

# Deposition of PCBs in mountains: The forest filter effect of different forest ecosystem types

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## Abstract

The effect of canopy composition and density on the forest filter effect (the deposition flux under the canopy and deposition to bare soil) for polychlorinated biphenyls (PCBs) was investigated for forests of the Italian Alps. Deposition fluxes were measured in situ using deposition samplers below canopies and in adjacent clearings at three altitudes (1100, 1400, and 1800 m above sea level). Forest sites were selected on the basis of canopy composition and density. Net forest fluxes (NFFs) were calculated by subtracting the deposition flux under canopies by deposition fluxes to clearings and represent the net contribution of forests to PCB deposition. NFF trends are discussed in relation to canopy development. Mean deposition velocities were also calculated and a direct correlation with the octanol air partition coefficient ( $K_{OA}$ ) was found. A leaf area index (LAI) was used to calculate a specific, canopy density-independent, deposition velocity for each forest type. This parameter can be used to calculate the deposition of PCBs in forests, given their LAI. Results show that forests significantly enhance the deposition of PCBs to soil and that this effect is controlled by temperature, leaf dynamics, and  $K_{OA}$ .

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## 1. Introduction

Atmospheric transport and deposition to soils and vegetation are key factors for the study of environmental exposure to persistent organic pollutants (POPs). Methods to evaluate atmospheric deposition fluxes by both direct and indirect measurements have been developed and applied in different scenarios (Strachan and Eisenreich, 1988; Galassi et al., 1993; Gatz et al., 1994; Gregor et al., 1996; Jurado et al., 2004). The uptake of POPs by vegetation is a relevant step by which pollutants enter the terrestrial food web (McLachlan, 1996; Gouin et al., 2002). Forests, in particular, may strongly influence deposition fluxes to the ground (Horstmann and McLachlan, 1996; Brorström-Lundén and Löfgren, 1998). The capacity of leaves to accumu-

late organic pollutants (Bacci et al., 1990; Reischl et al., 1987; Umlauf et al., 1994; Di Guardo et al., 2003), the extent of organic surface area, together with high soil organic matter content, and infrequent biomass harvesting create the conditions for forests to be an important storage or “retardation” compartment for POPs in the terrestrial environment.

A model known as the “forest filter effect (FFE)” proposed by McLachlan and Horstmann (1998), predicted that the average annual deposition of some POPs on forested soils is approximately three times greater than that on bare soil. In this model, forest canopies are seen as cumulative compartments (with lipid-soluble POPs accumulating on leaf surfaces and in leaf cuticular waxes) able to redirect POPs to the soil following different processes: rain washout, wax erosion, and transport due to litter fall. The model is expressed as a function of  $K_{OA}$  and  $K_{AW}$  (*n*-octanol/air and air/water partition coefficients, respectively) and predicts a low

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filter effect for compounds with  $\log K_{OA} < 7$  and  $\log K_{AW} < -6$  and pronounced effects for compounds with  $7 < \log K_{OA} < 11$  and  $\log K_{AW} > 6$ . Few experimental data are currently available to better characterize the filter effect (Horstmann and McLachlan, 1996, 1997a, b, 1998). Considering the large percentage of the planet surface involved, the global role of forests in the fate of semivolatile organic compounds is receiving greater attention (Wania and McLachlan, 2001; Wegmann et al., 2004). Considerable uncertainties still exist concerning the variability of the FFE for different ecological scenarios, given the few experimental data available. This is particularly true for mountains, where different forest types are generally present at different altitudes.

In this study, the FFE was estimated for certain organochlorine compounds using deposimeters in forests and clearing sites along an altitudinal gradient (from 1000 to 1800 m above sea level (a.s.l.)) in the Italian Western Alps. These forests are characterized by different compositions, densities, and leaf phenology. In the alpine scenario, environmental conditions could determine the presence of contamination hotspots due to enhanced deposition (Daly and Wania, 2004). The main goal of this study is to evaluate the deposition of polychlorinated biphenyls (PCBs) in an alpine scenario and, more specifically, to characterize the role played by different forest types in deposition fluxes to soils.

## 2. Materials and methods

### 2.1. Reagents

All solvents used were pesticide residue grade. Acetone and *n*-hexane were purchased from Fluka, Buchs, Switzerland. Methanol, dichloromethane, toluene, and chlorotrimethylsilane were purchased from Sigma–Aldrich, Seelze, Germany. Anhydrous sodium sulfate and florisol for residue analysis (60–100 mesh) were purchased from Merck, Darmstadt, Germany. Empore extraction disks (C-18, 47 mm) came from 3M, St. Paul, MN, USA, and gel permeation SX-3 beads (200–400 mesh) were purchased from Bio-Rad, Hercules, CA, USA. PCB single-congener analytical standards were purchased from AccuStandard, New Haven, CT, USA. Purities were above 98%.

