fraction to 15 μl.

The PAH clean-up was conducted according to the method in Kaupp and Sklorz (1996). The first step was gel-permeation chromatography using Biobeads SX8 (Bio Rad) and toluene. The sample was then applied to a column of activated silica gel and eluted with *n*-hexane/acetone (4 : 1). The solvent was concentrated to 0.5 ml for analysis.

The analysis of all compounds was conducted using HRGC/HRMS on a VG Autospec Ultima. The parameters employed for the analysis of the tetra- through octa-chlorinated PCDD and PCDF homologues are given elsewhere (Horstmann and McLachlan, 1995). Hexachlorobenzene, the PCBs and the PAHs were analysed on a DB-5MS column (J&W, 0.25 mm × 30 m, 0.25 μm film thickness) using negative EI at a resolution of 6000–9000. Six PCB peaks (IUPAC congeners 28/31, 52, 101/84/90, 153, 138/158, and 180) and 16 PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, triphenylene, chrysene, benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i) perylene, dibenz(a,h)anthracene and coronene) were quantified.

RESULTS AND DISCUSSION

Quality of the data

The recovery of the internal standards was $>70\%$ in all samples. The quantities of any given analyte found in the laboratory blanks (one blank was analysed with each 5–7 samples) were at least 5 times lower than the quantities present in the samples. The only exceptions were the gas-phase concentrations of the seven most involatile PAHs, which were discarded because of the high blanks. Despite the blank interferences the gaseous levels of these PAHs were $<10\%$ of the particle bound levels, indicating that they were virtually completely particle bound. No serious interferences or problems with the chromatography were observed for any of the compounds.

The concentrations of anthracene and perylene were very low and the agreement between parallel samples was poor. Hence, they were not included in the data set. For the other compounds good agreement was found between the parallel deposition samples. Since three parallel deposition samples were collected during the previous year's sampling, these data were used to estimate the precision of the deposition sampling method. The mean coefficient of variation for the PCDD/F homologues and 2,3,7,8-substituted isomers over the 12 month sampling period was 0.115 in the clearing and 0.195 in the coniferous forest. It was concluded that the higher values in the coniferous forest likely reflect the spacial heterogeneity of deposition there (Horstmann *et al.*, 1997).

The deposition fluxes measured in the deciduous forest in autumn with the laundry baskets were also in reasonable agreement with the fluxes determined with the Bergerhoff jars (e.g. the mean difference between the two methods for the PCDD/F homologues in October was 13%). Most of this deposition was associated with falling leaves (see below). The fluxes measured with the Bergerhoff jars were generally somewhat higher than those measured with the baskets, which may be due to leaves having been blown out of the baskets. The results indicate that the Bergerhoff jars were effective at collecting the falling leaves.

No parallel air samples were collected. However, in a previous study using the same sampler the median coefficient of variation from three parallel samples was 0.065 for the compounds studied here (Hippelein *et al.*, 1993). We consider this to be an upper estimate of method precision, since the current study was conducted with improved analytical procedures.

Deposition fluxes and ambient air concentrations

The annual bulk deposition fluxes at the three sites and the average gaseous and particle bound concentrations in the ambient air in the clearing are given in Table 1. The deposition fluxes of the PCDD and PCDF homologues were similar to those measured in the previous year (Horstmann *et al.*, 1997). The somewhat lower fluxes of the higher chlorinated congeners to the clearing may be related to the lower levels of

Table 1. Annual deposition fluxes at the three sites and average gaseous and particle- bound ambient air concentrations in the clearing

