Long-term atmospheric bulk deposition of polycyclic aromatic hydrocarbons (PAHs) in rural areas of southern Germany

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Abstract:

A novel passive sampling technique using a funnel-adsorber-cartridge device was adopted and validated in the field during a long-term monitoring program on the atmospheric deposition of polycyclic aromatic hydrocarbons (PAHs) in three rural regions of southern Germany. Apart from seasonal variations, fairly stable annual deposition rates around 200 µg m^{-2} $year^{-1}$ for the sum of PAHs were obtained. The time-integrating passive samplers showed that spatial variability due to topography was negligible and differences between open-field and forest deposition were within a factor of 2. Based on correlations with ambient temperature, advection was identified as the most important factor that controls the atmospheric deposition of PAHs. Gas-adsorption contributes significantly to the deposition of the semivolatile compounds in forests, but particle deposition seems to be the major pathway for all PAHs.

Keywords: passive sampler; monitoring; deposition processes; open-field; forest;

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Introduction

Atmospheric deposition is an important pathway of diffuse soil contamination with persistent organic pollutants (POPs) in rural areas (Leister and Baker, 1994). Hydrophobic persistent compounds tend to accumulate in soils and may thus accumulate to concentrations of concern (e.g. precautionary limits). Hence, there is a need for monitoring the atmospheric deposition of POPs for early recognition of trends and early development of environmental action plans. As the demand for monitoring increased, time-integrating passive sampling techniques become more and more important because they fulfil the demands of monitoring programs with limited analysis. Recently, several studies on passive air sampling for measuring air concentrations were published (Jaward et al., 2004; Farrar et al., 2005; Paschke and Popp, 2005; Söderström et al., 2005) and data on atmospheric deposition are often estimated from measured air concentrations (e.g., Gigliotti et al., 2005; Gioia et al., 2005). However, investigations using passive samplers for direct quantification of the atmospheric bulk deposition are only rarely reported (e.g., Matzner, 1984), and available long-term data are mostly based on extrapolated shorter-term measurements (e.g., Brorström-Lundϑn and Löfgren, 1998).

In this study we focus on the deposition of polycyclic aromatic hydrocarbons (PAHs), a compound group under discussion to be included into the Stockholm convention of the United Nations Environment Programme (UNEP) that was developed to regulate POPs in the environment (Richter and Steinhauser, 2003). Concentrations of PAHs are frequently reported for various environmental compartments. They occur not only widespread in soils and sediments, but enter also the food web and was detected in crops (Kulhanek et al., 2005) and cork used for wine bottles (Mazzoleni et al., 2005). Here we present results of a continuous two-year monitoring program that was conducted to quantify the atmospheric deposition of

PAHs, with the focus on spatial and temporal variabilities on different scales using novel passive deposition samplers.

Theory

Generally, the atmospheric deposition is separated into wet and dry deposition (Leister and Baker, 1994; Buehler et al., 1998; Brun et al., 2004). For both, several processes such as scavenging of vapour and particles, particle sedimentation, and surface gas absorption contribute to the overall flux. Bulk samplers do not discriminate any of the processes and, as a consequence, they record the sum of all of them.

Depending on their physical and chemical properties such as vapour pressure and solubility, PAHs occur in the atmosphere in the vapour phase as well as in the solid particle phase. From benz(a)anthracene on to the higher molecular weight compounds, PAHs are almost exclusively associated with particles, whereas the lighter molecular PAHs from naphthalene to pyrene occur predominantly in the vapour phase (semivolatile PAHs; Franz and Eisenreich, 1998; Dachs and Eisenreich, 2000). According to Wania et al. (1998a), the distribution of semivolatile organic compounds between any sorbing surface materials (suspended aerosols or any earth surface, e.g. soils, plants, bedrocks, water) and air depends mainly on temperature. Assuming chemical equilibrium between the two phases, the following empirical correlation was developed (Wania et al., 1998a):

$$\ln p_a = \quad m\,T^{-1} + b \qquad (1)$$

where p_a denotes the partial pressure of a given compound in the atmosphere and T the ambient temperature. If temperature driven gas exchange between the surface and the atmospheric gas phase leads to a quasi equilibrium, p_a denotes the equilibrium partial pressure between the gas phase and the surface with a reservoir of the substance on or in the surface. In that case, m is *negative*. For such a situation an increase in ambient temperature will cause outgassing of the compound from the surface, i.e. the net flux is upward and the surface is the source of the compound. Inversely, a decrease of ambient temperature will cause net deposition from the atmosphere to the surface.

If, on the other hand, the correlation between measured p_a and T^{-1} shows a *positive* slope *m*, equilibrium conditions between the surface and the gas phase do not exist since air concentrations are much higher than expected based on thermodynamical considerations. In that case, advection of the compound from other regions must lead to the high observed gas concentrations. This situation must lead to a net deposition of the compound to the earth surfaces.

In summary, a positive *m* indicates advection as the source of the compound, and net deposition at the site of observation. A negative *m* indicates equilibrium between atmosphere and earth surface with upward net flux from the surfaces as ambient temperature increase, and vice versa. Since Gioia et al. (2005) report a positive correlation between atmospheric deposition and air concentration of semivolatile organochlorine pesticides, we postulate an linear relationship between ($m\ T^{-1}$) and the logarithm of the vertical exchange flux, ln *F*.

Materials and methods

Study areas and field instrumentation

Three rural, mostly forested landscapes were selected following a transect from the western to the eastern borderline of Southern Germany: The “Seebach” area in the northern Black Forest, the “Lange Klinge” area in the Schönbuch Forest and the “Waldstein” area in the Fichtelgebirge mountains / Northern Bavaria. The bulk atmospheric deposition of PAHs was quantified with a passive funnel – adsorber cartridge sampling device, which was developed at the Center for Applied Geosciences, University of Tuebingen (Martin, 2000). The system was validated for PAHs and became a national standard (German Industrial Standard DIN 19739-2, 2003). It was extensively tested at the bench scale as well as in the field (a brief description follows below).