### 2.2. Sampling sites

Sampling was performed in 2003 at six sites (three forest sites plus three adjacent clearings) in the Lys Valley, Aosta, Italy, situated at 1100, 1400, and 1800 m a.s.l. in an alpine region (Figs. 1 and 2). These sites are not directly affected by local sources of contamination (Jaward et al., 2005). The Lys Valley is in the Western Alps and presents a North–South orientation, with the

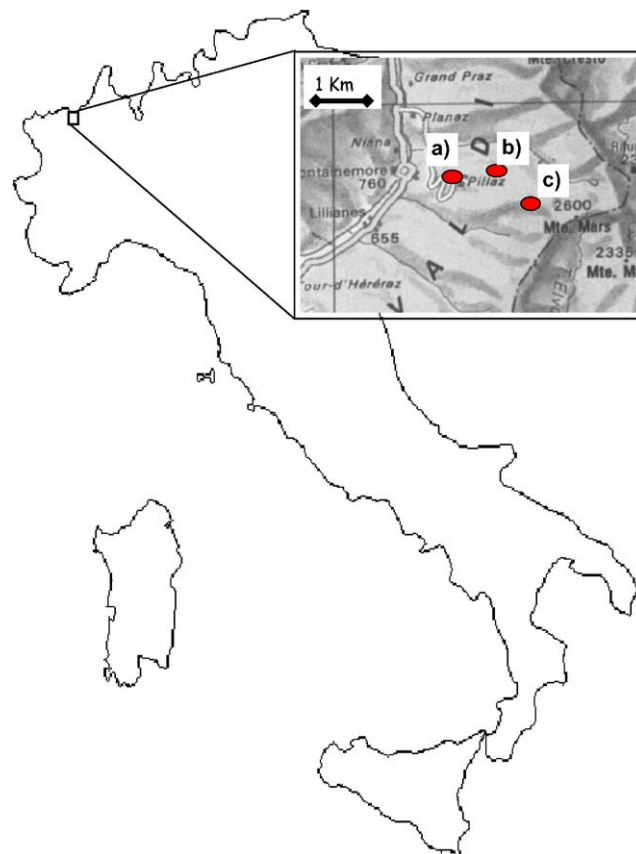


Fig. 1. Geographical location of sampling sites: (a) 1100, (b) 1400, and (c) 1800 m a.s.l.

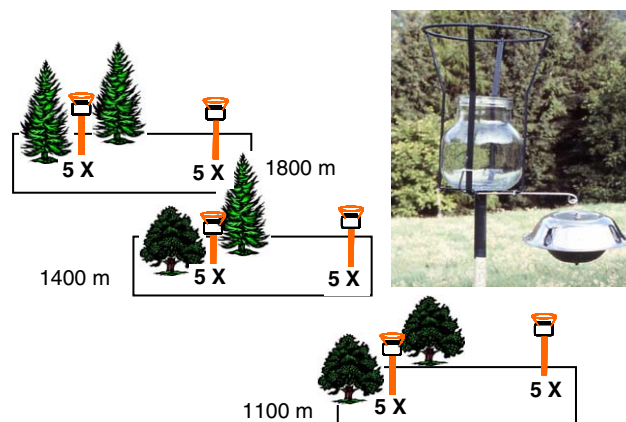


Fig. 2. Schematic representation of the experimental design.

main peak (Mount Rosa, 4634 m a.s.l.) at the northern extremity. All sampling sites were located on the east side of the valley, to normalize ecological conditions such as sun exposure and wind path. Deposition samplers within forest sites were located at least 100 m from the margins of the forest. Clearing sites were selected in the vicinity of the corresponding forest site, and samplers were located not less than 100 m from the forest margin to avoid possible interference due to the

possibility of falling leaves transported laterally by the wind (boundary effects).

### 2.3. Sampling

Bulk deposition collectors were deployed in forests, below the canopy, and in adjacent clearings. Deposition meters were assembled in accordance with the German VDI 2119 (Bergerhoff) standard method as reported by Horstmann and McLachlan (1997a), in which glass jars are deployed at a height of 2 m above the ground on poles equipped with a ring to prevent bird fouling. Glass jars had a capacity of 5 L and an opening with a diameter of 12 cm. At each site, five glass jars were deployed during four campaigns, as reported in Table 1. Following sampling, jars were sealed with hexane-rinsed aluminum foil under the plastic caps, brought to the laboratory, and stored at 5 °C until extraction. Pre-rinsed, sealed jars were located at the sites for the following sampling period.

### 2.4. Glass silanization

In order to reduce adsorption effects of PCB on the glass wall and improve the recovery for subsequent quantitative analysis, the jars were silanized prior to sampling. The coating procedure has been shown to reduce the glass adsorption of PCBs and to enhance extraction efficiency (Lung et al., 2000a, b).

