



# Atmospheric versus biological sources of polycyclic aromatic hydrocarbons (PAHs) in a tropical rain forest environment

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*Evidence of non-pyrolytic, biogenic production of PAHs is provided.*

## Abstract

To distinguish between pyrogenic and biological sources of PAHs in a tropical rain forest near Manaus, Brazil, we determined the concentrations of 21 PAHs in leaves, bark, twigs, and stem wood of forest trees, dead wood, mineral topsoil, litter layer, air, and *Nasutitermes* termite nest compartments. Naphthalene (NAPH) was the most abundant PAH with concentrations of 35 ng m<sup>-3</sup> in air (>85% of the  $\sum$ 21PAHs concentration), up to 1000  $\mu\text{g kg}^{-1}$  in plants (>90%), 477  $\mu\text{g kg}^{-1}$  in litter (>90%), 32  $\mu\text{g kg}^{-1}$  in topsoil (>90%), and 160  $\mu\text{g kg}^{-1}$  (>55%) in termite nests. In plants, the concentrations of PAHs in general decreased in the order leaves > bark > twigs > stem wood. The concentrations of most low-molecular weight PAHs in leaves and bark were near equilibrium with air, but those of NAPH were up to 50 times higher. Thus, the atmosphere seemed to be the major source of all PAHs in plants except for NAPH. Additionally, phenanthrene (PHEN) had elevated concentrations in bark and twigs of *Vismia cayennensis* trees (12–60  $\mu\text{g kg}^{-1}$ ), which might have produced PHEN. In the mineral soil, perylene (PERY) was more abundant than in the litter layer, probably because of in situ biological production. *Nasutitermes* nests had the highest concentrations of most PAHs in exterior compartments (on average 8 and 15  $\mu\text{g kg}^{-1}$  compared to <3  $\mu\text{g kg}^{-1}$  in interior parts) and high PERY concentrations in all compartments (12–86  $\mu\text{g kg}^{-1}$ ), indicating an in situ production of PERY in the nests. Our results demonstrate that the deposition of pyrolytic PAHs from the atmosphere controls the concentrations of most PAHs. However, the occurrence of NAPH, PHEN, and PERY in plants, termite nests, and soils at elevated concentrations supports the assumption of their biological origin.

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## 1. Introduction

The largest part of the PAH burden in temperate environments of the northern hemisphere results from

human activities like burning of fossil fuels, coal gasification, or oil refining (Howsam and Jones, 1998). Non-anthropogenic sources like volcanic eruptions or natural vegetation fires are generally thought to be less important, as shown by the coincidence of energy consumption and PAH concentrations in archived soils (Jones et al., 1989) and dated sediments (Christensen and Zhang, 1993; Lima et al., 2003) over more than a century.

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The knowledge of the distribution and sources of PAHs, among other organic pollutants, in the tropical environment is very limited (Jones and de Voogt, 1999; Wilcke, 2000), but it is essential to understand and predict the global dynamics and temporal trends of these compounds. While several studies report PAH concentrations and possible sources in the aquatic environment (e.g., Laflamme and Hites, 1978; Zakaria et al., 2002; Zhou and Maskaoui, 2003), studies on terrestrial soils and plants are largely missing (Wilcke, 2000). In recent years, evidence was presented that there are biological sources of the PAHs naphthalene (NAPH), phenanthrene (PHEN), and perylene (PERY) in the tropics, which may contribute significantly to the environmental load in rural background areas (Wilcke et al., 2000, 2003, 2004). In soils from different ecological zones of Brazil, one of NAPH, PHEN, or PERY dominated the mixture of PAHs while high-molecular weight fire markers were almost absent (Wilcke et al., 2003). The same was true for NAPH and PHEN in soils and plants from the Brazilian savanna region, the Cerrado (Wilcke et al., 2004).

Evidence for a biological production of NAPH has been derived from its presence in *Magnolia* flowers (Azuma et al., 1996) or flower scents of different *Annonaceae* species from the Amazon rain forest (Jürgens et al., 2000). Daisy et al. (2002) have shown that NAPH is produced by *Muscodor vitigenus*, an endophytic fungus of a liana growing in the Peruvian Amazon region. High NAPH concentrations in *Coptotermes formosanus* termite nests of subtropical North America (Chen et al., 1998a,b) and nests of various termite genera from tropical Brazil (Wilcke et al., 2000, 2003) suggest a NAPH synthesis by termites or associated microorganisms. As *C. formosanus* followed NAPH-marked paths, Chen et al. (1998a) assumed that NAPH acts as a signaling compound. Wiltz et al. (1998) and Wright et al. (2000) reported that NAPH inhibited the growth of insect pathogenic fungi, suggesting that NAPH may form part of the termites' defensive system. Naphthalene concentrations were also particularly high in nests of *Nasutitermes* sp. (Wilcke et al., 2000), a genus relying exclusively on chemical colony defense (Martius, 1994). However, NAPH has not been detected as a major component in gland secretes of different *Nasutitermes* species (Baker and Walmsley, 1982; Braekman et al., 1983; Valterová et al., 1989).

Microbial production of PERY in recent anaerobic sediments and soils has been recognized for a long time (Wakeham et al., 1980; Venkatesan, 1988), and it is suspected also for PHEN (Wakeham et al., 1980; Wickström and Tolonen, 1987). The high concentrations and depletion in  $^{13}\text{C}$  of PERY extracted from termite nests and soils from the Amazon basin compared to fossil fuel-derived PERY indicated that biological production also occurs in termite nests

(Wilcke et al., 2002). From these results we concluded that there might be large plant- and/or termite-related sources of PAHs in tropical rain forests. However, frequent large-scale burning of rain forests by man may also cause a significant input of pyrogenic PAHs (Freeman and Cattell, 1990; Radzi bin Abas et al., 1995).

The distribution among different environmental compartments can give hints on the sources. Leaves and bark of trees most closely represent the current atmospheric PAH concentrations (Ockenden et al., 1998) and are therefore used for biomonitoring of airborne pollution (Alfani et al., 2001; Hwang et al., 2003). On the other hand, stem wood receives PAHs probably only from internal sources (i.e. plant metabolism or endophytic organisms), as any translocation of PAHs with an octanol–water partition coefficient  $>10^4$  in the plant is unlikely (Simonich and Hites, 1995).

The same may be true for nests of *Nasutitermes*, a dominant termite genus in Amazonian rain forests (Constantino, 1992; Martius, 1994). This genus feeds mainly on wood and builds arboreal carton nests at several meters height, which are connected to the ground by galleries (i.e. artificial tunnels) along the tree trunk. The nests can be differentiated morphologically in a thin outer wall, an inner wall, and a nursery. While the last two compartments receive PAHs inputs either from digested wood used for construction or from internal synthesis, the outer wall and galleries receive PAHs also from atmospheric deposition.