The samplers were distributed over the study areas to account for spatial variability of atmospheric PAH-deposition. Topographical differences and differences between open field and forest deposition were quantified. The field instrumentation in the northern Black Forest and in the Schönbuch Forest is shown in Fig. 1. In the Fichtelgebirge mountains, the samplers were placed in the vicinity of a meteorological station of the Bayreuth Institute of Terrestrial Ecosystem Research (BITÖK) at the "Waldstein" site (50°08'40"N, 11°51'55"E, 765 m a.s.l), one on a clearance (Pflanzgarten) and another one inside the forest. A detailed description of the site is given in Matzner (2004). In the forests the funnel of the bulk samplers were equipped with a 0.5 mm sieve (stainless steel) in order to separate the litterfall (spruce needles) from the throughfall.

Sampling and analysis

The bulk deposition passive sampling system consists of a borosilicate glass funnel and a large adsorption cartridge packed with Amberlite® IRA-743 (Fig. 2). While bulk deposition percolates through the funnel and cartridge, PAHs from both the water and particle phases are collected from the wet and dry deposition, by adsorption and filtration, respectively. Each cartridge contained about 15 g of the adsorber material, which was fixed on top and at the bottom with glass wool plugs. In the field, the sampling systems were housed in an aluminum box. After sampling periods of about 60 days, the cartridges were replaced by new ones. After each sampling period the funnels were purged with 200 mL acetone in order to collect adsorbed and deposited PAHs from the glass surfaces. Blanks (cartridges containing the adsorber material) were carried along and analyzed during each sampling campaign to check potential background contamination from transport and handling. After transfer into the lab, the cartridges were sequentially solvent extracted in 4 steps (50 mL for each) with the same acetone used before for the cleaning of the funnels (i.e. the purge solution). As internal standards, five deuterated PAHs were added to the extracts: naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12. For the removal of co-extracted water residues, 10 mL cyclohexane and about 2 L millipore-water were added in order to transfer the PAHs into the cyclohexane phase by liquid-liquid extraction. After 48 h the cyclohexane was sipped off and the extracts were further purified using common column chromatography with coupled polar (Al_2O_3, 5% deactivated) and non-polar (SiO_2, 5% deactivated) adsorbents.

The litterfall in the forest samplers was sequentially extracted with an Accelerated Solvent Extractor (ASE 300, Dionex), two times with acetone at 100 °C and then with toluene at 150 °C. Internal standards were added and clean-up was done as described above. The quantification of PAHs was carried out using a HP 5890 gas chromatograph (carrier gas: Helium; column: DB-5 Zebron phenomenex, 30 m, 0.25 mm I.D.) equipped with an HP 7673 autosampler and an HP 5972 A mass spectrometer. The following PAHs were quantified: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b+k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene.

Properties of the adsorber and field validation

The adsorber Amberlite$^{®}$ IRA-743 is an macroporous polystyrene coated with N-Methylglucamin as a functional group that allows water to wet the material. The large grain sizes of 0.5 – 0.7 mm results in good permeability and thus prevents accumulation of water at the top and subsequent overflow. Furthermore, it allows a good drainage of the cartridge, which is important during periods of frost when freezing water would destroy the glass cartridge. The adsorber material does not shrink nor swell during drying or wetting and has a sufficient sorption capacity to avoid breakthrough of target compounds through the cartridge. Further advantages are high recovery rates during extraction with acetone, no degradation of trapped target compounds during the sampling period , and finally high precision of the deposition rates.

The system was thoroughly checked and validated (Martin, 2000; Martin and Grathwohl, 2002). In brief, for all PAHs recoveries >80% in extracts of spiked cartridges (in most cases >90%) were obtained. The breakthrough was assessed in the field using a second adsorption cartridge in series that did not show any significant enrichment of the PAHs after a sampling period of 61 days. Once adsorbed, PAHs were stable as proven by extractions of spiked cartridges after different periods of time up to 400 days. The precision was determined in a field test with 8 replicates. The coefficient of variation was 5.1 % for the PAH-sum and generally < 10 % for the single PAHs.

Results and discussion

Bulk deposition rates of PAHs

Since naphthalene frequently occurred as background contamination (indicated by the blank cartridges), probably due to uptake from the laboratory air, it was not considered for evaluation of results, which will be presented for the remaining 17 PAHs only.

As shown in Fig. 3, in all three study areas a distinct seasonal variation with higher deposition rates during winter and lower ones during summer were recorded using the bulk samplers during the 2 year monitoring program. The Northern Black Forest and the Fichtelgebirge

Mountains showed significantly higher deposition rates than the Schönbuch Forest. Mean annual deposition rates are summarized in Tab. 1. The compound specific annual deposition rates were fairly constant during the two years in each study area as shown in Tab. 1. Regional or spatial variability of the deposition rates could be caused by means of topographical differences as well as by differences between open-field and forest deposition, respectively. However, based on the range of variation of the deposition rates given for the Black Forest and the Schönbuch Forest (Fig. 3), relief-dependent variability seems to be very limited if the time-integrating passive sampling technique and sampling periods of about 2 months are employed. Only at the beginning of the sampling campaign some differences between the atmospheric deposition at the top of the hill and in the valley of the Seebach, northern Black Forest, were observed (the difference in altitudes between these two sampling stations was about 300 m). Comparing open-field and forest deposition, the throughfall in the forests were lower than the open-field deposition during almost all of the sampling periods. Considering the mean annual deposition rates (Tab. 1), the open-field ones were up to twice as high compared to the throughfall. In contrast, depending on the amount of litterfall, the bulk deposition rates in the forests exceeded the open-field ones during most of the sampling periods (Fig. 3). In case of the forest deposition, stem flow was not accounted for since in coniferous forests it contributes only to a minor extent to the bulk deposition (Matzner, 1984).

The higher deposition rates in the Fichtelgebirge mountains and the northern Black Forest, respectively, are most likely due to their proximity to high emission regions. The Black Forest obtains its pollution loads presumably from the highly industrialized Upper Rhine Valley in the West (Schiedek and Hinderer, 2001). In the case of the Fichtelgebirge mountains, inorganic atmospheric pollutants were traced back to emission areas of the Czech Republic in the East (Klemm and Lange, 1999). However, no correlation was found between PAH deposition rates and precipitation or wind speed and direction, respectively, in this study (data not shown). A reasonable assessment of the source regions could not be established due to the lack of data concerning PAH concentrations in the different air masses, which are a prerequisite for the calculation of back trajectories. Hence, the source regions for PAH deposition in the different study areas remain unknown.