Each glass jar was cleaned initially with soap and tap water and then rinsed with 0.5 L of Milli-Q water. Jars were oven-dried by heating to 150 °C. After cooling they were rinsed with acetone and *n*-hexane. A 5% solution of chlorotrimethylsilane in toluene was added to the jars and left for 15 min. The solution was later exchanged with methanol for an additional 15 min. Ultimately, jars were rinsed several times with acetone and *n*-hexane before being sealed.

### 2.5. Sample extraction and clean-up

Before extraction, PCB 40 and PCB 128 were added to each sample as recovery standards (RS). These two

compounds were chosen in order to monitor the losses of the entire range of measured PCBs, assuming that RSs have an analytical behavior comparable to the similarly chlorinated congeners in the samples. RSs were quantified, as for the other congeners, using the internal standards added at the end of the treatment. Large vegetal material collected by the sampler (e.g., leaves, branches, etc.) was separated from water using solvent-rinsed tweezers and stored at –20 °C until extraction. The liquid content of each five-jar set coming from the same site was filtered using a glass vacuum filter holder and a 47-mm-diameter glass fiber filter GD1UM (Whatman; Maidstone, Kent, UK) and a glass-wool prefilter. Water was extracted on-line using Empore 47-mm C<sub>18</sub> extraction disks (3 M, Neuss, Germany) previously rinsed with 20 mL of *n*-hexane and 20 mL of acetone and then activated with 10 mL of methanol. The Empore disk was then eluted with 5 mL of acetone and 30 mL of dichloromethane.

Each glass jar was further rinsed for 24 h with 300 mL of dichloromethane in an ad hoc rotary device capable of rinsing the glass walls. Solvent was collected, added to the eluate, and concentrated using a vacuum rotary evaporator (Büchi, Flawil, Switzerland) to a volume of 50 mL. The vacuum was set at 500 mbar. Glass jars were mechanically wiped using glass-wool handled with solvent-rinsed stainless steel tweezers. The previously separated large vegetal material was then added to the glass fiber filters and the glass-wool in cellulose thimbles (Schleicher and Schuell, Dassel, Germany), and the solvent was extracted with an all-glass automated Soxtec extractor (Velp Scientifica, Usmate, Italy) using 60 mL of a *n*-hexane:acetone (6:1) solution for 8 h. All fractions were eventually combined and concentrated using a vacuum rotary evaporator to 7 mL for clean-up.

Gel permeation clean-up was performed in accordance with US Environmental Protection Agency (USEPA) method 3640A (1998) using a 600-mm length, 26-mm-i.d. glass column filled with SX-3 beads (200–400 mesh) and coupled to an Agilent 1100 series HPLC system. The flow rate was set at 3.5 mL min<sup>-1</sup> and the run time was 72 min. Fractions were collected using the retention times of chemical markers according to the

Table 1  
Sampling campaign details (April–November 2003)

Campaign	Period	Mean temperature in °C			Rain (mm)
		1100 (m)	1400 (m)	1800 (m)	
1—Spring	19 April–23 June (63)	15.2	11.9	10.8	103
2—Early summer	23 June–1 September (69)	19.6	15.9	14.7	188
3—Late summer	1 September–21 October (50)	11.6	8.6	7.6	80
4—Autumn	21 October–23 November (33)	3.8	1.7	1.4	53 + 53 <sup>a</sup>

Numbers in parentheses are days of sampling. Mean temperature refers to the average temperature between forest and clearing sites.

<sup>a</sup>During this campaign an important snow episode occurred (530 mm). Snow was converted to a rain equivalent by assuming a density of 0.1 kg dm<sup>-3</sup> (Roebber et al., 2003).

USEPA (1998). A calibration solution was injected between every six samples.

Further clean-up was performed on concentrated samples using a 5-mm i.d. glass column packed with 2 g of activated Florisil and eluted with 5 mL of *n*-hexane.

PCB 30 and PCB 141 internal standards were added and the samples were finally concentrated under a gentle stream of N<sub>2</sub> up to 100 µL.

## 2.6. Instrumental analysis

Analyses were performed using a Hewlett–Packard (Palo Alto, CA, USA) 5890 Series 2 gas chromatograph (GC) equipped with dual ECD. Injection was split via a Y connector into two parallel columns: a 60-m DB-5 (J&W Scientific, Folsom, CA, USA) with an i.d. of 0.25 mm and a film thickness of 0.25 µm and a 60-m BP-50 (SGE International, Melbourne, Australia) with an i.d. of 0.25 mm and film thickness of 0.25 µm. The carrier gas (analytical-grade helium) flow rate was held at 1 mL min<sup>-1</sup>. The GC oven temperature program was as follows: initially at 90 °C held for 1 min, 25 °C min<sup>-1</sup> to 170 °C, 1 °C min<sup>-1</sup> to 260 °C, and then 15 °C min<sup>-1</sup> to 300 °C, held for 10 min.