	Deposition ($ng\,m^{-2}\,y^{-1}$)			Gaseous Conc. ($pg\,m^{-3}$)		Particle-bound conc. ($pg\,m^{-3}$)	
Compound	Clearing	Coniferous	Deciduous	May–April	May–Oct.	May–April	May–Oct.
Phenanthrene	32,200	105,000	252,000	7800	3600	1100	68
Fluoranthene	27,800	107,000	233,000	2000	630	1980	149
Pyrene	15,500	58,800	139,000	930	290	1480	122
Triphenylene/Chrysene	16,300	35,800	69,800	148	72	1250	121
Benzo[b]fluoranthene	18,900	32,800	54,300	153	22	1810	250
Benzo[k]fluoranthene	5310	10,100	16,700	47	6.3	490	75
Benzo[e]pyrene	7940	13,800	21,600			620	111
Benzo[a]pyrene	7450	15,200	20,600			710	94
Indeno[1,2,3-cd]pyrene	10,800	16,700	25,900			840	160
Benzo[ghi]perylene	6470	10,300	16,800			430	88
Dibenz[ah]anthracene	1370	2350	3330			96	17.1
Coronene	6350	9000	13,300			280	68
Hexachlorobenzene	150	584	1480	156	210	0.46	0.43
PCB 28/31	732	796	1410	13.5	20	0.20	0.23
PCB 52	291	370	980	7.6	11.5	0.143	0.16
PCB 101/84/90	160	471	1840	5.9	9.2	0.21	0.19
PCB 153	275	1230	3570	5.3	7.9	0.54	0.32
PCB 138/158	192	946	2480	2.7	4.0	0.40	0.22
PCB 180	123	630	1240	0.97	1.33	0.44	0.17
		($pg\ m^{-2}\ y^{-1}$)		($fg\ m^{-3}$)			($fg\ m^{-3}$)
ΣCl_4DD	1640	5870	12,000	26.8	14.5	26	3.6
ΣCl_5DD	3310	8530	13,600	17.5	15.5	57	9.6
ΣCl_6DD	7790	12,100	20,100	11.5	15.5	129	39
ΣCl_7DD	14,900	16,200	25,200	5.9	9.5	250	110
Cl_8DD	27,600	27,500	36,500	2.5	3.9	330	176
ΣCl_4DF	8220	32,400	55,700	191	104	153	18.5
ΣCl_5DF	8290	21,700	32,900	68	45	194	25
ΣCl_6DF	6810	11,100	16,800	16.3	17.6	145	31
ΣCl_7DF	4490	4970	7360	3.1	5.0	85	29
Cl_8DF	2420	2400	3360	0.51	0.73	41	14.7
2,3,7,8-Cl_4DD	23	107	216	0.46	0.28	0.66	0.10
1,2,3,7,8-Cl_5DD	237	435	708	0.93	0.86	4.2	0.87
1,2,3,4,7,8-Cl_6DD	429	504	826	0.57	0.79	6.0	2.3
1,2,3,6,7,8-Cl_6DD	561	709	1220	0.85	1.13	9.9	3.3
1,2,3,7,8,9-Cl_6DD	606	650	1190	0.61	0.83	10.0	3.5
1,2,3,4,6,7,8-Cl_7DD	7640	7740	12,300	2.83	4.5	135	61
2,3,7,8-Cl_4DF	532	2140	3410	7.2	4.3	9.2	1.39
1,2,3,4/7,8-Cl_5DF	605	1740	2570	4.9	3.1	15.1	1.97
2,3,4,7,8-Cl_5DF	697	1630	2360	3.3	2.9	16.3	2.8
1,2,3,4,7,8/9-Cl_6DF	734	1190	1990	1.96	2.2	17.4	3.6
1,2,3,6,7,8-Cl_6DF	620	1070	1740	1.53	1.79	13.3	3.1
2,3,4,6,7,8-Cl_6DF	757	1180	1730	1.05	1.38	15.5	4.5
1,2,3,4,6,7,8-Cl_7DF	2770	3280	4680	2.04	3.3	52	17.4
1,2,3,4,7,8,9-Cl_7DF	318	282	479	0.14	0.25	7.6	2.5

precipitation during this study (741 vs 888 mm in 1994/1995).

The ambient air concentrations displayed annual cycles typical for these compounds in Central Europe (König *et al.*, 1993; Hiester *et al.*, 1995; Hippelein *et al.*, 1996; Kaupp *et al.*, 1996; Dörr *et al.*, 1996), the PCDDs, PCDFs and PAHs displaying a strong maximum in winter, the PCBs a minimum. The gas/particle partitioning was also consistent with previous measurements in the area (Hippelein *et al.*, 1996) and with current partitioning theory, the gaseous fraction increasing with increasing temperature and volatility of the compound (with the exception of the PAHs, which behaved as if they were less volatile than their vapour pressures relative to the other compounds would indicate). A notable exception was benz(a) anthracene, which was virtually absent from the gas phase during the summer. This suggested that this compound is subject to photodegradation in the gas phase. Due to this suspected instability it was not included in the final data set.

Both the particle bound and gaseous concentrations were systematically lower under the forest canopies than in the clearing, suggesting that the forests influenced the contaminant levels in the atmosphere, as has been reported by others (Hornbuckle and Eisenreich, 1996). For this reason the data from the clearing were used to calculate the deposition velocities.

Calculation of deposition velocities

In calculating the deposition velocities it was assumed that the particle-bound deposition velocity should be the same for all compounds within a chemical family. This assumption is based on the observation that the particle size distribution of PCDDs/PCDFs is the same for all homologue groups (Kaupp *et al.*, 1994), and that the particle-size distributions of different PAHs are also similar to each other (Katz and Chan, 1980; Venkataraman and Friedlander, 1994). This suggests that within their respective families these compounds are associated with the same particles. This being the case, the particle-bound deposition velocities for individual compounds in each of these substance groups should be the same.