The seasonal trend of PAH deposition rates in rural areas was already described in several publications (Brorström-Lunden and Löfgren, 1998; Golomb et al., 2001; Garban et al., 2002; Motelay-Massei et al., 2003; Brun et al., 2004) and quantitatively similar values are published in the literature (Tab. 2). The higher PAH deposition rates during winter season are on the one hand due to enhanced emissions (residential heating; Golomb et al., 2001). On the other hand, snow scavenging can contribute significantly to the PAH deposition rates (Franz and Eisenreich, 1998; Wania et al., 1998b; Carrera et al., 2001).

Transport and deposition processes

In order to compare the open-field deposition with the forest deposition in a qualitative way, the PAH distribution patterns were determined by calculating the percentages of the individual PAHs in relation to the sum of all quantified PAHs for each sampling period and station. Hence, measurements in different compartments, such as PAH-concentrations on needles (litterfall) and deposition rates, become comparable as well as data sets with large quantitative variabilities (due to e.g. seasonal variations of deposition rates). All data were compiled and plotted with respect to the different compartments (Fig. 4). Forest deposition was split into bulk (throughfall and litterfall) and litterfall only.

As shown in Fig. 4, higher percentages of the semivolatile compounds (acenaphthylene – pyrene) were observed in the forested areas. Between pyrene and chrysene, this trend is reversed and the high molecular weight PAHs (benz(a)anthracene – benzo(ghi)perylene) showed higher enrichment in open-field deposition. The trend reversal is exactly in the transition zone of preferred vapour phase transport (from acenaphthylene to pyrene) and particle-bound transport, respectively (Franz and Eisenreich, 1998).

According to Horstmann and McLachlan (1998), no difference in wet deposition rates between open-field and forest is assumed. Hence, the shift in the distribution pattern with respect to the different compartments must be related to dry deposition. Furthermore, the semivolatile PAHs are relatively enriched in the forest compared to the open field stations. In addition, the highest percentages for the semivolatile PAHs were obtained in the litterfall of the forest deposition (Fig. 4). Since these are the PAHs that occur in the vapour phase in the atmosphere (in contrast to the PAHs from benz(a)anthracene to benzo(ghi)perylene that are entitled as the particle associated PAHs in Fig. 4), dry gaseous deposition of semivolatile PAHs, i.e. partitioning into needles, is expected to be responsible for the shift in the PAH distribution pattern between the different compartments.

This conclusion is confirmed by the fact that gas exchange fluxes were estimated to contribute a substantial fraction of the air-water transfer for the semivolatile PAHs (Dickhut and Gustafson, 1995). Furthermore, according to Böhme et al. (1999) and McLachlan (1999), equilibrium between plant surfaces and the atmosphere regarding uptake of semivolatile PAHs can be assumed after 15 weeks in temperate climates resulting in an enrichment of these compounds in forests compared to open-field deposition. In a recent study, Krauss et al. (2005) could attribute the leaf uptake of these compounds to equilibrium partitioning in a tropical rain forest as well. Thus, for the perennial conifers of the different study areas, equilibrium subsequent to diffusive gaseous uptake is supposed to lead to the higher percentages of semivolatile PAHs in the forests and, as a consequence, the lower percentages for the particle associated PAHs. Since the sum of all compounds is always 100 %, higher percentages of semivolatile PAHs must lead to lower ones for the particle associated compounds. Considering the particle associated PAHs only (Fig. 5), the distribution patterns of the different compartments match quite well.

In summary, gaseous dry deposition contributes significantly to the forest deposition. Nevertheless, the most important deposition process concerning PAHs is particle-associated deposition. This will be discussed now in the following section.

At the Waldstein study area, meteorological parameters such as temperature, wind (speed and direction), and precipitation were continuously recorded over the entire investigation period (Klemm et al., 2006). Apart from temperature, no correlation between the PAH deposition rates and other meteorological parameters could be observed (data not shown). The relationship between mean ambient temperature and atmospheric deposition of two PAHs is shown in Figure 6. One of the semivolatile (phenanthrene) and one of the particle associated PAHs (benzo(a)pyrene) was selected as representatives for that purpose. A similar trend with almost parallel running slopes of the regression lines was obtained for both, the semivolatile and the non-volatile compound, respectively, and all of the other PAHs show the same trend as well. In general, high ambient temperatures are correlated with low deposition rates, and vice versa, which reflects the seasonal trend of emissions and the resulting bulk deposition rate (see above). Assuming a direct link between the deposition fluxes F of PAHs and the atmospheric concentrations of these compounds, the positive regressions between F and T^1 in Fig. 6 indicates that the atmospheric concentrations of the PAHs are higher at lower temperatures.

Similar trends are reported in the recent literature for particle bound, non-volatile PAHs (Buehler et al., 2001). However, for other POPs (e.g. pesticides such as HCBs, PCBs) an inverse relationship with high atmospheric concentrations during warm periods and lower ones during cold periods is often described (Wania et al., 1998a; Buehler et al., 2001; Murayama et al., 2003; Gioia et al., 2005). The latter relationship has to be expected if only thermodynamically driven gaseous exchange between the earth surface and the atmosphere controls the concentration in each compartment. However, this is not the case for the PAHs. Whereas PAHs are currently released into the atmosphere from primary sources during combustion of fossil fuels, atmospheric PCBs are mainly derived from secondary sources due to volatilisation from e.g. buildings. Therefore, atmospheric PCB concentrations are shown to be a function of temperature with increasing vaporization during summer (Dickhut and Gustafson, 1995), whereas the PAH concentrations follows the trend of primary emissions which are higher during winter season (Prevedouros et al., 2004). Our study shows that a similar correlation is evident also between the deposition flux and temperature. Thus, advection controls the deposition and atmospheric concentrations of PAHs in rural areas, even of semivolatile PAHs.