The objectives of our study were (i) to monitor – to our knowledge for the first time – the PAH concentrations in different compartments of a tropical rain forest and (ii) to assess the sources of PAHs (atmospheric versus biological) by examining their distribution among internal and external, atmosphere-exposed, plant and termite nest compartments and by relating PAH concentrations in air to those in external plant parts.

## 2. Materials and methods

### 2.1. Study sites

The study area was located in the *terra firme* (i.e. never flooded) region approximately 30 km north of the city of Manaus, state of Amazonas, Brazil. The mean annual precipitation is about 2100 mm with a maximum of 200–300 mm per month from December to May and less than 100 mm between July and September. The mean monthly temperatures are between 25 and 27 °C (Irion et al., 1997). The natural vegetation is primary lowland tropical rain forest, which is mixed with fallow land, agricultural land, and secondary forests in the study area. The soils are deeply weathered Xanthic Ferralsols (FAO-UNESCO, 1997) derived from tertiary sediments.

## 2.2. Samples

Particulate and gaseous PAHs in air were sampled by drawing air with a membrane pump at a rate of ca.  $0.5 \text{ m}^3 \text{ h}^{-1}$  through a glass fiber filter (55 mm diameter, Schleicher and Schüll GF-6) followed by an adsorbent cartridge filled with 15 g of XAD-2. Three air samples were taken at a secondary forest site at 1.5 m height between 20 and 29 September 2001, corresponding to 26.8, 28.2, and  $36.0 \text{ m}^3$  of air. For comparison, one sample was taken in the city of Manaus (28–29 September 2001), corresponding to  $23.7 \text{ m}^3$  of air. The daytime temperature was ca.  $33 \text{ }^\circ\text{C}$ , the night-time temperature was  $26 \text{ }^\circ\text{C}$ , the weather was sunny with a short rainfall every second to third day. After the sampling, the glass fiber filters were wrapped in aluminum foil and the XAD-2 traps were sealed. Samples were stored at  $-18 \text{ }^\circ\text{C}$  until analysis.

Plant samples were collected within an area of about  $10 \text{ km}^2$  from one primary forest stand and three secondary forest stands in September 2001. The latter had established themselves in the last 15 years on abandoned plantations and were dominated by *Vismia* spp. At the primary forest stand, 10 species of different families were sampled: *Attalea attaleoides* (Barb. Rodr.) Wess. Boer., Arecaceae; *Rinorea racemosa* (Mart.) Kuntze, Violaceae; *Psychotria medusula* Müll. Arg., Rubiaceae; *Naucleopsis ternstroemiiflora* (Hildbr.) C.C.Berg, Moraceae; *Swartzia cuspidata* Benth., Fabaceae; *Swartzia ulei* Harms, Fabaceae; *Ocotea floribunda* (Sw.) Mez, Lauraceae; *Socratea exorrhiza* (Mart.) H. Wendl., Arecaceae; *Myrcia* sp., Myrtaceae; and *Pourouma ferruginea* Standl., Cecropiaceae. At two different secondary forest stands we sampled six of the most abundant tree species of different families: *Vismia cayennensis* (Jacq.) Pers., Clusiaceae; *Pourouma cuspidata* Mildbr., Cecropiaceae; *Xylopia nitida* Duval, Annonaceae; *Miconia tormentosa* (Rich) D.Don, Melastomataceae; *Loreya spruceana* Benth. ex Triana, Melastomataceae; and *Parkia decussata* Ducke, Fabaceae. At the third site *L. spruceana* was absent, and thus only the other five species were sampled. We collected leaves, bark, twigs (up to 1 cm diameter), and stem wood of one 4–7 m tall tree of each of the above mentioned species. All leaf, bark, and twig samples were cut to pieces of 2–8 mm within 4 h after sampling. All samples were stored in closed aluminum containers at  $-18 \text{ }^\circ\text{C}$ . The stem wood samples were cut in frozen state with a blade-cutting mill in Berlin.

We sampled four arboreal nests of the termite genera *Nasutitermes* (outer wall, inner wall, nursery, and gallery) at 4–8 m height. Two nests were located near the edge of a primary forest facing a plantation, the other two at the edges of secondary forests facing a forest clearing. We took one soil and one litter layer sample near each termite nest combining five subsamples

representatively collected from an area of  $25 \text{ m}^2$ . In the same area, a composite dead wood sample was also collected. Termite nest (termites were carefully removed), dead wood, organic layer, and soil samples were homogenized and stored in aluminum containers at  $-18 \text{ }^\circ\text{C}$ .

## 2.3. Analyses

We determined organic carbon (OC) and total nitrogen in air-dried aliquots of all samples by dry combustion using a Leco CN-2000 analyzer. The frozen samples (XAD-2, glass fiber filters, plants, soils, termite nests) were extracted with hexane:acetone 2:1 by pressurized solvent extraction using an ASE 200 (Dionex, Sunnyvale, CA) as described in Krauss and Wilcke (2003). We evaporated the extracts to 1 ml and dried them by filtration over anhydrous  $\text{Na}_2\text{SO}_4$ . The extracts were purified by solid phase extraction on aluminum oxide/silica gel columns (Krauss and Wilcke, 2003) and evaporated to approximately  $500 \mu\text{l}$  before PAH measurement.

We separated 21 PAHs in all extracts by gas chromatography (Agilent 6890, Palo Alto, CA) using an Agilent/J&W DB5-ms fused silica capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ ) and quantified them with mass spectrometry (Agilent 5973) with electron ionization at 70 eV in selected ion monitoring mode: naphthalene (NAPH), acenaphthylene (ACENY), acenaphthene (ACEN), fluorene (FLUO), phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLUA), pyrene (PYR), benz(a)-anthracene [B(A)A], chrysene + triphenylene (CHRY), benzo(b + j + k)fluoranthenes [B(BJK)], benzo(a)pyrene [B(A)P], benzo(e)pyrene [B(E)P], perylene (PERY), indeno(1,2,3-cd)pyrene (IND), dibenz(a,h)anthracene (DIBE), benzo(ghi)perylene [B(GHI)], coronene (COR). The GC conditions were the same as described in Krauss and Wilcke (2003). For quantification we used eight perdeuterated PAHs as internal standards, which were spiked to the samples after extraction. The recoveries of the internal standards ranged from  $72 \pm 20\%$  (mean  $\pm$  standard deviation) to  $86 \pm 10\%$  relative to FLUA-D<sub>10</sub> spiked to the extracts prior to injection.

## 2.4. Quality assurance and quality control

We used solvents of HPLC or residue analysis grade; all other chemicals were at least of 'pro analysi' grade. All vessels used for analysis were pre-cleaned with ethyl acetate followed by acetone and heated at  $300 \text{ }^\circ\text{C}$  overnight. We ran one analytical blank with every batch of 15–20 samples to check background contamination during the extraction and purification steps. To remove background contamination, we corrected PAH concentrations by subtracting the mean of the analytical blanks.