Use was also made of the anticipated similarity between the gaseous deposition velocities of different compounds. The only physical–chemical property of the compound expected to influence the gaseous deposition velocity is the diffusivity in air. The compounds studied here have similar diffusivities (a reflection of their similar size), and hence for a given canopy the deposition velocities should be similar. This is, of course, only true as long as the compound does not approach a partitioning equilibrium with the vegetation. Once this happens the deposition flux begins to decrease, leading to a reduction in the (apparent or net) deposition velocity.

To calculate the deposition velocities, the deposition fluxes measured in the clearing were first subtracted from the fluxes measured below the canopies. It has been shown for PCDDs/PCDFs that the deposition flux measured in the clearing with glass bulk deposition samplers consists almost entirely of wet deposition and particle sedimentation (Horstmann and McLachlan, 1997). Assuming that the flux measured below the canopy is approximately equal to the flux to the canopy, flux below canopy minus flux to the clearing gives the canopy interception I, here defined as the flux to the canopy through particle impaction/diffusion and dry gaseous deposition. As with deposition, the interception is given per square meter (horizontal) ground surface.

The particle-bound deposition velocities of the six almost completely particle-bound PAHs were calculated by dividing the interception fluxes by the particle-bound concentrations in the air C_P,

$$v_P = I/C_P. \tag{4}$$

The average of these six deposition velocities $\bar{v}_P$ was then calculated and applied to the determination of the gaseous deposition velocity for the remaining PAHs. It was multiplied by the particle-bound ambient air concentrations to give the interception flux due to particle deposition I_P,

$$I_P = \bar{v}_P C_P. \tag{5}$$

This was subtracted from the total interception flux to give the interception flux due to gaseous deposition I_G, which was then divided by the gaseous ambient air concentration C_G to arrive at the gaseous deposition velocity,

$$\mathrm{v}_G = (I - I_P)/C_G = I_G/C_G. \tag{6}$$

In the case of the PCDDs/PCDFs there were no congeners that were virtually completely particle bound so the particle-bound deposition velocity could not be calculated independently. Instead, a value was chosen that minimised the variation in the gaseous deposition velocities between the 10 PCDD/PCDF homologues. This approach was justified because none of the PCDDs/PCDFs approached a partitioning equilibrium (see below). This particle-bound deposition velocity was also employed for the calculation of the gaseous deposition velocities of the PCBs, but since the canopy interception of the PCBs was almost completely due to gaseous deposition, this assumption had little impact on the results.

Over 90% of the annual excess deposition below the deciduous canopy occurred in October, November and—to a lesser extent—December, indicating that the excess deposition was almost exclusively associated with leaf fall. Hence, the average air concentrations during the period in which the leaves were on the trees (May–October) were used to calculate the deposition velocities at this site (see Table 1).

The strong seasonal variation in the gaseous and particle-bound concentrations presents problems when estimating the average deposition velocities to the coniferous canopy. Referring to equations (2) and (3), it is only mathematically permissible to calculate the mean deposition velocity v from N/C when C is constant over time. Whereas the concentrations of most compounds showed little or only moderate seasonal variation (this can be seen by comparing the 12-month and 6-month means in Table 1), the annual variation in the monthly means of the particle-bound concentrations of some PAHs exceeded a factor of 100. It then becomes important to consider whether the average deposition velocity is uniform throughout the year, or whether it too shows seasonal variation. When it is higher in summer, then the air concentrations in summer have to be weighted more heavily in calculating v, and *vice versa*. Higher deposition velocities can be expected during the summer at this site due to the higher solar radiation and reduced frequency of stable atmospheric conditions. In the absence of quantitative information, we arbitrarily weighted the air concentrations from the six summer months three times more than the concentrations from the six winter months (e.g. we took the mean of the 12 month mean and the six month mean concentrations in Table 1).

The deposition velocities were calculated by taking the difference between two or three measured values. This procedure is very sensitive to measurement error. The annual deposition flux is the sum of 12 monthly deposition fluxes, which are in turn the means of two samples. As a first approximation, the coefficient of variation for the annual deposition flux is equal to the coefficient of variation for the sampling method divided by $\sqrt{24}$. Using the mean coefficients of variation for the deposition methods given above, this amounts to 0.02 for the clearing and 0.04 for the forested sites, respectively. Since the larger error for the forest sites dominates the calculation of the difference, the standard deviation of the interception fluxes can be expected to be in the order of 4% of the total deposition to a given forest site. Hence, only those values were utilised in the deposition velocity calculations for which the respective canopy interception flux (gaseous I_G or particle-bound I_p) was at least 20% of the total deposition flux below the canopy (with one exception, see below).