Taking into account the different transport processes (gaseous vs. particle bound), one would expect different slopes for the different selected compounds in Fig. 6. However, this is not the case. Since similar slopes were obtained for both the semivolatile and the particle associated compounds, a common deposition mechanism is assumed. Gaseous deposition of benzo(a)pyrene is very unlikely due to the low vapour pressure of that compound. Therefore, particle associated deposition should be the governing process. It does not mean that phenanthrene as an representative for the semivolatile PAHs is transported exclusively on particles in the atmosphere, but the deposition process seems to be dominated by the particle-phase fraction. The PAH distribution pattern in Fig. 4 clearly indicate the occurrence of gaseous semivolatile PAHs, but the slopes of Fig. 6 indicate that particle associated transport is the major transport process even for the semivolatile PAHs in southern Germany.

A hypothesis: atmospheric deposition of PAHs is related to deposition of carbonaceous particles

Since particles play a major role in the overall fate of the PAHs in the environment, the deposition of particles should be taken into account as well as the contaminants. Moreover, there are good reasons to address the deposition of particle associated PAHs to the deposition of one specific subclass of the aerosol: the carbonaceous particles. Firstly, pyrolysis is the common source for the PAHs and the carbonaceous particles. Secondly, black carbon or soot particles, respectively, are the carriers for the PAHs during atmospheric transportation (Dachs and Eisenreich, 2000). In fact, similar carbonaceous particles could be identified in atmospheric deposition samples and soils (Gocht, 2005).

In order to highlight the plausibility of carbonaceous particles as carriers for the PAHs during atmospheric transportation and deposition, a simple model calculation based on PAH-concentrations and the content of carbonaceous particles in rural soils was conducted and will be discussed briefly. In natural top-soils, the content of carbonaceous particles on the soil organic matter is about 1% (Schmidt and Noack, 2000). Assuming a soil organic matter content of top-soils of 5% leads to a content of carbonaceous particles of 0.05%. Taking now a PAH concentration of 1 mg Kg^{-1} in top-soils into consideration (such concentrations are often reported in the scientific literature, e.g. Krauss et al., 2000) and relating this to the content of carbonaceous particles, leads to a concentration of 2 g Kg^{-1} on those particles. This matches the measured PAH-concentration range on particles in smoke of burning wood (Fine et al., 2002) or coal (Wornat et al., 2001), respectively.

Currently, it is not known if the PAHs in soils are exclusively attributed to the carbonaceous particles. However, these particles are very strong adsorbents for the PAHs in the atmosphere

(Dachs and Eisenreich, 2000) and future research needs to investigate the role of carbonaceous particles during atmospheric deposition of anthropogenic contaminants such as PAHs.

Conclusions

Annual deposition rates of individual PAHs, as determined using passive samplers and sampling periods of 6-8 weeks were fairly stable. The spatial variability of deposition rates in rural areas of southern Germany was within a factor of 2 and the deposition rates followed a seasonal trend with higher rates during winter and lower ones during summer. Gaseous uptake of semivolatile PAHs plays an important role in forests resulting in an enrichment of these compounds compared with open-field deposition. Apart from that, particle-associated deposition seems to be the most important process regarding PAHs. It is hypothesized that the deposition of PAHs is strongly related to the deposition of carbonaceous particles.

The described passive sampling system provides very robust results. As a main advantage of the sampling system, long-term monitoring programs can be conducted with a limited number of samples. The funnel-adsorber-cartridge system gives the opportunity to use sampling periods of 2 months or even longer, whereas most of the sampling systems in the cited publications used 1-week sampling periods. Furthermore, because of the relative little spatial variation at this time-scale in rural areas, a limited number of sampling sites can be used in trend studies.

To further study the relative roles of particle bound versus gas phase concentrations, respective concentration measurements are mandatory.

Acknowledgements

The paper benefited from a critical review by Jonathan Barber and two anonymous reviewers. Financial supports by grants from BWPLUS (Lebensgrundlage Umwelt und ihre Sicherung, contract number BWR22006), state of Baden-Wuerttemberg, Germany, AquaTerra, Integrated Project in the 6th Framework Programme of the European Union (contract number 505428), and the German Federal Research Ministry (BMBF) through grant PT-BEO 51-0339476D are gratefully acknowledged. The UMEG (Umweltmessungen Umwelterhebungen und Gerätesicherheit) support us in the development of the passive samplers.

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Figure captions

Fig. 1: Map of the study areas in southern Germany (upper part) and distribution of deposition samplers in the investigation area of the Schönbuch Forest (“Lange Klinge”, right hand side on the lower part of the figure) and the northern Black Forest (“Seebach”, left hand side of the lower part).

Fig. 2: Sketch of the passive sampler device. Amberlite® IRA 743 was used as adsorber.

Fig. 3: Atmospheric deposition of PAHs (∑ of all measured PAHs excluding naphthalene) in rural landscapes of southern Germany in ng m^{-2} d^{-1}. Note the different scales of the ordinate axis in the different study areas. The bars indicate the range of variation in the different study areas.

Fig. 4: PAH distribution pattern of open-field deposition (n = 54), forest bulk deposition (n = 34) and concentrations of spruce needles (n = 30). PAHs are arranged with respect to their physico-chemical properties (highest solubility / vapour pressure on the left, lowest on the right hand side). Percentages were calculated with respect to the PAH-sum of each measurement (i.e. 100% represents the PAH-sum). The bars of variation indicate 1 standard deviation from the arithmetic means

Fig. 5: PAH distribution pattern of open-field deposition (n = 54), forest bulk deposition (n = 34) and concentrations of spruce needles (n = 30) for the particle associated PAHs only. The bars indicate 1 standard deviation from the arithmetic means.

Fig. 6: Correlation between open-field atmospheric deposition of phenanthrene (semivolatile) and benzo(a)pyrene (non-volatile, i.e. particle associated), respectively, and ambient temperature (mean values of each sampling period) at the “Waldstein” study area, Fichtelgebirge Mountains, northern Bavaria.