Analyses were conducted for PCBs. Congeners, by homologue group, were tri-PCB 28/31; tetra-PCB 52, 44, 49, 64, 74, 70; penta-PCB 104, 101, 99, 97, 87, 110, 118, 105; hexa-PCB 136, 151, 149, 132/153, 138, 156; hepta-PCB 188, 187, 183, 174, 177, 180; octa-PCB 201, 203, 194.

## 2.7. Quality assurance/quality control

One field-blank sample was included for every six samples measured. No blank correction was performed. Detection limits were defined as three times the blank values and varied between 110 and 300 pg per impaction surface of five jars (= 0.226 m<sup>-2</sup>), depending on congener and sample category. Preliminary recovery tests were conducted in the lab on artificially composed samples, with recoveries averaging 90%. Additionally, PCB 40 and PCB 128 were added to each field sample before extraction as RS. The amount of RS (PCB 40 and PCB 128) added to each sample was similar to detected quantities. Preliminary measurements showed that both congeners were below detection limits in environmental samples. Recoveries were 75% for PCB 40 and 86% for PCB 128. All samples were corrected individually for recovery. The analyses of reference standard material were performed using a reference sediment sample (BCR, European Community, No. 392) in order to validate the analytical procedure.

## 2.8. Vegetation and meteorology

The vegetation composition was estimated at each forest site, considering the relative abundance of

dominant tree species in 2500 m<sup>2</sup> (Pignatti, 1995). The canopy density was measured using the leaf area index (LAI) (Chen et al., 1997). The LAI is a measure of the leaf area per unit of ground area (i.e., m<sup>2</sup> leaf m<sup>-2</sup> ground). The trend of foliar growth was monitored by measuring growth rate (in terms of dry weight increase) of 30 leaves at approximately 1-week intervals. The final weight was assumed to represent completed growth. Similarly, litter fall intensity was estimated by empirically evaluating the amount of leaves remaining on trees at each week interval. A total of eight LAI measurements were made at each site during the period of maximum leaf development using a LAI 2000 sensor (Li-Cor, Lincoln, NE, USA). The temperature was recorded hourly at each clearing and forest site throughout the campaign using six Testo 174 data loggers (Testo, Lenzkirch, Germany) equipped with an NTC-temperature sensor with a resolution of 0.1 °C. Precipitation in the Lys Valley was monitored during sampling campaigns by a meteorological station situated a few kilometers away from the sampling sites. Snow events were measured by recording, after each event, the height of the fresh snow.

## 3. Results

### 3.1. Deposition measurements

Table 2 displays a summary of deposition fluxes (ng m<sup>-2</sup> month<sup>-1</sup>) measured at each site. Fluxes were calculated as follows:

$$\text{Deposition flux} = \frac{\text{total sequestered amount (ng)}}{0.056 \text{ (m}^2\text{)}} (30/d_s),$$

where 0.056 (m<sup>2</sup>) is the interception surface of five jars and *d<sub>s</sub>* is the number of days of each sampling campaign.

Fig. 3 reports comparisons of monthly deposition fluxes for selected PCBs (28/31, 52, 101, 118, 132/153, 138, 180) measured in this study with previously published data. Forest and clearing data were averaged in order to have one forest and one clearing deposition value per sampling period. This was done to simplify the comparison among sites, given the small differences of deposition values measured at the different heights for the same sampling period. Net depositions in forests followed a seasonal trend, showing the highest fluxes in autumn (410 ng m<sup>-2</sup> month<sup>-1</sup>) and the lowest (64 ng m<sup>-2</sup> month<sup>-1</sup>) during the warmer part of the summer.

### 3.2. Meteorological data

Fig. 4 summarizes the meteorological data. The difference between the minimum and the maximum

Table 2  
Summary of results: deposition fluxes ( $\text{ng m}^{-2}\text{month}^{-1}$ )

