# COMPARISON OF PAH CONCENTRATIONS IN SEMIPERMEABLE MEMBRANE DEVICES, LOW VOLUME ACTIVE SAMPLER, AND SPRUCE NEEDLES

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**Introduction**
Polycyclic aromatic hydrocarbons (PAH) are produced mainly by incomplete combustion processes and some of them are known to be carcinogenic. These compounds are characterized for a wide range of physicochemical properties as vapour pressure, lipophilicity and gas particle partitioning that determine their different compartment affinities of them in the environment. One compartment of crucial importance among the sinks of POPs is vegetation being in the mass transfer flux an intermediate compartment between air and soil. [1,2,3,4] Bioaccumulation in leaves depends not only on vegetation and micrometeorological conditions but also on PAH molar volume.[5] Vegetation canopy as natural passive sampler system allows quantify both the compounds retained within the leaf compartment and those deposited with particles on the leaf surface. Semi-permeable membrane devices (SPMD) can be used alternatively; they are appropriate for compounds which are predominantly in the vapour phase but can also uptake compounds from particles deposited on the membrane when lipid diffused through it.[6,7]

The accumulation and distribution of PAH were analysed in spruce needles and SPMD devices chosen as passive samplers meanwhile the active sampling provided us with the PAH air concentration. Correlations among compounds were calculated with results obtained from the active and passive samplers and used to find relationships between them. The study area is the Bavarian and Bohemian Forest (Central Europe); the four sites were chosen for their similar climate, soil and forest properties and their great distance to possible emission sources. The analytical determinations concerned 18 compounds of the PAH family. The aim of this study was to determine strength and weakness of the different methods applied related to the sampling of persistent compounds in mountainous forest areas.

**Materials and Methods**
The site characteristics at the sampling sites; Mitterfels, Ruckowitzschachten and Haidel, located in Eastern-Bavaria and Boubin located in western Bohemia (Sumava National Park) were already presented by Kirchner *et al.* as well as the sampling description.[8] In addition, active sampling campaigns wit a low volume (LowVol) sampler (Digitel blower, DPA96) were conducted in the periods August - October 2003, October 2003 - January 2004, January - March 2004, September - October 2004 and October 2004 - January 2005 at Haidel. Spruce needles (*Picea abies* (L.) Karst), ½, 1 ½ and 2 ½ years of age, were sampled in October 2003 and October 2004. SPMDs were deployed for ½ and 1 ½ years at the sampling sites and collected in October 2003 and 2004, respectively. SPMD tubes (23 cm X 2.5 cm, membrane thickness 67.4 µm) were filled with 0.7 ml triolein (1,2,3-tris[cis-9-octadecenoylglycerol]). SPMDs were transported in hermetic clean glass vials to and from the place of deployment to prevent possible contaminations. SPMDs in quadruplicates were placed in weather huts made of natural, untreated wood at 3.0 m above the ground in small forest clearings. After being collected, these devices were stored without being cleaned on their surface. XAD cartridges and their respective back-up cartridges were also transported in sealed glass cylinders. Samples from LowVol cartridges corresponding to the periods August - October 2003 and September - October 2004 were collected at the same time like SPMDs and needles. Cartridges, needles, SPMDs and SPMDs blanks were kept under identical storage conditions at -28°C prior to analysis.

LowVol cartridges were extracted with a mixture *n*-hexane/acetone 3:1 in a Soxhlet extraction system for 24 hours. Before extraction, the cartridges were spiked with deuterated PAH standards (Cambridge Isotope Laboratories, USA). The extracts were reduced and then eluted with a mixture *n*-hexane/dichloromethane 1:1 on a mixed column filled with 10 g silica gel, 5 g $Al_2O_3$ and 2 g $Na_2SO_4$ from the bottom to the top. After that, the reduced extracts were eluted through a C18 modified silica column and finally concentrated to 20 µl.