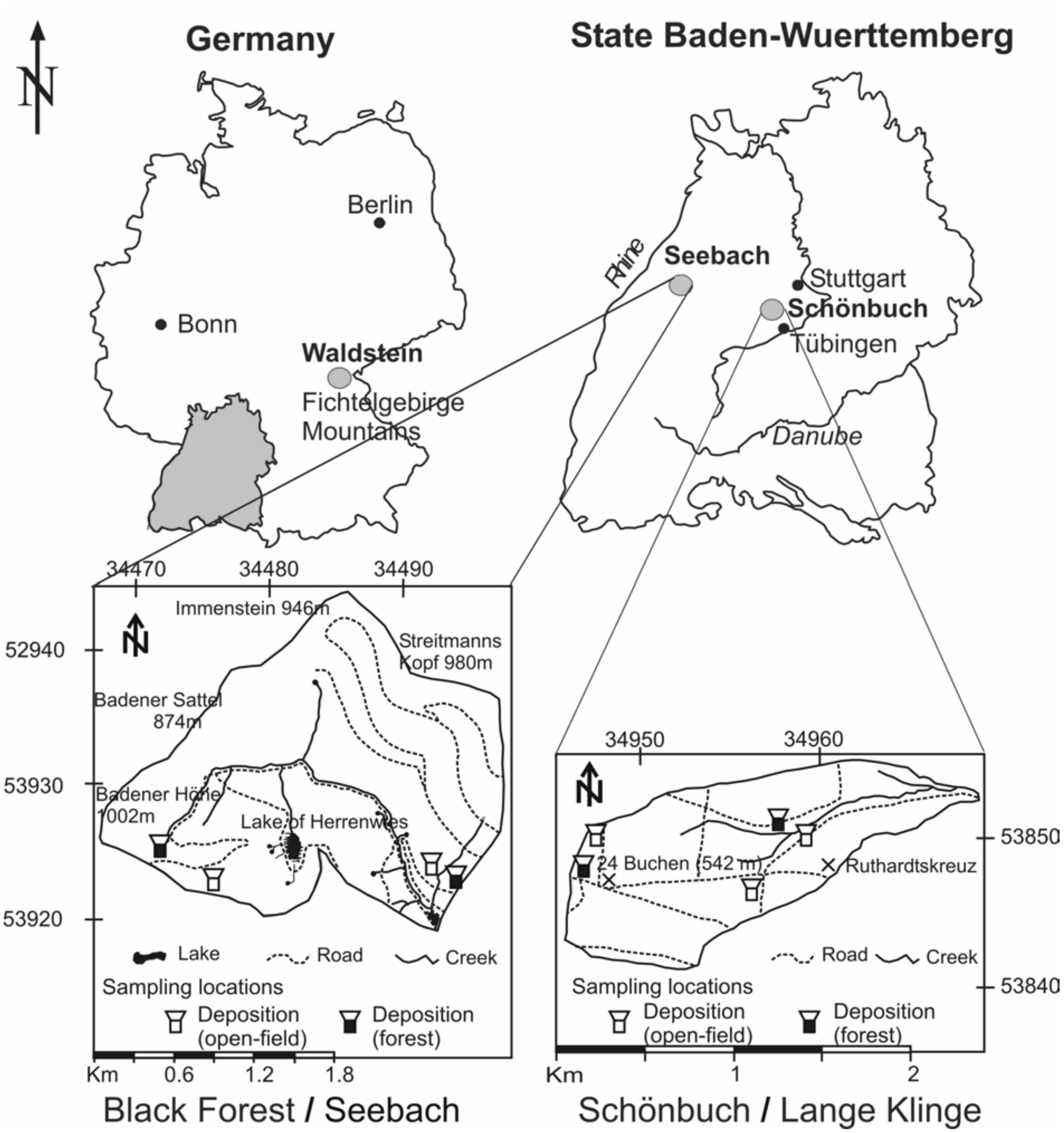
N
Germany
State Baden-Wuerttemberg
Berlin
Bonn
Waldstein
Fichtelgebirge
Mountains
Rhine
Seebach
Stuttgart
Schönbuch
Tübingen
Danube
34470
34480
34490
52940
53930
53920
Immenstein 946m
Streitmanns
Kopf 980m
Badener Sattel
874m
Badener Höhe
1002m
Lake of Herrenwies
Lake
Road
Creek
Sampling locations
Deposition
(open-field)
Deposition
(forest)
Km
0.6
1.2
1.8
Black Forest / Seebach
34950
34960
53850
53840
24 Buchen (542 m)
Ruthardtskreuz
Road
Creek
Sampling locations
Deposition
(open-field)
Deposition
(forest)
Km
1
2
Schönbuch / Lange Klinge

Fig. 1

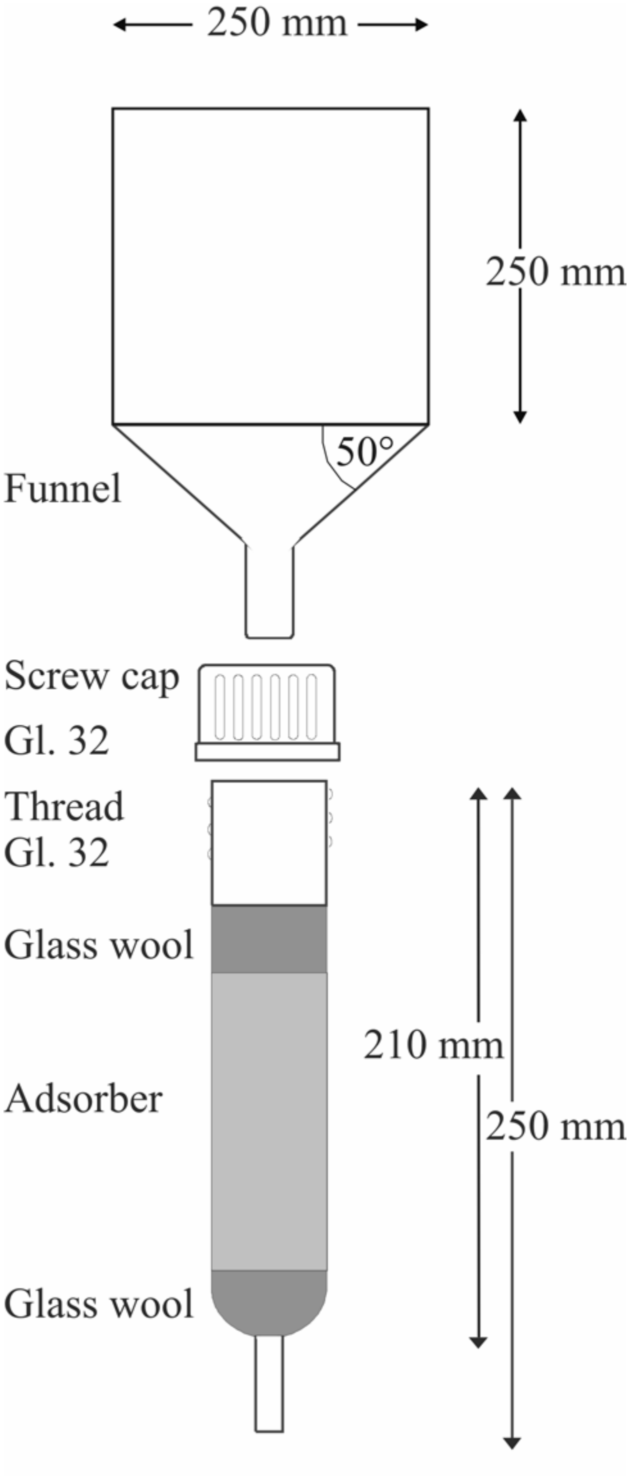
250 mm
250 mm
50°
Funnel
Screw cap
Gl. 32
Thread
Gl. 32
Glass wool
210 mm
Adsorber
250 mm
Glass wool