Particle-bound deposition velocities

The particle-bound deposition velocities are summarised in Table 2. There is very good agreement between the deposition velocities calculated for the six PAHs, the coefficient of variation being 0.16 and 0.13 for the coniferous and deciduous canopies, respectively. No values could be calculated for PCDD/PCDF deposition to the coniferous canopy since the deposition fluxes of the primarily particle-bound hepta- and octachlorinated congeners to the clearing and below the spruce stand were virtually identical (see Table 1).

The average deposition velocities to the deciduous canopy are similar to representative values estimated for the deposition of particulate sulphates to deciduous forests (Voldner *et al.*, 1986). Interestingly, the deposition velocities for the PAHs to the coniferous canopy were 15 times lower than the deciduous canopy values. This can be attributed in part to the influence of differences in canopy turbulence and surface properties on particle advection and diffusive deposition to the canopy surfaces. This influence is reflected in the differences in the gaseous deposition velocity, which was a factor of 5 higher to the deciduous canopy (see below). A further contributing factor may have been seasonal variation in the deposition velocity as discussed above. The deposition velocity to the deciduous canopy reflects only the six summer months, while the value for the coniferous canopy is a weighted average over the year. According to the weighting scheme selected, the summer deposition velocity should be 50% higher than the annual average, but this factor may be higher. Finally, it is possible that other properties of the canopies not reflected in the dry gaseous deposition velocity contributed to the differences in dry-particle-bound deposition.

Table 2. Long-term average dry particle-bound deposition velocities of SOCs to two forest canopies (flux due to particle sedimentation not included)

Compound	Deposition velocity ($cm\,s^{-1}$) Coniferous[a]	Deciduous[b]
Benzo[e]pyrene	0.051	0.78
Benzo[a]pyrene	0.061	0.88
Indeno[1,2,3-cd]pyrene	0.038	0.60
Benzo[ghi]perylene	0.047	0.74
Dibenz[ah]anthracene	0.055	0.73
Coronene	0.048	0.65
Mean (6 PAHs)	0.050	0.73
PCDDs/PCDFs	—	0.2

[a] Annual average calculated by weighting the particle-bound air concentrations for May–October three times more than for November–April.

[b] Average for May–October.

Although the particle-bound interception flux of the higher chlorinated $Cl_{7\text{-}8}DD/F$ to the deciduous canopy was only 12–15% of the total deposition flux, the deposition velocity is included in Table 2 because it suggests a distinctly different behaviour for the PCDDs/PCDFs compared to the PAHs. The 4 times lower deposition velocity for the PCDDs/PCDFs might be the result of sampling/analytical error, but a deviation of this magnitude is considered unlikely. An underestimation of the PAH fluxes in the clearing due to photodegradation of the PAHs in the Bergerhoff jars would lead to an elevated deposition velocity for the PAHs, but this hypothesis can be discarded since similar results are obtained if the flux under the conifer canopy is used instead of the flux in the clearing as the measure of wet deposition/particle sedimentation. One plausible explanation for the difference in the deposition velocities is that the particle-size distribution of the particle-bound PAHs and PCDDs/PCDFs differ. Parallel measurements of the particle-size specific concentrations of PAHs and PCDDs/PCDFs would be valuable for evaluating this hypothesis.

Gaseous deposition velocities

The calculated gaseous deposition velocities are summarised in Table 3. The values obtained for the PCDDs/PCDFs are in very good agreement, the means being $0.78 \pm 0.15\,cm\,s^{-1}$ for the coniferous and $3.6 \pm 0.65\,cm\,s^{-1}$ for the deciduous canopy. The fact that the deposition velocity did not increase with increasing volatility (decreasing degree of chlorination) indicates that these compounds did not approach a partitioning equilibrium. The one exception was the ΣCl_4DF, for which somewhat lower values were obtained than for the other PCDDs/PCDFs. This suggests that some of the more volatile Cl_4DF isomers might have approached equilibrium. The fact that 2,3,7,8-Cl_4DF does not also show lower values is

Table 3. Long-term average gaseous deposition velocities of SOCs to two forest canopies, calculated pseudo-plant/air partition coefficients^{a} and octanol/air partition coefficients