	1800 <sup>a</sup> F	1800 C	1400 F	1400 C	1100 F	1100 C
<i>Spring</i>						
PCB 28–31	19.1	7.8	18.9	3.0	9.3	4.6
PCB 52	12.2	5.7	10.8	2.4	9.5	4.2
PCB 101	19.6	8.3	27.7	12.9	20.4	5.7
PCB 118	22.8	6.1	20.7	20.7	12.0	4.9
PCB 132/153	12.4	8.0	15.2	8.0	10.6	7.5
PCB 138	18.3	5.3	21.9	12.3	24.6	7.2
PCB 180	11.9	6.5	9.7	6.0	8.8	5.5
<i>Early summer</i>						
PCB 28–31	5.0	1.8	8.3	1.2	7.2	1.4
PCB 52	2.3	nq	4.3	0.9	6.6	1.2
PCB 101	11.3	2.7	15.0	3.0	16.5	2.0
PCB 118	8.6	3.3	8.4	2.2	10.6	2.4
PCB 132/153	6.3	4.1	7.1	1.7	8.4	2.3
PCB 138	11.1	4.1	14.4	6.0	13.5	4.9
PCB 180	13.3	3.6	7.0	2.7	7.0	2.4
<i>Late summer</i>						
PCB 28–31	2.8	6.7	24.7	nq	19.2	3.1
PCB 52	nq	14.7	17.7	2.8	41.4	13.7
PCB 101	nq	9.9	50.5	3.2	56.8	12.9
PCB 118	43.8	12.2	40.5	11.1	31.3	8.1
PCB 132/153	3.5	12.6	65.4	2.0	nq	38.9
PCB 138	11.8	14.3	38.5	nq	nq	nq
PCB 180	18.0	13.4	31.8	2.8	nq	4.6
<i>Autumn</i>						
PCB 28–31	138.8	38.2	59.6	12.0	64.7	20.6
PCB 52	44.6	19.1	61.4	14.6	58.6	12.4
PCB 101	19.2	18.0	53.2	18.3	43.7	16.7
PCB 118	70.4	9.3	64.6	8.8	26.5	8.7
PCB 132/153	78.6	9.9	35.8	9.8	32.0	8.3
PCB 138	131.5	21.7	66.6	29.7	50.2	11.1
PCB 180	63.4	10.3	nq	10.7	23.9	9.6

F, forest; C, clearing; nq, not quantifiable. Each sample was composed of the content of five glass jars.

<sup>a</sup>Altitude in meters above sea level.

daily mean temperature was around 22 °C. Precipitation amounts per period of sampling are reported in Table 1. Major precipitation events (180 mm) occurred during the early summer campaign. Rain and snow episodes occurred during sampling periods. In particular, a snow episode during the autumn campaign (53 cm of snow at ground level) capped the samplers for a few days before melting completely. For this event an equivalent amount of 53 mm of rain was estimated, assuming a snow density of  $0.1 \text{ kg dm}^{-3}$  (Roebber et al., 2003).

### 3.3. Vegetation development

Forest sites were characterized by different compositions in terms of the relative abundance of species (Table 3). Evergreen coniferous species, namely spruce (*Picea abies* (L.) Karsten), represented only 10% and 5% of the forest sites at 1400 and 1800 m a.s.l., respectively. The forest at 1800 m was predominantly composed of larch (*Larix decidua* Miller), a deciduous conifer. The forest

density was significantly different among sites, with the LAI value ranging between 1.7 and 4.8.

The seasonality of leaf appearance also differed between sites. During most of the spring, foliar biomass was almost absent at the 1800-m site (with the exception of spruce). Leaves started to appear at the 1100-m forest site around the beginning of sampling. The delay in leaf appearance at the 1400- and 1800-m sites was of approximately 20 and 30 days, respectively. During both summer campaigns all forests showed the maximum amounts of biomass (the trend of foliar biomass evolution is shown in Fig. 4).

## 4. Discussion

### 4.1. Deposition fluxes

Measured deposition fluxes for selected PCBs (28/31, 52, 101, 118, 132/153, 138, 180) were in the same range

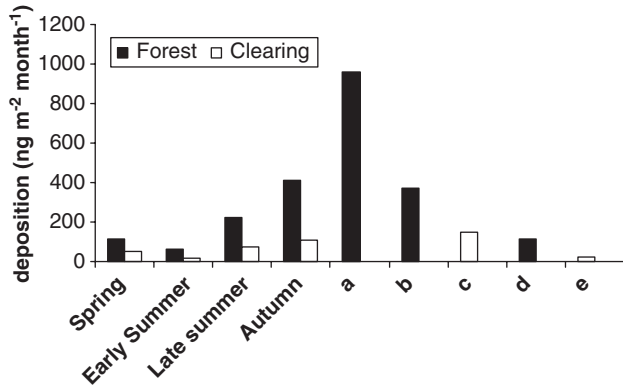


Fig. 3. Comparison of deposition fluxes for selected PCBs (28/31, 52, 101, 118, 132/153, 138, 180) measured in each campaign to previous published data: Horstmann and McLachlan (1998b), (a) deciduous forest, (b) coniferous forest, (c) clearing; Brorström-Lundén and Löfgren (1998), (d) coniferous forest (spruce) and (e) clearing. Data for the forest and clearing sites were averaged (arithmetic mean) in order to give one forest and one clearing concentration deposition per sampling period. This was done to simplify the comparison among sites given the small differences of values of deposition measured at the different heights for the same sampling period. Monthly fluxes were calculated based on the mean annual deposition fluxes reported.