Fig. 2

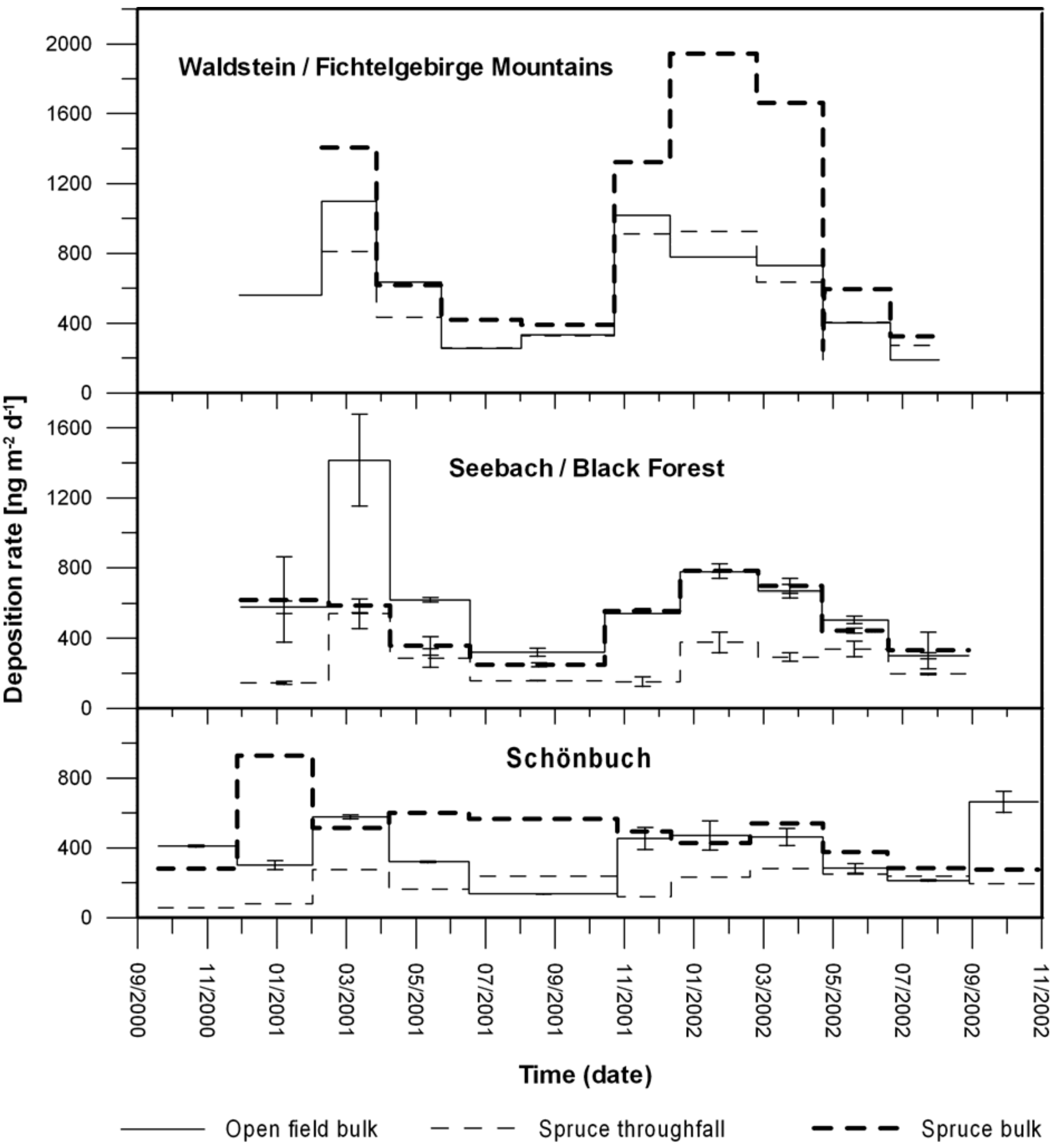
Waldstein / Fichtelgebirge Mountains
Seebach / Black Forest
Schönbuch
Deposition rate [ng m^{-2} d^{-1}]
0
400
800
1200
1600
2000
0
400
800
1200
1600
0
400
800
09/2000
11/2000
01/2001
03/2001
05/2001
07/2001
09/2001
11/2001
01/2002
03/2002
05/2002
07/2002
09/2002
11/2002
Time (date)
Open field bulk
Spruce throughfall
Spruce bulk