	Deposition velocity (cm s^{-1})		log K_{PA}^{a}		log K_{OA}
Compound	Coniferous^{b}	Deciduous^{c}	Coniferous	Deciduous	(25°C)
Phenanthrene	0.035^{d}	0.37^{d}	7.38	7.57	7.60^{e}
Fluoranthene	0.15^{d}	1.9^{d}	7.95		8.81^{e}
Pyrene	0.16^{d}	2.4^{d}	7.98		8.81^{e}
Triphenylene/chrysene	0.25	3.5			10.63^{f}
Hexachlorobenzene	0.0074^{d}	0.039^{d}	6.92	6.72	6.90^{g}
PCB 28/31		0.21^{d}		7.77	7.92^{h}
PCB 52	0.026^{d}	0.38^{d}	7.49	7.95	8.22^{h}
PCB 101/84/90	0.13^{d}	1.15^{d}	8.19		8.80^{h}
PCB 153	0.46	2.6			9.37^{h}
PCB 138/158	0.70	3.6			9.51^{h}
PCB 180	1.4	5.3			9.88^{h}
$\Sigma\mathrm{Cl_4DD}$	0.64	4.5			
$\Sigma\mathrm{Cl_5DD}$	0.98	4.1			
$\Sigma\mathrm{Cl_6DD}$	0.94	4.5			
$\Sigma\mathrm{Cl_7DD}$		4.6			
$\Sigma\mathrm{Cl_4DF}$	0.51	2.8			
$\Sigma\mathrm{Cl_5DF}$	0.72	3.3			
$\Sigma\mathrm{Cl_6DF}$	0.73	3.2			
$\Sigma\mathrm{Cl_7DF}$		2.5			
2,3,7,8-$\mathrm{Cl_4DD}$	0.70	4.3			10.14^{i}
1,2,3,7,8-$\mathrm{Cl_5DD}$	0.66	3.2			10.72^{i}
1,2,3,4,7,8-$\mathrm{Cl_6DD}$		2.6			11.17^{i}
1,2,3,6,7,8-$\mathrm{Cl_6DD}$		3.1			11.21^{i}
1,2,3,7,8,9-$\mathrm{Cl_6DD}$		3.6			11.49^{i}
1,2,3,4,6,7,8-$\mathrm{Cl_7DD}$		3.8			11.87^{i}
2,3,7,8-$\mathrm{Cl_4DF}$	0.88	4.2			9.42^{i}
1,2,3,4/7,8-$\mathrm{Cl_5DF}$	0.89	3.9			10.10^{i}
2,3,4,7,8-$\mathrm{Cl_5DF}$	0.92	3.4			10.09^{i}
1,2,3,4,7,8/9-$\mathrm{Cl_6DF}$	0.63	3.3			10.64^{i}
1,2,3,6,7,8-$\mathrm{Cl_6DF}$	0.79	3.6			10.68^{i}
2,3,4,6,7,8-$\mathrm{Cl_6DF}$	0.99	3.8			10.79^{i}
1,2,3,4,6,7,8-$\mathrm{Cl_7DF}$		2.6			11.25^{i}

[a] This pseudo-K_{PA} value is the quotient of the deposition flux divided by the canopy volume density and the average gaseous concentration for October (deciduous stand) or for the whole year (coniferous stand). It is not a thermodynamically defined equilibrium partition coefficient.

[b] Annual average calculated by weighting the gaseous air concentrations for May–October three times more than for November–April.

[c] Average for May – October calculated using the average gaseous air concentrations for this period.

[d] These are net deposition velocities which are lower than the physical deposition velocities since these compounds approached a partitioning equilibrium

[e] Harner and Bidleman (1997).

[f] Calculated from Mackay *et al.* (1992)

[g] Harner and Mackay (1995).

[h] Kömp and McLachlan (1997b).

[i] calculated from Govers and Krop(1996).

not inconsistent with this explanation, since this congener is one of the least volatile $\mathrm{Cl_4DF}$ isomers.

These deposition velocities are high compared to values reported for PCDDs/PCDFs to grass and corn crops (McLachlan, 1996), which is not surprising given the higher surface roughness of the forest canopies. They are also high compared to deposition velocities for many inorganic gases (Voldner *et al.*, 1986). Gaseous deposition velocities to forest canopies of this magnitude are generally only reported for inorganic constituents which react on leaf surfaces such as HNO_3 (Voldner *et al.*, 1986; Voldner and Sirois, 1986). This is consistent with the fact that the SOCs in this work are also deposited to the surface of the cuticles (Reischl *et al.*, 1987; Umlauf *et al.*, 1994b), whereas other inorganic air pollutants for which measured deposition velocities are available are taken up primarily through the stomata. The cuticle offers a much larger receptor surface than the stomata, leading to higher deposition velocities.