The lower limit of determination of PAHs was estimated from the smallest peak (signal-to-noise ratio

>3:1 in the chromatograms) that could be integrated and was about  $0.01 \text{ ng m}^{-3}$  for each PAH for the air samples and  $5\text{--}20 \text{ ng kg}^{-1}$  for the solid samples. We tested the accuracy of PAH quantification by analyzing the certified reference materials “CRM 104 – PAH contaminated soil” (Resource Technology Corporation, Laramie, WY, USA). The average measured PAH concentrations of three replicates were 88% (range 75–108%) of the reference values.

### 2.5. Calculations and statistical evaluation

All given concentrations are based on dry weight. The sum of the concentrations of all 21 PAHs is referred to as  $\sum 21\text{PAHs}$ . The 18 clearly pyrogenic PAHs (i.e. all except for NAPH, PHEN, and PERY) are referred to as “pyrogenic PAHs” and the sum of their concentrations is called  $\sum 18\text{PAHs}$ .

The  $K_{\text{OA}}$  values of the PAHs at standard conditions (101.3 kPa, 25 °C) were taken from Horstmann and McLachlan (1998) or, if no literature data were available, calculated from the subcooled liquid vapor pressures (taken from Mackay et al., 1992) according to Harner and Bidleman (1996) using the equation for non-ortho polychlorinated biphenyls. Because a gas chromatographic separation of chrysene and triphenylene, and of the benzo(*b*, *j*, and *k*)fluoranthenes was not possible, we used as an approximation of the compound properties of the most abundant compounds in these mixtures, i.e. chrysene and benzo(*b*)fluoranthene, respectively.

Statistics was performed with STATISTICA for Windows 5.1 (StatSoft of Europe, Hamburg, Germany). Correlation and regression followed the least-squares method. We identified significant differences of the concentrations of individual PAHs between two compartments using a *t*-test for dependent samples (“paired differences” test). The significance level was set at  $P < 0.05$ . To compare the PAH concentrations in plant compartments of the same species between the three secondary forest sites, we used the non-parametric Friedman’s two-way analysis of variance. To compare PAH concentrations and patterns among different species at the secondary forest sites, we used the non-parametric median test, which is equivalent to the parametric one-way analysis of variance. The use of parametric methods was in both cases not meaningful, because means and variances were correlated.

## 3. Results and discussion

### 3.1. Air

The sum of the PAH concentrations ( $\sum 21\text{PAHs}$ ) in the air samples (sum of gaseous and particulate phase) at the secondary forest site was, on average,  $35 \text{ ng m}^{-3}$ .

While NAPH accounted for 85% of  $\sum 21\text{PAHs}$ , we detected no five- and six-ring PAHs except for the B(BJK) in the gaseous or particulate phase (Table 1). The concentrations of individual PAHs were similar or lower than those reported for other tropical or temperate forest sites (Vasconcellos et al., 1998; Horstmann and McLachlan, 1998; Howsam et al., 2000).

The PAH concentrations at the secondary forest site were 10 or more times lower than at an urban location in Manaus. The sampling location in Manaus showed also a predominance of NAPH (93% of  $\sum 21\text{PAHs}$ ). Compared with other tropical and temperate urban locations, PAH concentrations in the air of Manaus were at the lower end of the reported range (Harrison et al., 1996; Panther et al., 1999; Lee et al., 2001; Liu et al., 2001).

The distribution of PAHs among the gaseous and particulate fractions was in the range of data reported for European locations in the summer (Harrison et al., 1996; Horstmann and McLachlan, 1998; Howsam et al., 2000).

### 3.2. Plants

Leaves had in general the highest  $\sum 21\text{PAHs}$  of all plant compartments (mean  $593 \mu\text{g kg}^{-1}$ ) followed by bark (mean  $363 \mu\text{g kg}^{-1}$ ) and twigs (mean  $167 \mu\text{g kg}^{-1}$ ), although twigs and bark of some tree species had higher concentrations than the leaves. Stem wood consistently had the lowest  $\sum 21\text{PAHs}$  (mean  $51 \mu\text{g kg}^{-1}$ ). The  $\sum 18\text{PAHs}$  followed the same order and thus reflected the exposure of the plant surfaces to the atmosphere and the ratio of the exposed surface to volume of the compartment. However, there were large variations of up to a factor of 100 in  $\sum 18\text{PAHs}$  concentrations for the same compartment among different trees. This may be explained by variations in exposure times, morphologies, and/or microclimatic conditions, which all control PAH accumulation by plants from the air (Barber et al., 2004). The PAH concentrations of the different compartments of the same tree species at all three secondary forest sites were similar. This indicated that the three studied secondary forest sites received similar PAH inputs.

Naphthalene was by far the dominant PAH in all plant compartments and accounted, on average, for 94% of the  $\sum 21\text{PAHs}$  in leaves, 91% in bark, 88% in twigs, and 81% in stem wood. Phenanthrene was the second most abundant compound contributing, on average, 1.3% to the  $\sum 21\text{PAHs}$  in leaves, 3.3% in bark, 4.4% in twigs, and 9.7% in stem wood. Its concentrations were, on average, highest in bark, followed by leaves, while twigs and stem wood had similar concentrations (Table 2). The differences between the compartments were less pronounced than for

Table 1

Total concentrations of PAHs ( $C_{\text{air}}$ ) in air samples of Amazonia (means  $\pm$  standard deviations), and ratio of particle-bound ( $C_{\text{p}}$ ) to gaseous PAH concentration ( $C_{\text{G}}$ )