Fig. 3

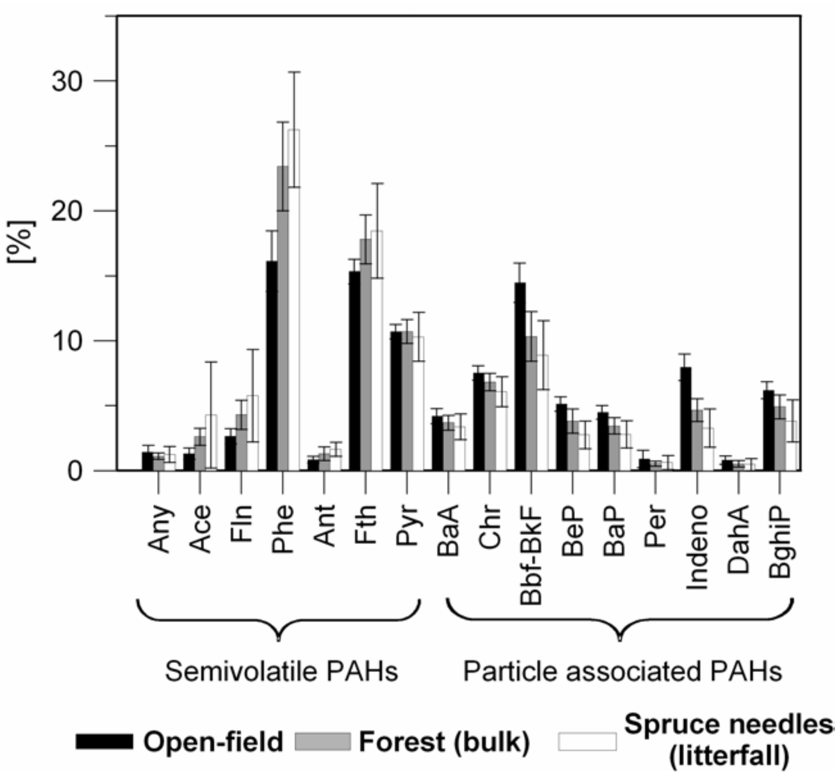
[%]
0
10
20
30
Any
Ace
Fln
Phe
Ant
Fth
Pyr
BaA
Chr
Bbf-BkF
BeP
BaP
Per
Indeno
DahA
BghiP
Semivolatile PAHs
Particle associated PAHs
Open-field
Forest (bulk)
Spruce needles (litterfall)

Fig. 4

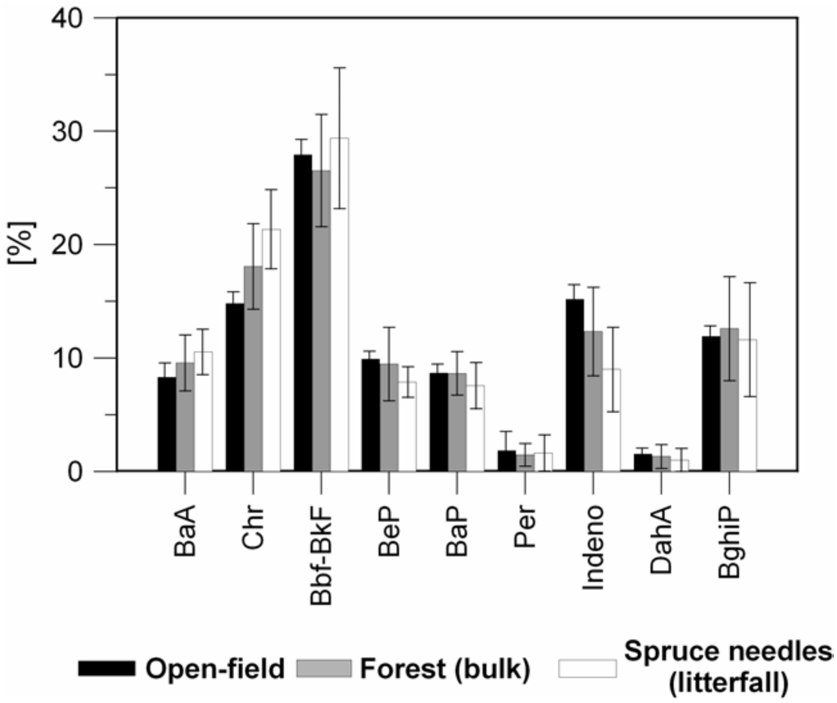
[%]
0
10
20
30
40
BaA
Chr
Bbf-BkF
BeP
BaP
Per
Indeno
DahA
BghiP
Open-field
Forest (bulk)
Spruce needles (litterfall)

Fig. 5

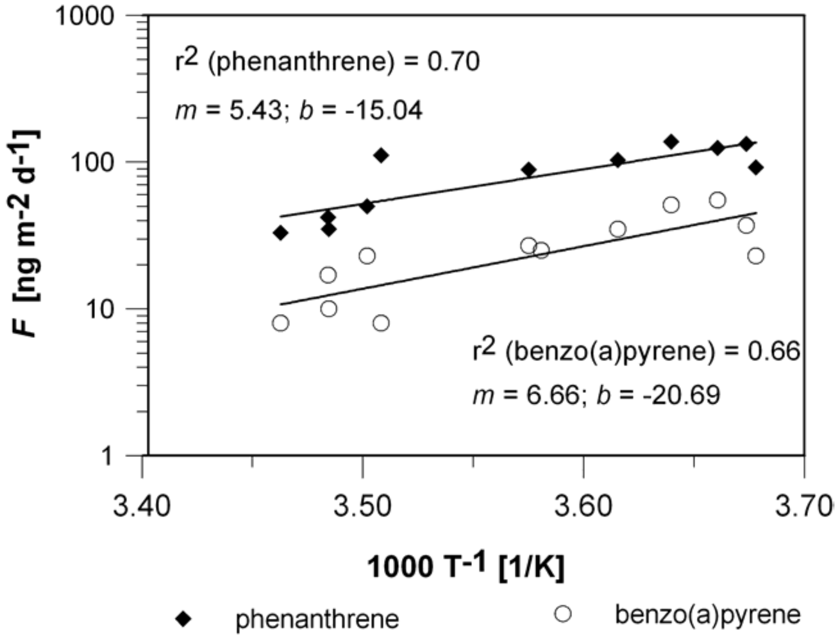
1000
100
10
1
F [ng m-2 d-1]
3.40
3.50
3.60
3.70
1000 T-1 [1/K]
r2 (phenanthrene) = 0.70
m = 5.43; b = -15.04
r2 (benzo(a)pyrene) = 0.66
m = 6.66; b = -20.69
◆ phenanthrene
○ benzo(a)pyrene

Fig. 6

Table 1: Mean annual deposition rates of PAHs in rural areas of Southern Germany in µg m^{-2} $year^{-1}$.