The average gaseous deposition velocity for the PCDDs/PCDFs to the deciduous forest was 5 times higher than to the coniferous forest. Error in the values for the coniferous stand due to incorrect seasonal weighting of the air concentrations are insignificant in this case, since in contrast to the particle phase many of the gaseous concentrations (e.g. ΣCl_5DD, ΣCl_6DF, 1,2,3,7,8-Cl_5DD, 2,3,4,7,8-Cl_5DF, 1,2,3,4,7,8-Cl_6DF) were relatively constant over the year. The differences between the two canopies may nevertheless be partly due to higher average deposition velocities in summer than in winter, but it is felt that differences in the canopy turbulence and the mass transfer directly at the leaf/needle surface were likely also important.

Returning to Table 3, it can be seen that the deposition velocities of triphenylene/chrysene and the higher chlorinated biphenyls agree quite well with those of the PCDDs/PCDFs. This is consistent with the postulated independence of the gaseous deposition velocity from the physical–chemical properties of these compounds, given their similar gaseous diffusivities.

With increasing chemical volatility the calculated gaseous deposition velocities of the PCBs and PAHs decrease. This indicates that these compounds reached an air/canopy partitioning equilibrium. As equilibrium is approached the accumulation of chemical in the canopy slows since the deposition is now in part counteracted by volatilisation of chemical from the canopy. In this case the calculated deposition velocities do not represent the physical transport of gaseous chemical to the canopy. These are net deposition velocities describing the net transport.

A pseudo-canopy/air partition coefficient can be calculated using equation (1). The volume densities of the deposited foliage V were estimated from the measured leaf fall for the deciduous site ($440\,\mathrm{g\,dw\,m^{-2}}$) and from the annual litter fall for the coniferous site ($121\,\mathrm{g\,dw\,m^{-2}}$). These were divided by the dry weight fraction (assumed to be 40%) and the fresh foliage density (assumed to be $0.9\,\mathrm{kg}\,\ell^{-1}$) to yield the volume densities of $0.0012\,\mathrm{m^3\,m^{-2}}$ (deciduous) and $0.00034\,\mathrm{m^3\,m^{-2}}$ (coniferous). The pseudo-partition coefficients were then calculated for all compounds with net deposition velocities at least 5 times lower than the average values measured for the PCDDs/PCDFs (see Table 3). In the case of a partitioning equilibrium, the plant concentrations reflect the air concentrations at the time of deposition. For the deciduous canopy the gaseous air concentrations in October were employed, since the excess canopy deposition occurred almost exclusively in October/November. For the coniferous canopy the average annual concentrations were employed to reflect the relatively homogenous distribution of the excess canopy deposition throughout the year.

In Table 3, $\log K_{PA}$ is seen to increase with decreasing volatility of the compound. Several laboratory studies have shown the vegetation/air partition coefficient of hydrophobic chemicals to be related to the octanol/air partition coefficient K_{OA} (Bacci *et al.*, 1990; Paterson *et al.*, 1991; Tolls and McLachlan, 1994), which also increase with decreasing volatility (see Table 3). Both K_{PA} and K_{OA} are a strong function of temperature (Kömp and McLachlan, 1997a; Harner and Mackay, 1995), and hence in order to compare the K_{PA} and K_{OA} values it was necessary to temperature-correct the K_{OA} values from 25°C to the temperature at the time of deposition using a van't Hoff-type equation. The average temperature in October (11°C) was used for the deciduous canopy, the average annual temperature (8°C) for the coniferous canopy. The enthalpies of phase change were taken from Harner and Bidleman (1997) for the PAHs (a value of $80\,\mathrm{kJ\,mol^{-1}}$ was assumed for triphenylene/chrysene), Harner and Mackay (1995) for hexachlorobenzene, Kömp and McLachlan (1997b) for the PCBs and McLachlan *et al.* (1995) for the PCDDs/PCDFs.

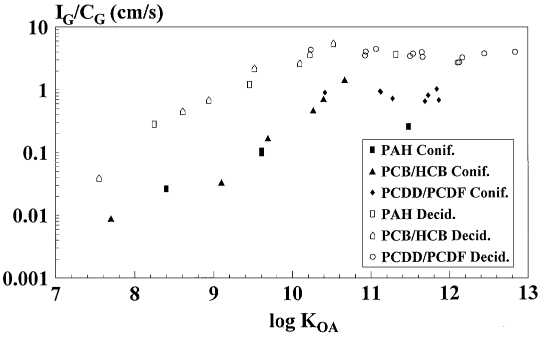

Fig. 1. Plot of the quotient of the annual gaseous canopy interception I_G and the gaseous air concentration C_G vs the octanol/air partition coefficient K_{OA} at ambient temperature (see text for details).