	Manaus, Amazonia, urban, $n = 1$		Amazonia, secondary forest, $n = 3$		Amazonia <sup>a</sup> , forest, range $n = 16$	Bayreuth, Germany <sup>b</sup> , forest, mean May–October		Meathop, NW England <sup>c</sup> , forest, mean summer	
	$C_{\text{air}}^{\text{d}}$ (ng m <sup>-3</sup> )	$C_{\text{p}}/C_{\text{G}}$ (-)	$C_{\text{air}}^{\text{e}}$ (ng m <sup>-3</sup> )	$C_{\text{p}}/C_{\text{G}}$ (-)	$C_{\text{p}}$ (ng m <sup>-3</sup> )	$C_{\text{air}}$ (ng m <sup>-3</sup> )	$C_{\text{p}}/C_{\text{G}}$ (-)	$C_{\text{air}}$ (ng m <sup>-3</sup> )	$C_{\text{p}}/C_{\text{G}}$ (-)
NAPH	862	0.001	26 $\pm$ 9	0.010	n.q. <sup>f</sup>	n.q.		n.q.	
ACENY	11	0.001	1.4 $\pm$ 1.1	0.005	n.q.	n.q.		n.q.	
ACEN	2.7	0.008	0.3 $\pm$ 0.1	0.064	n.q.			0.11 $\pm$ 0.03	
FLUO	9.9	0.003	0.6 $\pm$ 0.1	0.037	n.q.			0.41 $\pm$ 0.06	
PHEN	25	0.009	1.6 $\pm$ 0.3	0.105	n.d.–0.1	3.7	0.019	3.5 $\pm$ 0.5	0.049
ANTH	1.5	0.013	0.07 $\pm$ 0.01	0.479		n.q.		0.08 $\pm$ 0.02	
FLUA	3.5	0.044	0.32 $\pm$ 0.07	0.276	0.001–0.85	0.78	0.237	0.78 $\pm$ 0.16	0.054
PYR	3.3	0.033	0.17 $\pm$ 0.07	0.275	0.001–0.17	0.41	0.421	0.35 $\pm$ 0.05	0.094
B(A)A	0.2	0.136	0.02 $\pm$ 0.01	1.12	0.003–0.22	n.q.		0.05 $\pm$ 0.01	0.667
CHRY	0.7	0.154	0.03 $\pm$ 0.02	0.744	0.006–0.61	0.19	1.68	0.08 $\pm$ 0.01	0.429
B(BJK)	0.5	0.602	0.03 $\pm$ 0.03		0.002–1.8	0.35	11.6	0.30 $\pm$ 0.07	0.247
B(A)P	n.d. <sup>g</sup>		n.d.		0.001–0.66	0.09		0.04 $\pm$ 0.01	3.33
B(E)P	n.d.		n.d.		0.001–1.1	0.11		n.q.	
PERY	n.d.		n.d.		0.003–0.12	n.q.		n.q.	
IND	n.d.		n.d.		0.003–0.66	0.16		n.q.	
DIBE	n.d.		n.d.		0.001–0.17	0.02		n.q.	
B(GHI)	n.d.		n.d.		0.007–0.75	0.09		0.04 $\pm$ 0.01	
COR	n.d.		n.d.		n.q.	0.07		n.q.	

Literature data are given for comparison.

<sup>a</sup> Vasconcellos et al. (1998).

<sup>b</sup> Horstmann and McLachlan (1998).

<sup>c</sup> Howsam et al. (2000).

<sup>d</sup> Collected 28–20 September 2001.

<sup>e</sup> Collected 20–29 September 2001.

<sup>f</sup> Not quantified.

<sup>g</sup> Not detected.

NAPH. The next most abundant compounds were in all samples FLUA, PYR, CHRY, and B(BJK) contributing 1–4% of the  $\sum 21\text{PAHs}$  concentrations with mean concentrations of 0.5–1.2  $\mu\text{g kg}^{-1}$  in stem wood, 1.3–2.1  $\mu\text{g kg}^{-1}$  in twigs, and 2.5–5.5  $\mu\text{g kg}^{-1}$  in bark and leaves. Perylene concentrations were low in all compartments, exceeding 1  $\mu\text{g kg}^{-1}$  only in three leaf samples.

The mean individual contributions of all PAHs to the  $\sum 21\text{PAHs}$  concentrations, except NAPH, tended to increase in the order leaves  $\leq$  bark  $\leq$  twigs  $<$  stem wood (data not shown). However, standard deviations were large. This constant distribution pattern of all PAHs, except NAPH, among the different plant compartments suggests that they were accumulated in the plants by the same processes.

Except NAPH, PAH concentrations in leaves (32  $\mu\text{g kg}^{-1}$ ) were similar to those in a mixed forest at a remote location in northern England (23–59  $\mu\text{g kg}^{-1}$  without COR; Howsam et al., 2000), but lower than those of pine needles from background sites of Korea, Mexico, and the United States (ca. 50–140  $\mu\text{g kg}^{-1}$  without PERY; Hwang et al., 2003) or maple leaves from rural central United States (220  $\pm$  52  $\mu\text{g kg}^{-1}$  without PERY and DIBE; Wagrowski and Hites, 1997).

The NAPH concentrations in leaves of our study sites were much higher than in temperate climates.

Howsam et al. (2000) reported NAPH concentrations of ca. 3  $\mu\text{g kg}^{-1}$  (<7% of the sum of PAH concentrations) for a mixed forest in the UK, and Alfani et al. (2001) detected 15–76  $\mu\text{g NAPH kg}^{-1}$  in *Quercus ilex* leaves along a rural–urban gradient in Naples, Italy, where the sums of PAH concentrations were 107–4600  $\mu\text{g kg}^{-1}$ . The most abundant PAH in leaves from rural locations is usually PHEN, followed by FLUA, PYR, CHRY, and B(BJK) (Wagrowski and Hites, 1997; Howsam et al., 2000; Hwang et al., 2003), while at urban locations the percentages of FLUA, PYR, CHRY, B(BJK) increase relative to PHEN with increasing total PAH concentrations (Wagrowski and Hites, 1997; Alfani et al., 2001; Hwang et al., 2003).

In the compartments of trees from the Brazilian Cerrado, mean concentrations of all PAHs except NAPH were higher than in our study (Wilcke et al., 2004). The mean NAPH concentrations in stem wood at both sites were similar, but they were up to 30 times higher in bark, twigs, and leaves from Amazonia than from Cerrado. The contribution of NAPH to the  $\sum 20\text{PAHs}$  concentrations in different compartments of trees from a typical Cerrado stand was 25% (leaves), 37% (twigs), 39% (bark), and 55% (stem wood; Wilcke et al., 2004) and thus higher than in temperate forests but not as high as in our study. In leaves from the

Table 2  
Naphthalene, phenanthrene, perylene,  $\Sigma$ 18PAHs, organic carbon (OC) concentrations, and C/N ratios in different compartments of an Amazonian rainforest ecosystem (means and ranges)

Compartment	Plants						Termite nests					
	Leaves 27 ( $\mu\text{g kg}^{-1}$ )	Bark 26 ( $\mu\text{g kg}^{-1}$ )	Twigs 23 ( $\mu\text{g kg}^{-1}$ )	Stem wood 27 ( $\mu\text{g kg}^{-1}$ )	Dead wood 4 ( $\mu\text{g kg}^{-1}$ )	Litter layer 4 ( $\mu\text{g kg}^{-1}$ )	Topsoil 4 ( $\mu\text{g kg}^{-1}$ )	Nursery 4 ( $\mu\text{g kg}^{-1}$ )	Inner wall 4 ( $\mu\text{g kg}^{-1}$ )	Outer wall 4 ( $\mu\text{g kg}^{-1}$ )	Gallery 4 ( $\mu\text{g kg}^{-1}$ )	
Naphthalene	560 (289–973)	329 (73–1001)	143 (27–425)	42 (11–78)	208 (179–246)	327 (192–477)	23 (15–32)	116 (75–158)	92 (70–107)	95 (65–115)	114 (38–160)	
Phenanthrene	8.1 (0.35–26)	13 (1.2–105)	5.7 (n.d.–27)	4.5 (n.d.–23)	17 <sup>a</sup> (–)	5.2 (1.9–9.7)	0.5 (n.d.–0.78)	0.4 (n.d.–0.53)	0.2 (n.d.–0.28)	10 (8.1–15)	6.3 (4.2–7.2)	
Perylene	0.45 (0.05–3.2)	0.22 (n.d.–0.75)	0.24 (n.d.–0.50)	0.23 (n.d.–0.48)	2.7 (n.d.–3.0)	0.5 (n.d.–0.7)	0.8 (0.10–2.0)	1.2 (1.2–20)	86 (15–193)	58 (33–86)	73 (69–104)	
$\Sigma$ 18PAHs	24 (2.5–80)	21 (3.3–100)	18 (1.8–181)	3.9 (0.61–7.8)	4.0 (0.90–11)	23 (18–28)	2.0 (0.46–3.2)	2.6 (0.68–3.7)	2.8 (0.61–5.6)	15 (7.1–21)	7.9 (6.5–10)	
OC	454 (377–511)	446 (320–501)	454 (372–544)	458 (391–497)	457 (415–485)	473 (451–490)	33 (22–39)	480 (450–519)	472 (414–501)	468 (464–480)	453 (430–469)	
C/N	26 (13–42)	46 (14–77)	67 (18–150)	138 (59–364)	61 (40–82)	33 (23–46)	15 (14–17)	52 (28–80)	45 (37–60)	40 (31–51)	39 (35–46)	