Fig. 3). These data are referred to as the 1995–1996 campaign. Other deposition flux measurements are available for forest (spruce) and clearing sites of the Swedish West Coast (Brorström-Lundén and Löfgren, 1998) (columns (d) and (e) in Fig. 3). These data were measured in the spring of 1995 and were very close to the values of our spring campaign (this paper). The differences between Horstmann and McLachlan’s (1998) results and the data presented here can be justified by the differences in air concentration, which were about two–three times higher by Horstmann and McLachlan’s measurements. Similarly, the air concentrations measured in Brorström-Lundén and Löfgren (1998) and shown in Fig. 3 are comparable to those of our spring campaign (this paper).

The deposition data measured at different altitudes allow the calculation of an FFE, originally defined by McLachlan and Horstmann (1998) as (deposition flux to canopy)/(deposition flux to bare soil) for the selected sites and here defined (for the sake of clarity) as

$$FFE = \frac{\text{deposition flux under canopy}}{\text{deposition flux to clearing}}$$

The FFE for the sites in this work varied between two and four and was within the same range reported by Horstmann and McLachlan (1998) and Brorström-Lundén and Löfgren (1998), confirming the results previously published for this category of compounds.

Deposition data presented in this paper were inversely correlated to temperature (Fig. 4) and generally increased from spring to autumn, when the maximum values were found. This is of course related to litter fall, which represents a substantial loading of PCBs for the soil environment. The FFE was higher in the early summer campaign compared to the spring, probably due to the full development of the canopy at all sites (Fig. 4).

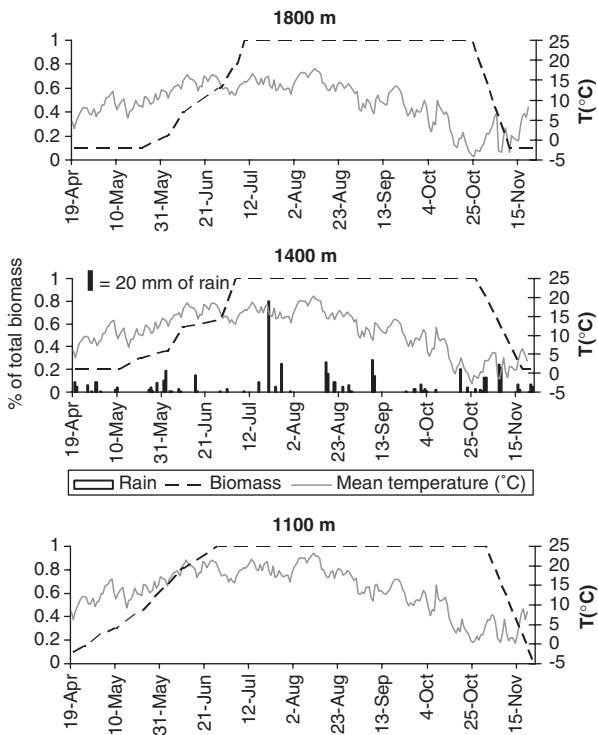


Fig. 4. Overview of meteorological and vegetation parameters.

as that of data reported by Horstmann and McLachlan, (1998) (Fig. 3). Data from the autumn campaign (this paper) were similar to the data of Horstmann and McLachlan (1998) for coniferous forest (column b in Fig. 3), while their data from deciduous forest were approximately two–eight times greater (column a in

#### 4.2. Net forest fluxes

In order to evaluate the contribution of any given forest type to deposition, it is worthwhile to calculate the net forest flux as

$$NFF = \text{deposition flux under canopy} - \text{deposition on clearing.}$$

Given the temperature dependence of the depositions outlined above, we decided to subtract its influence when calculating the net forest flux (NFF). This index can be regarded as a temperature-independent deposition flux specific for each forest site.

The NFF trends for a sum of selected PCBs are reported in Fig. 5. This comparison was performed only for the spring, early summer, and autumn campaigns due to quantification problems in the late summer samples. Coeluting interferences occurred in the chromatograms for the late summer samples, making a

Table 3  
Forest species composition and leaf area index (LAI) ± standard deviation at each site

Sites	Dominant species (estimated relative abundance)	Measured LAI (m <sup>2</sup> m <sup>-2</sup> )
1100 m a.s.l.	Chestnut ( <i>Castanea sativa</i> ) (33%) Hazelnut ( <i>Corylus avellana</i> ) (33%) Maple ( <i>Acer pseudoplatanus</i> ) (33%)	3.86 ± 0.27
1400 m a.s.l.	Beech ( <i>Fagus sylvatica</i> ) (90%) Spruce ( <i>Picea abies</i> ) (10%)	4.78 ± 0.17
1800 m a.s.l.	Larch ( <i>Larix decidua</i> ) (95%) Spruce ( <i>P. abies</i> ) (5%)	1.74 ± 0.23