The procedures for the sample preparation, clean up and quantification of PAHs in needles were already described.[9] Regarding the SPMDs, they were cut into slices, spiked with deuterated PAH standard mixture (Cambridge Isotope Laboratories, USA) and extracted for 24 hours with 100 ml cyclohexane each by use of a rotating shaking machine. The further clean up for PAHs was the same as for XAD cartridges. The compounds were determined by high resolution gas chromatography (HRGC) on a Rtx-CLPesticidesII column (Restek, Germany). The GC is coupled with a high resolution mass spectrometer MAT95 (Thermo Electron GmbH, Germany) operated in single ion monitoring mode.

The PAH quantified were the 16 priority pollutants of US EPA Acenaphthylene (ACL), Acenaphthene (AC), Fluorene (FL), Phenanthrene (PHE), Anthracene (AN), Fluoranthene (FA), Pyrene (PY), Benz(a)anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbFA), Benzo[k]fluoranthene (BkFA), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IP), Dibenz[a,h]anthracene (DBahA), Benzo[g,h,i]perylene (BghiP). Naphthalene was excluded due to its high volatility meanwhile Benzo[e]pyrene (BeP), Perylene (PE) and Benzo(b)naphtho(1,2-d)thiophene were added to this list. Results were given in air concentration (pg m$^{-3}$) for the active measurements, in mass per dry weight (ng kg$^{-1}$) for needles and total amount of each compound per tube (ng tube$^{-1}$) for SPMDs. Quadruplicates of SPMDs blanks were done for the first sampling period (½ year) and duplicates for the extended period (1 ½ year). Duplicates of the clean-up blanks were also conducted as an internal quality control. The standard recoveries for PAH were in the range of 50-90 % for all investigated samples.

**Results and Discussion**

Regarding the active samplers, PAH were correlated among them, showing the whole PAH family the same trend to a concentration increase in early and late winter and a decrease of concentration in the warmer seasons. For instance, this is particularly remarkable for the heavy molecular weight PAH i.e.: BbFA, BkFA, BeP and BaP presenting a strong correlation between them with at least $r^2$=0.93. The lower molecular weight PAH are not so well correlated, neither among them nor with the heavier molecular weight PAH. Higher concentrations of PAH are determined during the late winter time meanwhile the lower concentrations are detected in summer. To illustrate this, PHE reached the highest concentration in late winter with 4.7 ng m$^{-3}$ air in comparison to 0.8 ng m$^{-3}$ air observed in summer, meanwhile the carcinogenic BaP fluctuated between 120 to 14 pg m$^{-3}$ air. Previous studies in a semi urban zone showed also this temporal trend.[10] FL and PHE are the compounds detected in higher concentrations in all sampling campaigns. PHE represents in the studied campaigns between 33-50 % of the whole PAH. The compounds FA and PY are also present in all the sampling campaigns with percentages between 9.5-14.5 and 4.5- 6.8, respectively. The lower molecular weight PAH are in higher concentrations than higher molecular weight PAH.

Correlations in needles between compounds present no general trend but some correlations are found between compounds with similar physicochemical characteristics. A correlation between Pyrene (PY) and Fluoranthene (FA) in needles is observed with $r^2$=0.93. These compounds have similar properties as surface area, molecular volume, water solubility and octanol/water partition coefficient that can determine similar needle uptake. Prediction of vegetation-atmosphere partition coefficients, gave very similar values for them.[1,11] Thus, this can explain the similar behaviour found in needles. BeP and BaP are correlated also in needles with $r^2$= 0.91. Perylene (PE) correlates with BaP ($r^2$= 0.95), which could be expected due to their physicochemical similarities as well as for their similar vegetation-atmosphere partition coefficients.[12] PAH relative distribution in needles is different to that determined in air (figure 1). Low molecular weight PAH as PHE, FL and ACL are present in air in relatively higher concentrations than in needles. However, intermediate and high molecular weight PAH tend to accumulate in higher percentage in needles than low molecular weight PAH. The predominant compound in needles is FA, representing more than 20 % of the whole PAH concentration, meanwhile PHE, one of the predominant compounds in air, decreases in the leave compartment to a value around 12 % of the whole PAH.