<sup>a</sup> Compound was detected in only one sample.

Cerrado, PHEN, NAPH, ACEN, and FLUO were the most abundant compounds; in bark and twig samples from the Cerrado, the contribution to the sum of PAH concentrations decreased in the order, NAPH = PHEN > PYR > FLUA > FLUO > ACEN (Wilcke et al., 2004). The PAH concentrations and patterns in leaves of the Amazonian rain forest are thus more similar to those of remote forests from temperate locations than to those of the Cerrado; a remarkable exception, however, is the prominence of NAPH.

To assess a possible biological production of individual PAHs, we compared PAH concentrations and patterns among different tree species and plant compartments. In stem wood, we did not detect significant differences in the concentrations of any PAH among different species of the secondary forest. *Vismia cayennensis* had significantly higher concentrations of PHEN in bark (on average  $60 \mu\text{g kg}^{-1}$ ) and twigs ( $16 \mu\text{g kg}^{-1}$ ) than all other species (range  $1\text{--}21 \mu\text{g kg}^{-1}$  in bark, and  $0.8\text{--}11 \mu\text{g kg}^{-1}$  in twigs). The same was also true for the contribution of PHEN to the  $\Sigma$ 21PAHs. The concentrations of PHEN were also increased in leaves of *V. cayennensis* ( $12 \mu\text{g kg}^{-1}$ ), *P. cuspidata* ( $17 \mu\text{g kg}^{-1}$ ), and *L. spruceana* ( $10 \mu\text{g kg}^{-1}$ ), but along with high concentrations of one or more of FLUO, PYR, FLUA, CHRY, or B(BJK). Therefore a biological production of PHEN by *V. cayennensis* seems possible. Our results indicate that this production might be located in the bark of stems and twigs. In the leaves, however, PHEN probably mainly originated from the atmosphere.

Naphthalene concentrations were not significantly different among different species indicating that the possible NAPH biogenesis would be a common feature of all studied trees. The distribution among the different plant compartments (increasing concentrations from inner to outer parts) either could be attributable to biological NAPH sources located in the outer parts, or the NAPH concentrations in the outer plant parts reflected a combination of biological and atmospheric sources. Highest NAPH concentrations in the leaves are in contrast to the findings in the Cerrado where leaves had the lowest mean NAPH concentrations of all plant compartments (Wilcke et al., 2004). This might indicate a higher impact of atmospheric NAPH inputs in Amazonia than in the Cerrado.

### 3.3. Plant–air distribution

The distribution of nonpolar organic compounds between plants (particularly their leaves) and air (plant–air distribution coefficients,  $K_{PA}$ ) in equilibrium is a function of the octanol–air partition coefficient ( $K_{OA}$ ; Paterson et al., 1991; Tolls and McLachlan, 1994; McLachlan, 1999). To assess whether the leaves of our study plants had PAH concentrations in equilibrium with those of the air, we calculated leaf–air distribution

coefficients ( $K_{LA}$ ; in  $\text{cm}^3 \text{g}^{-1}$ ) for all PAHs by dividing their mean concentration in all leaves (in  $\text{ng g}^{-1}$ ) by their mean gaseous concentration at the secondary forest site (in  $\text{ng cm}^{-3}$ ). In spite of the limited number of air samples and when NAPH is omitted, a plot of the log-transformed mean  $K_{LA}$  of all studied plants against  $\log K_{OA}$  (average values shown in Fig. 1) reveals two different sections, one for compounds with  $\log K_{OA} \leq 7.5$  (ACEN, ACENY, FLUO, PHEN, ANTH) and one for compounds with  $\log K_{OA} \geq 7.5$  (FLUA, PYR, B(A)A, CHRY, B(BJK)), respectively. Similar relationships with  $\log K_{OA}$  were observed for the average bark–air distribution coefficients ( $K_{BA}$ ) and twig–air distribution coefficients ( $K_{TA}$ ), when NAPH again was omitted (not shown).

These observed  $\log K_{PA}$ – $\log K_{OA}$  relationships fit well into the framework of McLachlan (1999): plants take up organic compounds up to  $\log K_{OA} < 8.5$  by equilibrium partitioning with the gas phase (Section 1), for  $8.5 < \log K_{OA} < 11$  by kinetically limited gaseous deposition (Section 2), and for  $\log K_{OA} > 11$  by particle-bound deposition (Section 3). An uptake by equilibrium partitioning is indicated by a strong dependence of  $\log K_{PA}$  on  $\log K_{OA}$ , which can be seen for the left-hand Section 1 ( $\log K_{OA} \leq 7.5$ ) in Fig. 1 and is given by the equations

$$\log K_{LA} = 0.56 \log K_{OA} + 2.54, \quad r = 0.97 \quad (1)$$

$$\log K_{BA} = 0.90 \log K_{OA} + 0.23, \quad r = 0.95 \quad (2)$$

$$\log K_{TA} = 0.70 \log K_{OA} + 1.42, \quad r = 0.82 \quad (3)$$

The calculated slopes of the  $\log K_{PA}$ – $\log K_{OA}$  relationships ( $\log K_{OA} \leq 7.5$ ) were within the range

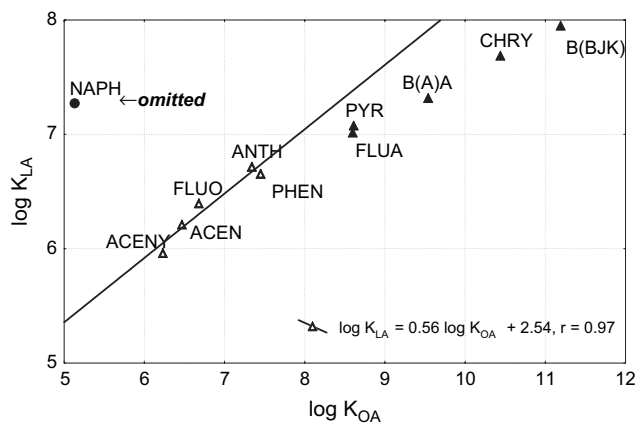


Fig. 1. Relationship between  $\log K_{OA}$  (octanol–air partition coefficient) and  $\log K_{LA}$  (ratio of the average concentration in leaves and the average concentration in air collected at secondary forest sites) of 11 PAHs in Amazon forests. The regression line only includes PAHs with a  $\log K_{OA} < 7.5$ . Naphthalene was omitted from the regression.

reported for *Lolium multiflorum* grass (0.91; Tolls and McLachlan, 1994), *Pinus sylvestris* (0.35–0.52; Ockenden et al., 1998), and pasture (0.32–0.47; Thomas et al., 1998).