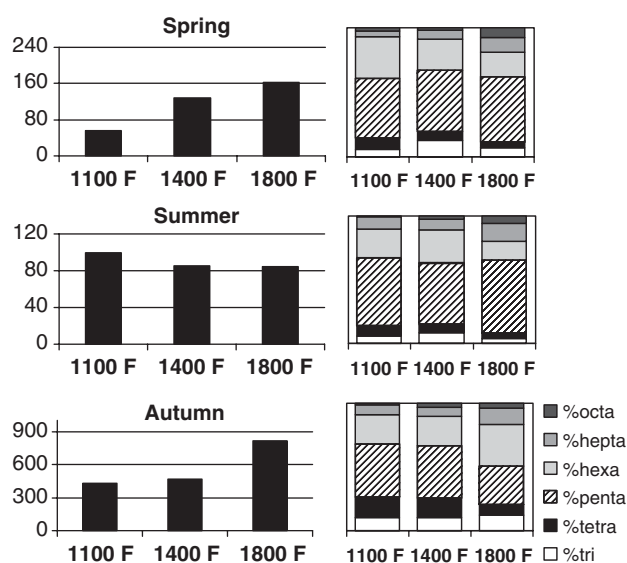


Fig. 5. (left) Net forest flux (NFF) for the sum of selected PCBs (28/31, 52, 74, 101, 99, 97, 87, 110, 118, 136, 149, 132/153, 138, 187, 174, 180, 203, 201, 194). NFF is calculated as (deposition flux in forest) — (deposition flux in clearing). (right) Percentages of homologue groups of PCB sum (F indicates the forest site).

reliable quantification impossible. Forests substantially enhance deposition fluxes in comparison to clearings. Net deposition from the canopy ranged between 80 and 800 ng m<sup>-2</sup> month<sup>-1</sup> depending on the altitude and the seasonally variable biological response. This tremendous variability over time was also documented for the deciduous forest of Horstmann and McLachlan (1997a). The highest variability among different forest types occurred in spring and autumn, while fluxes recorded in the summer were much more homogenous. Both in spring and in autumn, the greatest deposition was recorded at 1400 and 1800 m. During the spring campaign, differences in the NFF between sites were within a factor of two, with the highest value (163 ng m<sup>-2</sup> month<sup>-1</sup>) recorded at the 1800-m site. In spring the 1400- and 1800-m sites were probably characterized by the deposition of spruce needles (the only conifer present with persistent needles), while the lower value found at the 1100-m site was probably

related to the appearance of fresh leaves, which could have efficiently reduced the fraction of pollutant available for deposition.

The above-mentioned hypothesis is supported by additional investigations of the physiology of growing leaves. Leaves are in a stage of net uptake with respect to organic contaminants due to their continuous exposure of fresh organic surfaces during the growing period. In addition, during that stage of development, wax erosion cannot be considered significant in overall terms, given the moderate temperatures and the small amount of wax on leaf surfaces (Horstmann and McLachlan, 1996). During the early summer, differences in NFF were within a factor of 1.2. A possible explanation for the general reduction in fluxes could be the revolatilization of PCBs from the canopy due to elevated ambient temperatures. This hypothesis is also supported by the PCB patterns determined, in which the low-chlorinated congeners made a considerably minor contribution to the total PCB burden.

Finally, in the autumn samples the NFF increased significantly by a factor of 5–10 due to litter fall. The occurrence of a different predominant deposition mechanism is also reflected in the PCB fingerprint (Fig. 5). At all sites the relative importance of tri- and tetra-PCBs increased by a factor of 1.7–2.3. In particular, at the 1800-m site the relative importance of tri- and tetra-CB increased from 9% to 20%.

#### 4.3. Deposition velocities: relation to forest parameters

The NFFs calculated above are obviously related to the forest characteristics and also to the specific environmental/contamination conditions of the sites investigated. In order to generalize the results to any contamination situation, it may be useful to normalize NFFs by dividing them by the air concentration values measured in the respective clearings (Jaward et al., 2005):

$$\text{Net deposition velocity} \\ = \text{NFF/air concentration in clearings.}$$