Region	Type of deposition		Any	Ace	Fln	Phe	Ant	Fth	Py	BaA	Chr	Bbf-BkF	BeP	BaP	Per	Indeno	DahA	BghiP	∑ PAH
Seebach																			
2001	Open-field		2.17	1.48	4.88	27.32	2.01	32.77	21.72	8.31	17.84	37.89	13.77	10.50	1.49	21.12	2.53	14.68	220.48
	Forest	throughfall	0.84	2.47	3.50	16.64	0.76	16.10	8.65	2.80	5.63	11.81	4.38	3.55	0.49	6.07	0.45	4.59	88.73
		bulk	1.42	4.70	7.22	32.91	1.71	30.00	16.63	5.81	10.09	16.71	6.12	5.46	0.89	8.48	1.11	8.33	157.60
2002 [a]	Open-field		2.59	2.48	5.75	27.40	1.77	27.49	19.10	6.79	14.96	26.93	8.85	8.47	1.42	13.43	1.72	11.00	180.16
	Forest	throughfall	1.77	2.52	4.68	18.91	1.10	13.50	9.05	3.72	6.54	11.70	3.72	4.19	0.76	5.65	0.74	4.33	92.88
		bulk	2.28	4.65	9.40	43.68	2.22	28.67	19.07	6.87	12.47	18.02	5.77	6.57	1.18	8.34	1.11	12.19	182.49
Schönbuch																			
2001	Open-field		1.45	1.51	3.33	21.55	0.95	18.50	13.07	4.35	8.90	18.20	6.74	4.90	0.78	8.79	0.98	7.78	121.77
	Forest	throughfall	1.09	2.15	2.61	16.85	0.71	17.55	8.80	1.73	4.01	5.76	4.57	1.56	0.13	2.92	0.36	2.68	73.49
		bulk	2.13	6.63	13.03	58.14	6.25	36.62	19.31	6.48	11.33	21.91	10.39	5.01	1.05	7.38	0.73	6.69	213.08
2002	Open-field		3.22	2.40	3.87	28.76	1.46	26.62	20.09	8.56	13.93	26.06	8.37	8.66	1.44	16.82	1.31	10.96	164.68
	Forest	throughfall	1.79	1.74	2.80	16.17	1.01	15.17	9.91	3.25	6.15	8.26	3.00	3.53	0.39	5.20	0.30	4.02	82.12
		bulk	2.52	2.90	6.20	42.77	2.89	104.76	17.87	4.26	10.24	10.76	3.83	4.21	0.52	5.38	0.35	5.87	225.30
Waldstein																			
2001	Open-field		2.28	2.75	5.71	35.70	1.89	34.20	24.54	9.45	17.28	34.83	11.61	9.70	4.65	18.22	2.38	13.07	228.27
	Forest	throughfall	2.22	2.25	5.13	41.53	1.76	44.47	23.94	7.54	13.32	24.59	8.20	7.53	1.42	13.35	1.75	9.58	208.56
		bulk	2.95	7.69	13.46	81.78	3.43	72.39	37.59	11.76	20.77	36.72	11.57	11.00	2.15	17.15	2.15	12.68	345.25
2002 [b]	Open-field		2.57	3.18	6.09	36.14	2.36	32.14	23.72	8.92	17.23	30.04	9.65	9.70	4.82	15.70	2.04	11.88	216.17
	Forest	throughfall	2.75	2.85	6.05	45.03	2.47	39.58	23.96	7.47	14.14	25.72	8.05	8.32	2.03	13.80	1.66	9.31	213.18
		bulk	4.11	7.81	14.84	100.90	4.72	78.86	43.29	11.60	24.25	37.18	11.46	11.56	2.52	18.10	1.89	14.91	388.01

[a] 28.08.2001 – 29.08.2002

[b] 03.08.2001 – 02.08.2002

Table 2: Compilation of PAH deposition rates in rural areas in µg m^{-2} year^{-1} using different sampling methods.

Sampling method	**Study area**	**PAH$_{12}$ [a)]**	**BaP [b)]**	**Reference**
Bergerhoff	Germany		2.2-11.2	Matzner, 1984
Bergerhoff	Germany	142	7.4	Horstmann and McLachlan, 1998
Funnel-bottle	Germany		14.7-27.0	Schrimpff, 1984
Funnel-bottle	France	52-68	1.5	Garban et al., 2002
Funnel-bottle	France	46	1.5	Motelay-Massei et al., 2003
Funnel-adsorber-cartridge	High mountain areas, Europe	12.6-16	0.4-0.7	Fernandez et al., 2003
Funnel-adsorber-cartridge	Sweden	286	11.0	Brorström-Lunden et al., 1994
Funnel-adsorber-cartridge	Sweden	186	9.5	Brorström-Lunden and Löfgren, 1998
Funnel-bottle, wet-only	Hungary	393	13.0	Kiss et al., 2001
Funnel-adsorber-cartridge, wet-only	USA (Ches. Bay)	26.8-72.0	1.0-2.0	Dickhut and Gustafson, 1995
Funnel-adsorber-cartridge, wet only + calc. dry	USA (Ches. Bay)	135-184	6	Dickhut and Gustafson, 1995
Funnel-adsorber-cartridge, wet-only	USA (Ches. Bay)	72	2	Leister and Baker, 1994
Funnel-adsorber-cartridge, wet only + calc. dry	USA (Ches. Bay)	184	6	Leister and Baker, 1994
wet-only	USA (Gr. Lakes)		0.7-4.2	Buehler et al., 1998
wet-only	Canada	6.0-9.6	0.3-0.4	Brun et al., 2004
Air concentrations, calc. dry + calc. wet	USA, east coast	186	6.4	Gigliotti et al., 2005

[a)] Sum of phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b+k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene.

[b)] benzo(a)pyrene