The uptake of the compounds with  $\log K_{OA} > 7.5$  was kinetically limited, they did not reach equilibrium and the slope decreased correspondingly with increasing  $\log K_{OA}$  (McLachlan, 1999). Because we did not detect most five- and six-ring PAHs in the air, we could not identify the transition from kinetically limited to particle-bound deposition (Sections 2 and 3). It is therefore also possible that a part of the PAHs with  $\log K_{OA} > 7.5$  reached the plant in particle-bound form besides gaseous deposition. The slopes of the regression lines of  $K_{LA}$  on  $K_{OA}$  (only for PAHs with  $\log K_{OA} \leq 7.5$ ) showed a large variation among the different individual trees ranging from 0.33 to 1.46 ( $r = 0.64$ – $0.97$ ). Different slopes of the regression lines for different tree species may be attributable to differences in leaf morphology and microclimatic conditions (Barber et al., 2004). From the finding that all PAHs except NAPH show a plant–air distribution that fits well into the perception of PAH uptake by plants from air, we conclude that the source of all PAHs except a large part of NAPH is the atmosphere.

The only compound not fitting in this picture is NAPH, showing high concentrations in plant tissue compared to its concentrations in air. To reach the measured NAPH concentrations in leaves by equilibrium partitioning, the air concentrations should be 50 times higher than we have measured. One explanation might be that the NAPH concentrations in air show strong seasonal trends and were low at the time of sampling. The plant concentrations would in this case still reflect higher air concentrations of previous months. Barber et al. (2003) could show in depuration experiments that the loss of polychlorinated biphenyls from leaves after several weeks of gaseous uptake followed a two-stage kinetics. While about 40% of the PCBs were lost within hours, further 25% were lost within four weeks and 35% persisted in the leaves. Barber et al. (2003) did not find a dependence of depuration rates on  $\log K_{OA}$  for the PCBs (range of 8–12). Therefore, it would be possible that elevated NAPH concentrations in the plant samples persisted from previous periods with higher NAPH concentrations in air. However, this would imply even higher contributions of NAPH to the PAH concentrations in the air other than our sampling dates. Therefore, we consider the alternative explanation more likely that there is a biological production of NAPH in external tissues or by organisms of the phyllosphere.

Analytical artifacts, which could also account for the discrepancy between NAPH concentrations in plant tissue and air, can be ruled out; this would either be a loss of NAPH from the XAD-2 resin or a strong

contamination of plant material during the short time span of cutting. The latter was not found for termite nest or dead wood samples, which would have been affected in a similar way. The recovery of NAPH from XAD-2 was similar to that of all other PAHs. A significant chromatographic breakthrough of NAPH on the XAD-2 traps is despite high air temperatures during sampling unlikely, as we observed a breakthrough  $<5\%$  in the laboratory for sampling periods of 7 d and fluxes of  $5 \text{ m}^3 \text{ h}^{-1}$ , which exceeded the sampling periods (2–3 d) and fluxes ( $0.5 \text{ m}^3 \text{ h}^{-1}$ ) in this study considerably.

### 3.4. Dead wood

The sampled dead wood had undergone a considerable degradation, as indicated by an obvious loss of tensile strength and decreased C/N ratios ( $61 \pm 17$ ) as compared to stem wood ( $137 \pm 77$ ) while the OC content did not change (living wood:  $458 \pm 22 \text{ g kg}^{-1}$ ; dead wood:  $457 \pm 30 \text{ g kg}^{-1}$ ).

The  $\sum 21\text{PAHs}$  in dead wood ranged from 192 to  $247 \mu\text{g kg}^{-1}$ . While NAPH was predominant in all dead wood samples with concentrations from 179 to  $246 \mu\text{g kg}^{-1}$ , the concentrations of other PAHs were highly variable and in most samples only a few compounds were detectable (Table 2); PHEN was found in one sample at  $17 \mu\text{g kg}^{-1}$ , PERY in two samples at 2.0 and  $2.4 \mu\text{g kg}^{-1}$ , the  $\sum 18\text{PAHs}$  accounted for 0.9– $11.4 \mu\text{g kg}^{-1}$ . Wilcke et al. (2003) reported in general higher PAH concentrations for dead wood samples of Amazonia, particularly for NAPH. Dead wood sampled in the Cerrado had similar NAPH concentrations as in our Amazonian samples, but higher concentrations of other PAHs (Wilcke et al., 2004).

The concentrations of NAPH were, on average, five times higher in dead wood than in stem wood and the concentrations of ACEN, PYR, and PERY were also significantly higher in dead wood. However, the average  $\sum 18\text{PAHs}$  concentrations were similar in stem wood and dead wood. This indicates an uptake of NAPH and perhaps to a lesser extent pyrogenic PAHs from the atmosphere because of its longer exposure to the atmosphere, or it again points to a biological production, particularly of NAPH. Whether PERY and PHEN, showing both higher concentrations in dead than in stem wood (Table 2), had a biological origin (e.g., input by degrading organisms) cannot be assessed because of the low number of samples in which these compounds were detected.

### 3.5. Litter layer

The  $\sum 21\text{PAHs}$  concentrations in the litter layer ranged from 217 to  $517 \mu\text{g kg}^{-1}$ . Naphthalene was the dominant compound ( $192\text{--}477 \mu\text{g kg}^{-1}$ ), followed by PHEN ( $1.9\text{--}9.7 \mu\text{g kg}^{-1}$ ), CHRY ( $3.3\text{--}5.5 \mu\text{g kg}^{-1}$ ),

B(BJK) ( $2.9\text{--}5.4$ ), and FLUA ( $1.6\text{--}5.1 \mu\text{g kg}^{-1}$ ). Mean concentrations are given in Table 2. In contrast to this, litter layers of a temperate forest in Germany receiving exclusively pyrogenic PAHs (Krauss et al., 2000) and showing a composition of the PAH mixture which is typical for temperate organic layers (Wilcke, 2000), had lower NAPH concentrations, but approximately 10–50 times higher concentrations of all other PAHs (Fig. 2). If NAPH was omitted, there was a close correlation between the concentrations of individual PAHs in the Amazonian and temperate litter layers ( $r = 0.85$ ) indicating that the PAH mixtures were similar except the high abundance of NAPH at the tropical site. This strongly indicates that the PAHs in litter layers from Amazonia consisted of a mixture of pyrogenic PAHs and a separate source of NAPH, which is likely biological.