The influence of K_{OA} on the gaseous deposition behaviour is illustrated in Fig. 1. The quotient of the gaseous interception flux to the canopy I_G and the gaseous concentration C_G is plotted against the temperature-corrected $\log K_{OA}$ values. For compounds with $\log K_{OA} > 10$, the May–October mean and the weighted annual mean gaseous concentrations were used for the deciduous and coniferous canopies, respectively. For compounds with $\log K_{OA} < 10$, the October concentrations were used for the deciduous forest, the annual means for the coniferous site.

All compounds with $\log K_{OA} > 10.5$ did not approach a partitioning equilibrium. The quotient of the gaseous interception flux and the gaseous concentration in this part of the figure is equal to the gaseous deposition velocity (about $3.5\,\mathrm{cm\,s^{-1}}$ for the deciduous stand and $0.8\,\mathrm{cm\,s^{-1}}$ for the coniferous stand). The low value for triphenylene/chrysene in the coniferous stand (just above the legend in Fig. 1) can be attributed to the extreme sensitivity of its gaseous interception flux to the seasonal weighting of the particle bound concentrations.

All compounds with $\log K_{OA} < 10$ approached a partitioning equilibrium. A linear relationship between the $\log(I_G/C_G)$ and $\log K_{OA}$ is apparent for each canopy. The following linear regressions were obtained:

$$\log(I_G/C_G) = \begin{cases} 0.76 \log K_{OA} - 6.97, \quad r^2 = 0.95 \\ \qquad \text{(deciduous canopy in cm s}^{-1}\text{)} & (7) \\ 0.68 \log K_{OA} - 7.39, \quad r^2 = 0.94 \\ \qquad \text{(coniferous canopy in cm s}^{-1}\text{)} & (8) \end{cases}$$

These can be converted into relationships for the pseudo-partition coefficient as a function of K_{OA} using equation (1) and the estimated values for V:

$$K_{PA} = \begin{cases} 14\ K_{OA}^{0.76} \text{ (deciduous canopy)} & (9) \\ 38\ K_{OA}^{0.69} \text{ (coniferous canopy).} & (10) \end{cases}$$

The exponents of the K_{OA} term in equations (9) and (10) are distinctly less than 1. Most laboratory studies to date have suggested that K_{PA} should be linearly proportional to K_{OA} (Bacci *et al.*, 1990; Paterson *et al.*, 1991; Tolls and McLachlan, 1994). However, in a comparison of the plant/air partitioning of PCBs in different plants it was recently shown that the exponent of the K_{OA} term can vary widely. Exponents between 0.57 and 1.15 were obtained for the five grassland species tested (Kömp and McLachlan, 1997c). The exponents obtained for the spruce and beech/oak canopies fall within this range. However, it should be remembered that these are pseudo-partition coefficients that are not measured at a defined equilibrium state but rather in a constantly changing environment. For instance, varying environmental temperatures have a strong influence on K_{PA}. Compounds with lower K_{OA} values will respond more rapidly to the temperature-induced changes in K_{PA} than compounds with higher K_{OA} values (Kömp and McLachlan, 1997a), leading to different effective "equilibrium temperatures" for different compounds. Furthermore, there is strong evidence that a significant portion of the deposition flux in the spruce canopy is not associated with the falling needles (litter fall), but rather arises from erosion of chemical from the needle surface followed by deposition (Horstmann and McLachlan, 1996). This is thought to be caused by the erosion of cuticular waxes where a large fraction of these chemicals are stored in the needles (Reischl *et al.*, 1987; Umlauf *et al.*, 1994b). Since cuticular waxes that have been lost from spruce needles are replaced (Kurbasik, 1989), it can be expected that the eroded contaminant will also be replaced in the needles. Including the non-litter fall deposition flux in the calculation of the pseudo-K_{PA} value will thus tend to overestimate the true K_{PA} value.

It is interesting that a log K_{OA} of 10 represents the dividing point between equilibrium and non-equilibrium for both canopies. One might expect that more compounds would reach equilibrium in the coniferous canopy, since the needles are exposed for about 5 yr as opposed to 6 months for the oak and beech leaves. However, the longer exposure time is largely cancelled out by the 5 times lower gaseous deposition velocities to the coniferous canopy.