This percentage distribution is observed at the four sampling sites in the periods of October 2003 and 2004. Comparing PAH concentration distribution in needles and air at Haidel, higher amounts of 5 and 6 ring PAH are found in needles of all ages than in air (Figure 1). Furthermore, the 2 benzene ring compounds are in lower percentage in needles than in air. Thus, less accumulation of low molecular weight PAH is observed in the leaf compartment in comparison to the high molecular weight PAH. There is no correlation between concentrations of PAH in air and needles.
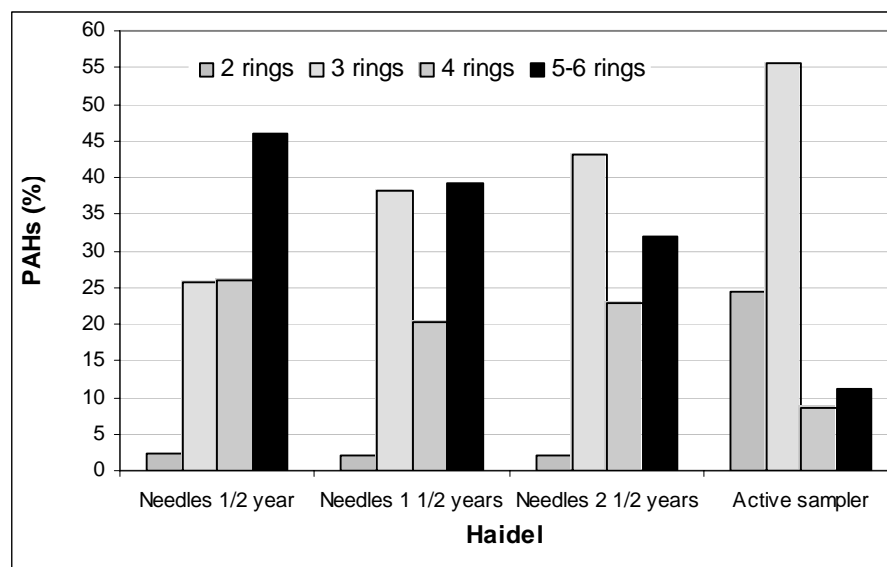


**Figure 1**: PAHs distribution (%) in needles ½, 1 ½ and 2 ½ years old and active sampler at Haidel. Sampling October 2003. The number of benzene rings was considered for the classification where BbFA, BkFA were included in 5-6 rings.

In SPMDs, two groups presented correlations: one between Chrysene and Fluoranthene and the other between BaA, BeP, BaP, PE and BghiP. Chr and FA have similar chemical stability indicated by their similar hardness values.[12] The physical properties, surface area and volume are similar between the compounds as well as the octanol-water partition coefficient (log $K_{ow}$) within both groups. This suggests that properties like spatial molecular distribution, stability of the compound and hydrophobicity, have an effect on the PAH uptake in SPMDs. The percentage distribution of PAH related to their number of aromatic rings did not present significant differences in the ½ and 1 ½ years exposure devices as shown in figure 2a.

SPMDs tend to accumulate low molecular weight PAH in comparison to the needles in the same time span. Actually, the heavy molecular weight PAH are mainly found in the particulate phase, being this characteristic an impediment for the uptake of these compounds through the membrane device. Thus, this implies that more percentage of 3 aromatic ringed PAHs related to the whole sample are found in SPMDs than in needles. In spite of this fact, the compound Benzo(b)naphtho(2,1-d)thiophene is found in needles and SPMDs 1 ½ years exposed but not in SPMDs of shorter exposition time.