To assess transformation processes and possible additional PAH sources in the litter layer, we estimated the PAH concentrations in litter fall from literature values of litter composition and compared them with the PAH concentrations in the living plant tissues. For our calculations we used litter fall data from Rodrigues et al. (2001) who reported that at a primary forest stand close to our study area litter fall consisted of 78.4% leaves, 15.7% woody matter, and 5.9% flowers and fruits. At a secondary forest site of comparable age (14 years) and species composition as our secondary forests, 81.7% of the litter fall were leaves, 10.5% woody matter, and 7.8% flowers and fruits (Rodrigues et al., 2001). Similar

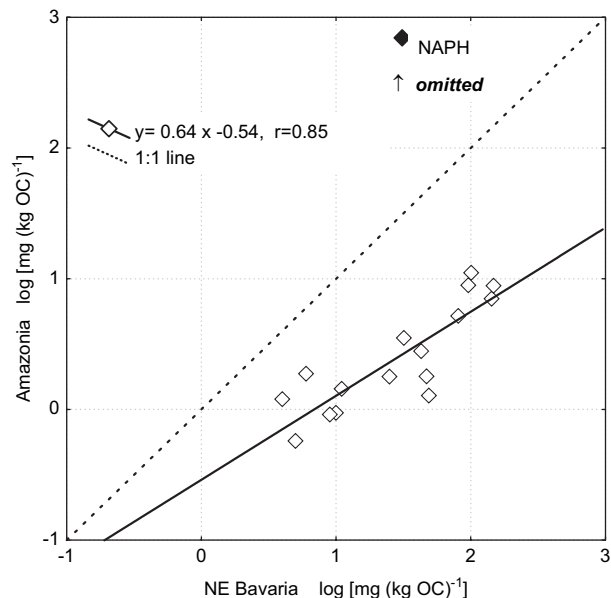


Fig. 2. Relationship between the OC-normalized concentrations of individual PAHs in litter layers of Amazon forests (average of 4 sites) and in litter layers of temperate forests in northeastern Bavaria considered as representative for a variety of temperate forests (Krauss et al., 2000; average of 18 sites). Naphthalene was omitted from the regression.

findings have been reported by Martius et al. (in press) for primary and secondary forests near Manaus where the litter fall in primary and secondary forest and in polycultures consisted of 67–82% of leaves, 8–14% of fine wood, 0.1–2.8% of coarse wood, and 3–9% of fine matter (including flowers and seeds) indicating that the values used for our PAH flux estimation are reasonable. To calculate PAH concentrations in the litter fall, we assumed that the concentrations in woody matter and flowers/fruits were the same as in twigs.

The PAH concentrations and the composition of the PAH mixture in the litter layer and the values estimated for the litter fall were in general similar. Additionally, we did not detect significant differences in the composition of the PAH mixture between leaves or twigs and litter layers. Thus, the composition of the PAH mixture and the PAH concentrations in the litter layer resembled those in fresh litter fall, indicating that no significant transformation of the PAHs occurred during the short lifetime of the thin litter layer. There were no hints to additional PAH sources for the litter layer.

### 3.6. Mineral topsoil

The PAH concentrations of the mineral topsoil samples ( $\sum 21\text{PAHs}$ :  $16\text{--}38\ \mu\text{g kg}^{-1}$ ) were at the lower end of the range in tropical topsoils ( $7\text{--}397\ \mu\text{g kg}^{-1}$  for the sum of 16 PAHs; Wilcke, 2000). Naphthalene was by far the most abundant compound ( $15\text{--}31\ \mu\text{g kg}^{-1}$ , Table 2). The concentrations of all other PAHs in general did not exceed  $0.5\ \mu\text{g kg}^{-1}$  and were considerably lower than those in temperate forest topsoils of northeastern Bavaria (Krauss et al., 2000).

To reveal the fate of PAHs during organic matter transformation from litter to mineral soil, we calculated enrichment factors by dividing the average OC-normalized concentrations of individual PAHs in mineral soil by those in the litter layer (Krauss et al., 2000). For all PAHs, the enrichment factors were  $\geq 1$  (Fig. 3), indicating that the PAHs entering the soil together with organic matter from the litter layer were accumulated relative to less recalcitrant organic compounds. The enrichment factors were not related to compound properties such as the octanol–water partition coefficient ( $K_{OW}$ ), which was the case for temperate forest soils (Krauss et al., 2000).

The enrichment factor of PERY was four times higher than that of all other PAHs suggesting a formation of this compound in the mineral soil. The studied topsoils revealed no macroscopic features of temporarily reducing conditions. Nevertheless, anoxic microsites may develop during the rainy season (Bundt et al., 1997) facilitating formation of PERY. Furthermore, Wilcke et al. (2000, 2003) have shown that termites or associated organisms might produce PERY and introduce it to the soil.

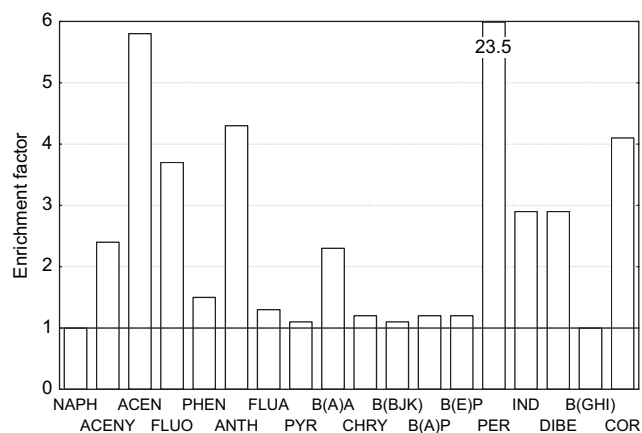


Fig. 3. Average enrichment factors (=OC-normalized concentration in topsoil divided by OC-normalized concentration in litter layer) in Amazon forests.