The values obtained represent the net deposition velocity ( $\text{cm s}^{-1}$ ), dependent only on the type of forest investigated. Deposition velocities were comparable to those calculated by Horstmann and McLachlan (1998). It should be noted that their deposition velocities were annual averages and therefore included the contribution of litter fall to deposition. The calculation of the NFF was performed for the early summer period, when foliar biomass was fully present, no substantial litter fall had occurred, and deposition mechanisms related to leaf erosion were not favored. Measured velocities are probably related primarily to forest-specific parameters, such as stand density and leaf composition. Net deposition velocities appeared to increase with the extent of chlorination, and thus these values were plotted against  $K_{\text{OA}}$ , corrected for ambient temperature (Fig. 6a).  $K_{\text{OA}}$  values, and their variation with temperature, were taken from Li et al. (2003). This behavior was also shown by Horstmann and McLachlan (1998) over an annual cycle. We decided to restrict the domain of PCBs plotted to chemicals with a  $\log K_{\text{OA}}$  between 8.5 and 10.5. Above  $\log K_{\text{OA}}$  10 compounds were shown to follow different deposition mechanism that did not satisfy the linear trend described by the regression (Horstmann and McLachlan, 1998). The regression shows a good correlation of forest type and deposition velocities, in which broadleaf species (1100- and 1400-m sites) are grouped together and the “pure conifer” site reveals a different behavior. This trend is similar to that shown by Horstmann and McLachlan (1998), even though conifers appear much more similar to broadleaf species in the present study. This can be explained by the short sampling time and the particularly low canopy

density at the 1800-m site. In order to exclude the overlying variability caused by the specific forest density (Table 3) and the increasing deposition due to increasing forest density, deposition velocities were divided by the LAI of each forest site. The LAI represents an index of the total foliar biomass accumulating pollutant from the air and a measure of the density of surface available for exchange with the atmosphere. The obtained ratio was then correlated to the  $K_{\text{OA}}$  values (Fig. 6b). This operation has the effect of removing the influence of canopy density on deposition fluxes. Two significantly different trends are apparent, representing the effect of the forest on deposition. Broadleaf forests appear to exhibit a comparable behavior, while coniferous forest show a higher capability to enhance the deposition of higher chlorinated PCBs. This “canopy-type-specific” velocity could be used to predict velocities for any forest type of similar composition by multiplying the velocity by the LAI. These results are more useful when predicting the role of forests in multimedia models (Cousins and Mackay, 2001).

## 5. Conclusions

This work contributes to the elucidation of the significance of forests as filters of airborne contaminants and as subsequent enhancers of soil contamination. A few papers were available on the subject and substantial uncertainty existed regarding the magnitude of the FFE in different environmental situations, especially in mountain sites. Here we first present a comparison of different forest types in which a mix of deciduous and persistent leaves is present. The results confirm the existing data and add additional information. Based upon the results, one can conclude that forest structures enhance the deposition of PCBs to soil. However, the extent of PCB deposition is strongly dependent on the seasonal time scale due to temperature and leaf evolution.

PCB fluxes are inversely correlated with temperature, and this was postulated to be dependent on the gas-partitioning equilibrium between air and canopies, occurring mainly for more volatile compounds. Calculated deposition velocity is directly correlated to the  $K_{\text{OA}}$ . The role of the canopy density parameter LAI was extrapolated, allowing an evaluation of the influence of forest composition on deposition velocities. This extrapolation has the advantage of allowing the calculation of deposition velocities for forest types with a species composition similar to those of the three sites analyzed but characterized by different canopy density. Such forest type-specific deposition velocities can be used to calculate the filter effect of forests on a regional level, where spatially explicit LAI values can be entered for the different areas. Such information can, for instance,

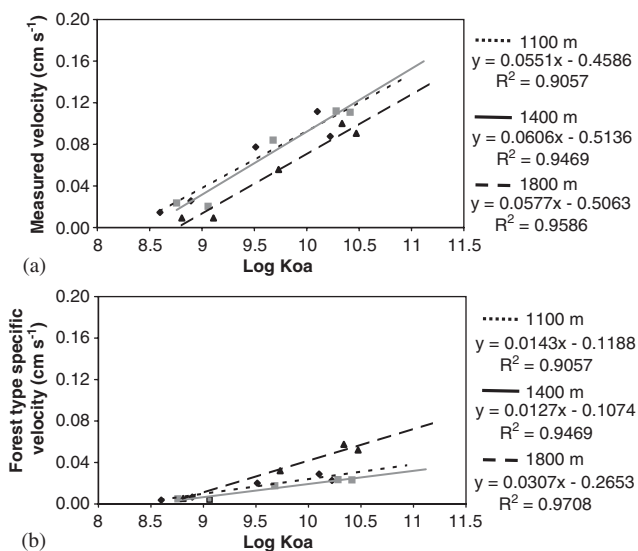


Fig. 6. (a) Dependence of net deposition velocity measured at the three sites during early summer on  $\log K_{\text{OA}}$ . (b) Net deposition velocities normalized by the LAI.

be used to predict the effect of forests in regulating the movement of POPs in the air/biomass/soil system on a global scale.

However, more work must be done to further characterize the cycle of POPs and other contaminants on a forest level, at which species composition, environmental conditions, and many other factors may substantially vary in time and space.

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