CONCLUDING DISCUSSION

Figure 1 could theoretically be extended to include particle-bound deposition, but for the six strongly particle-bound PAHs no gaseous concentrations could be reliably determined. Instead, the quotient of the total interception flux and the particle-bound concentration I/C_P was plotted against the quotient of the particle bound and gaseous air concentrations C_P/C_G (see Fig. 2). For the coniferous canopy the 12 month mean air concentrations were used, for the deciduous canopy the 6 month means. The six virtually completely particle bound PAHs were arbitrarily assigned C_P/C_G quotients between 40 and 90. All compounds with $\log K_{OA} > 9$ and where the total canopy interception exceeded 20% of the canopy deposition are plotted, including several in the transition region from primarily particle bound to primarily gaseous deposition that did not meet the criteria for the calculation of the deposition velocities. The right-hand side of Fig. 2 contains those compounds deposited primarily with particles. The levels of the plateaus correspond to the particle-bound deposition velocities for the two canopies. The lower levels for the PCDDs/PCDFs in the deciduous canopy discussed earlier are clearly seen. The increasing values of I/C_P in the left-hand portion of the graph reflect the added flux from dry gaseous deposition. The transition from one regime to the other is smooth. Surprisingly, this transition occurs at very high particle bound levels. Some compounds which were, on average, 90% particle-bound were deposited primarily in gaseous form.

The reason for this is the large difference between the gaseous and particle-bound velocities. The gaseous deposition velocities were 5–18 times higher for the deciduous canopy and 15 times higher for the coniferous canopy. This demonstrates the importance

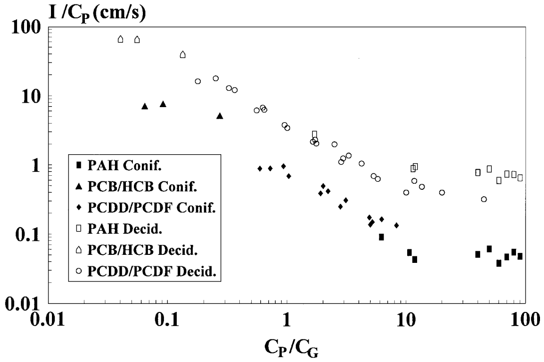

Fig. 2. Plot of the quotient of the annual total canopy interception I and the particle-bound concentration C_P vs the quotient of the particle-bound concentration and the gaseous concentration C_G (see text for details).

of gaseous diffusion as a mechanism for organic chemical deposition in forest ecosystems. Note again that the particle-bound deposition velocities determined here pertain only to particle diffusion and impaction. For the PCDDs/PCDFs deposition through diffusion can be expected to exceed deposition through impaction (Schröder *et al.*, 1997). Given the larger size and hence lower diffusivities of particles compared to gases, the lower deposition velocities for particles are to be expected.

In summary, the three deposition regimes described in equations (1)–(3) were identified for each of the forest canopies. Two properties were found to determine which deposition regime a given compound belonged to. For compounds with low K_{OA} values ($< 10^{10}$) the deposition to the canopy was governed by vegetation/gas phase partitioning. However, for compounds with higher K_{OA} values, the vegetation/air partition coefficient became so large that a partitioning equilibrium was not reached. The transition from this kinetically limited gaseous deposition to a dominance of particle-bound input was controlled by the gas/particle partitioning. It has recently been hypothesised that the gas/particle partitioning is also linearly proportional to K_{OA} (Finizio *et al.*, 1997), and as more measured K_{OA} values emerge it may be possible to describe the transition between all three regimes as a function of just this one physical-chemical property.

The deposition of all compounds can be predicted within a factor of two with equations (1)–(3) using the average deposition velocities for the canopy ($v_{G\mathrm{con}} = 0.78\ \mathrm{cm\,s^{-1}}$, $v_{G\mathrm{dec}} = 3.6\ \mathrm{cm\,s^{-1}}$, $v_{P\mathrm{con}} = 0.05\ \mathrm{cm\,s^{-1}}$, $v_{P\mathrm{dec}} = 0.73\ \mathrm{cm\,s^{-1}}$ (PAHs) or $0.2\ \mathrm{cm\,s^{-1}}$ (PCDDs/PCDFs)) and the relationships for the pseudo-K_{PA} given in equations (9) and (10). A major uncertainty remains in the determination of the particle bound deposition velocity in the coniferous canopy as a result of the pronounced annual cycle in the particle-bound concentrations. While it was assumed that the deposition velocity from May to October was on average 3 times higher than from November to April, an experimental determination of the seasonal variability is needed. Also, a more rigorous approach for the calculation of the partitioning behaviour is desirable, one that utilises true partition coefficients and accounts for their temperature variability.

The deposition velocities determined in this study are valid only for the canopies studied. Measurements in other canopies are required to establish the variability of the deposition velocities as a function of tree species, canopy structure and climate. However, the work presented here has served to demonstrate the influence of physical–chemical properties on deposition and has provided some deposition velocities that should be of value for performing initial evaluations of the role of forests in the environmental fate of organic contaminants.

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