### 3.7. Termite nests

The concentrations of NAPH, PHEN, PERY, and  $\sum 18\text{PAHs}$  were at the lower end of the range reported by Wilcke et al. (2003) for *Nasutitermes* nests of Amazonia (NAPH:  $111\text{--}3600$ ; PHEN:  $8\text{--}153$ ; PERY:  $4\text{--}600$ ;  $\sum 18\text{PAHs}$ :  $6\text{--}154\ \mu\text{g kg}^{-1}$ ). The reason for this difference is not clear. For pyrogenic PAHs, a contamination during sample drying as done by Wilcke et al. (2003) might have occurred, which would, however, not account for the high PERY concentrations. A higher input of pyrogenic PAHs in exposed parts of the nests is another possible explanation, probably due to a more intensive forest fire activity prior to the sampling campaign of Wilcke et al. (2003). It followed the 1997 El Niño event associated with extensive vegetation fires in the Amazon basin. However, this would not explain high NAPH or PHEN concentrations of interior parts. From the large variation in PAH concentrations among different *Nasutitermes* nests of Amazonia and other ecosystems of Brazil (Wilcke et al., 2003) we conclude that there is a strong regional or seasonal variation and/or differences among different *Nasutitermes* species, which were not studied so far.

Naphthalene and PERY were by far the most abundant individual PAHs in all compartments of *Nasutitermes* nests, followed by PHEN and all other PAHs (Table 2). The concentrations of NAPH were similar in all compartments, on average about  $100\ \mu\text{g kg}^{-1}$ , and those of PERY were lowest in the nursery and similarly high in all other compartments. The concentrations of PHEN and the  $\sum 18\text{PAHs}$ , as well as of some individual pyrogenic PAHs were significantly higher in the outer wall and the gallery than in the inner wall and the nursery.

Differences in organic matter composition cannot account for a different PAH accumulation capacity of

the compartments, as the whole nest was built from digested dead or living wood (Donovan et al., 2001; Amelung et al., 2002) and did not show significant differences in OC concentrations or C/N ratios (Table 2).

The higher concentrations of PHEN and the other 18 PAHs in gallery and outer wall clearly indicate an input from atmospheric deposition, as only these compartments are exposed to the atmosphere. If this was true, we would expect that the distribution of PAHs between air and exterior parts nests of *Nasutitermes* is similar to that between air and exterior parts of plants. To test this hypothesis, we calculated distribution coefficients outer wall – air ( $K_{OWA}$ ) and gallery – air ( $K_{GA}$ ) for all PAHs in the same way as for the leaves and plotted them against  $\log K_{OA}$  (shown for the outer wall in Fig. 4). The  $\log K_{OA}$ – $\log K_{OWA}$  and  $\log K_{OA}$ – $\log K_{GA}$  plots showed an almost identical pattern to that of  $\log K_{OA}$  versus  $\log K_{PA}$ . As for the plants, NAPH concentrations in outer wall and gallery were again higher than expected from equilibrium partitioning with air. When NAPH was omitted, the regression lines of  $K_{OWA}$  and  $K_{GA}$  on  $K_{OA}$  for  $K_{OA} \leq 7.5$  were given by Eqs. 4 and 5:

$$\log K_{OWA} = 0.66 \log K_{OA} + 1.73, \quad r = 0.88 \quad (4)$$

$$\log K_{GA} = 0.61 \log K_{OA} + 1.89, \quad r = 0.76 \quad (5)$$

For nursery and inner wall, in contrast, there were no correlations between  $K_{OA}$  and the distribution coefficients for  $\log K_{OA} \leq 7.5$  ( $r = 0.06$  and  $-0.13$ , respectively). These findings indicate that the outer compartments of the *Nasutitermes* nests received PAHs by gaseous deposition from the atmosphere. A subsequent redistribution of deposition-derived PAHs among the whole nest could be possible for volatile

PAHs, but not for the higher-molecular weight compounds. Therefore, the wood *Nasutitermes* is feeding on (Amelung et al., 2002), is likely to be the source of PAHs for the interior compartments, i.e. inner wall and nursery.

Inner wall and nursery had, on average, lower concentrations of NAPH, PHEN, and the pyrogenic PAHs than dead wood (Table 2); due to the large variation and the partly low number of observations the differences were only significant for NAPH, FLUA, and B(A)P. Compared with stem wood, the concentrations of PHEN and the pyrogenic PAHs were also lower in nursery and inner wall, but those of NAPH were significantly higher. When we assume that *Nasutitermes* feeds on both, dead and living wood, it seems likely that PHEN, NAPH, and the other pyrogenic PAHs are introduced into the nest with digested wood. The lower concentrations of these compounds in nests than in the stem and dead wood may indicate that additional input by deposition from the atmosphere was lacking or, that a certain percentage of these PAHs was degraded during digestion by *Nasutitermes* or subsequently in the nest. The PERY concentrations, however, were significantly higher in all nest compartments than in dead or living wood (Table 2). Apparently, PERY was produced in the *Nasutitermes* nest. This assumption corroborates earlier findings of Wilcke et al. (2000, 2003). The PERY concentration in the inner nest wall suggests that the defence area of the soldiers rather than the nursery (inhabited mainly by termite workers) is the location of PERY biosynthesis.

#### 4. Conclusions

The studied Amazonian rain forest had a lower PAH burden than many forest ecosystems in the temperate zone. From the distribution of PAHs among different compartments, and the similarity of the PAH patterns to those in temperate ecosystems, if NAPH, PERY, and partly also PHEN are disregarded, it is likely that all PAHs except for NAPH, PERY, and PHEN are entirely derived from biomass or fossil fuel combustion and are distributed in the environment via the atmosphere.

Naphthalene is by far the most abundant individual PAH in the whole ecosystem. The NAPH concentration in leaves was not in equilibrium with that in the air, pointing at additional NAPH sources to burning of biomass and fossil fuel. However, this additional source could not be clearly determined. Perylene shows elevated concentrations in the mineral soil and *Nasutitermes* nests where the concentrations of pyrogenic PAHs are low. We consider this as strong evidence for a production of PERY in these compartments. For PHEN, a biosynthesis in *V. cayennensis* seems possible due to the relatively high abundance in bark and twigs,

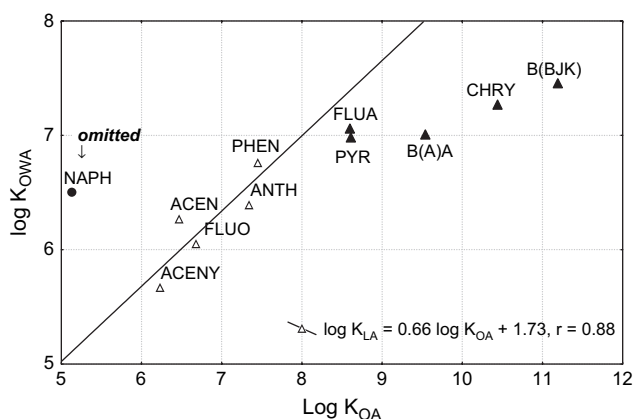


Fig. 4. Relationship between  $\log K_{OA}$  and  $\log K_{OWA}$  (ratio of the average concentration in outer walls of *Nasutitermes* nests and the average concentration in air) of 11 PAHs in Amazon forests. The regression line only includes PAHs with a  $\log K_{OA} < 7.5$ . Naphthalene was omitted from the regression.

but the contribution to the total PHEN storage in the rain forest remains to be elucidated.

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