The 3 aromatic ringed PAH group is composed of Phenantrene and Fluoranthene (Anthracene is not considered due to lack of chromatographic resolution and their small quantities) where PHE represents in average almost 50 % of the whole PAH presented in the samples and FA around 25 % in SPMDs exposed for ½ year. Bartkow *et al*, quantified PHE as the main compound of PAH (around 40 %) in SPMDs deployed for 32 days.[13] In SPMDs exposed 1 ½ years the increased proportional amount of 3 ringed PAH is due to an increase of FA that reached more than 30 % of the total PAH in the sample.

Lower molecular weight PAH that tend to be in the gaseous phase in major proportions are also dominant in SPMD devices as shown in figure 2b. Low molecular PAH presented a correlation between active and SPMD sampling. Even high molecular weight PAH, bound to particular material, correlated in both, SPMDs and active

samplers. Nonetheless, due to the low concentration of high molecular weight PAH, more studies for these compounds are necessary.



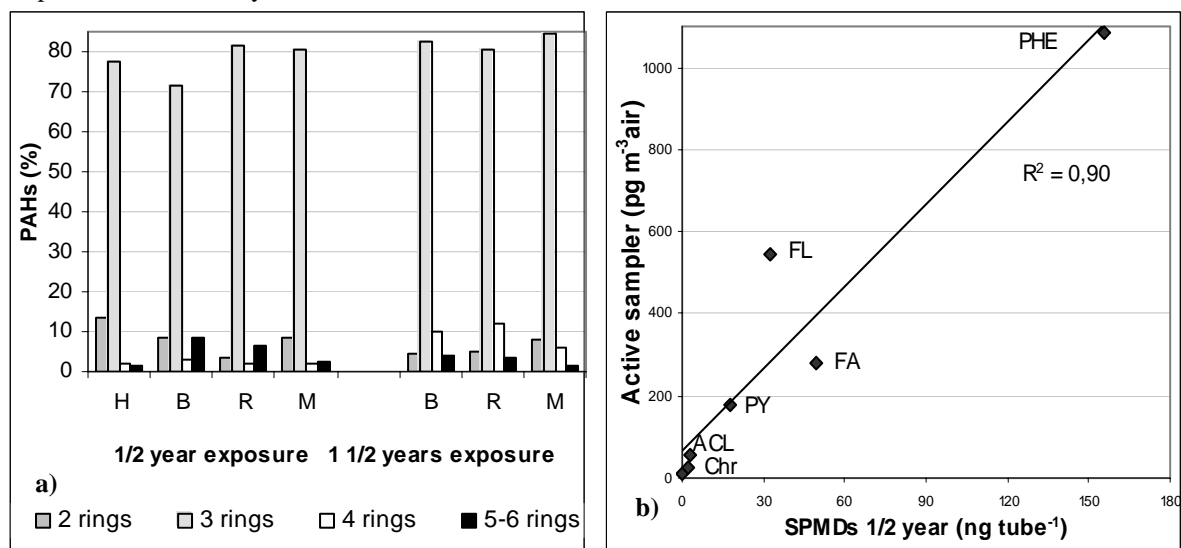**Figure 2**: **a)** PAHs distribution (%) in SPMDs ½ year and 1 ½ years exposure at 4 sampling sites. Site codes: H:Haidel, B:Boubin, R:Ruckowitzschachten and M:Mitterfels. **b)** PAHs concentrations in SPMDs ½ year exposure and active sampler 3 month exposure at Haidel.

In conclusion, the uptake of PAH in SPMDs and active samplers after ½ year exposure correlated linearly. Needles and SPMDs exposed longer times accumulate PAH without significant changes in their distribution patterns. In addition, there is a clear relationship between physicochemical properties of the compounds and the uptake rates. Compounds with similar properties exhibit similar behaviour, determining the good correlations obtained between them after the sampling analysis.

SPMDs appear to be a very feasible tool to detect low molecular weight PAH. On the other hand, needles are less "selective" than SPMDs, but can cover all the compounds analysed.

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