PAHs in Indoor and Outdoor Air from Decentralized Heating Energy Production: Comparison of Active and Passive Sampling

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Spatial and temporal variation of vapor- and particle-phase polycyclic aromatic hydrocarbons (PAHs) was determined in six urban and sub-urban locations in Kaunas, Lithuania during heating and non heating seasons. Two different sampling methodologies were used: passive (based on semipermeable membrane device, SPMD) and active (based on collection on filter and sorption). Sixteen priority PAHs as well as methylated PAHs were quantified in the collected samples. The sampled total amount of 16 PAHs investigated in SPMDs ranged from 10–138 ng/day outdoors, from 5–59 ng/day indoors during the winter sampling campaign. In summer these amounts varied from 11–19 ng/day outdoors and from 19–27 ng/day indoors. The total concentrations of vapor and particle-phase PAH in winter in actively taken samples varied from 49–286 ng/m³ outdoors and from 28–83 ng/m³ indoors. Seasonal differences as well as the influence of the fuel burning for domestic heating purposes on the PAH concentration outdoors were well reflected by the data obtained using the SPMD methodology.

Key Words: active/passive sampling, indoor/outdoor air pollution, PAH, SPMD

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) in the ambient air exist in a vapor phase or particle phase, depending on atmospheric conditions (ambient temperature, relative humidity, etc.), the nature (i.e., origin and properties) of the aerosol, and the properties of an individual PAH (1). In general, low-weight PAHs (with two, three, or four rings) are more volatile and exist mainly in the gas phase. Although the lighter PAH compounds are considered to be less toxic, they are able to react with other pollutants such as ozone, nitrogen oxides, and sulphur dioxide, to form diones, nitro- and dinitro-PAHs, and sulphuric acids, respectively, whose toxicity may be more significant (2).

In most urban, residential, and rural areas relying on residential and commercial heating, air pollution sources show a significant seasonality during the year (e.g., a relative enhancement during a cold winter). This effect is particularly pronounced when the fuels used for heating exhibit high PAH emissions (1,3). Wood combustion, especially in residential heating, is a significant PAH source in urban areas, especially in Northern Europe (4–8). Lithuania is also attributed to Northern Europe, with regards that individual house districts are mainly dominated by individual boilers. In vast majority of them various sorts of solid fuel is being burned, such as wood, peat, and coal. Burning of the calorific fraction of solid waste, although illegal, may also be the case (9).

There are numerous comparative studies reporting actively sampled vapor- and particle-phase PAH concentrations worldwide. In most cases, high volume sampling is employed, supplemented with glass fiber filters for particle collection and polyurethane foam (PUF) samplers (10–15) or XAD sorbent tubes (16) for sampling of vapor-phase PAHs. The use of semipermeable membrane devices (SPMDs) for air studies has not been so widespread. SPMDs were developed mainly for water sampling of organic pollutants. To use SPMDs for quantitative measurement of the air concentration, the sampling rate (R_S) or uptake rate constant (k_ua), as well as the SPMD-air partition coefficient (K_SA) have to be known. In water, the R_S of SPMDs is generally pre-calibrated in the laboratory at given temperatures. Calibrating the SPMDs prior to use requires tests of many different sampling conditions for a number of compounds. In addition, the field sampling conditions can be difficult to replicate and maintain over extended periods, making it complicated to generate pre-calibrated R_S values that reflect the true sampling situation (17). Instead, air pollution data obtained by SPMDs have been mostly interpreted by comparing the difference between sites in the amounts sequestered by the SPMD presenting data in ng/SPMD*day (4,5,15,18).

Several earlier studies on PAH distributions in Kaunas were mainly limited to the estimation of particle-phase concentrations (19,20). Average PAH concentrations at various locations in winter ranged between 32.7 and 75.1 ng/m³, which are higher than in most European towns (19). Krugly et al.
reported relatively high PAH levels in the vicinity of schools in Kaunas (3). The concentration of PAHs in the PM$_{2.5}$ fraction (Particles, smaller than 2.5 $\mu$m in diameter) ranged from 20.3–131.1 ng/m$^3$, while the vapor phase concentration of PAHs ranged from 67.2–372.5 ng/m$^3$. Kliucininkas et al. reported the concentration of PAHs in PM$_{2.5}$ fraction at indoor and outdoor sites in six urban homes in Kaunas (9). The outdoor PAH concentrations in the winter measurement campaign were higher (from 20.9–89.3 ng/m$^3$) compared to indoor measurements (from 5.1–60.0 ng/m$^3$). In this study, the effect of residential fuel combustion on local air quality was studied by measuring vapor- and particle-phase PAHs in the air in residential districts that uses wood and other sorts of solid fuel for heating and are located away from major traffic lanes.

**METHODOLOGY**

**Sampling Locations**

Six sampling locations were chosen in residential areas of Kaunas city (population 311,000; total area 157 km$^2$), Lithuania (Table 1). More detailed description of sampling sites is given by Kliucininkas et al. (9).

**Sampling Techniques**

Sampling was carried out during period of January/March and August/September, 2013.

During the cold season campaign (further referred to as “winter”), passive and active sampling outdoors and indoors was conducted at all six locations while during the summer campaign passive samplers were deployed at four locations (L2, L3, L5, L6), and active sampling was done at two locations (L2, L5).

The passive sampling employed SPMDs for gaseous phase PAH sampling. SPMDs were deployed for 28 days in each location, thus representing a long term average PAH levels.

The semipermeable membrane (ExposMeter AB, Sweden) is composed of a low-density non porous polyethylene (LDPE) tube containing triolein (IUPAC name - 2,3-Bis[[\(Z\)-octadec-9-enoyl]oxy]propyl \(Z\)-octadec-9-enoate). The ratio of polyethylene to triolein is 4:1. The membrane is 91.4 cm long and 2.5 cm wide, while the LDPE polymer is 75–90 $\mu$m thick. The nonporous membrane allows the nonpolar chemicals to pass through to the lipid where the chemicals are concentrated. Larger molecules having >600 Da and materials such as particulate matter and microorganisms are excluded (21).

SPMDs were attached to stainless steel holders (so called “spiders”). Some spiders were further placed into stainless steel “canister” type samplers. The samplers were designed to ensure sufficient air flow and to protect membranes.
| No. | Type of location | Type of ventilation | Active sampling measurement period | Passive sampling measurement period | House density, house/km² | Type of heating | Type of windows** | Outdoor temperature (passive sampl. period), °C weekly | Wind speed, m/s | Relative humidity,% |
|-----|------------------|---------------------|-----------------------------------|-----------------------------------|--------------------------|----------------|-----------------|-----------------------------------------------|--------------|-----------------|
| L1  | Urban            | Natural             | 01.20 - 01.25                     | 01.20 - 02.16                     | 1000–1400                | S-B, NG       | P, DP           | -13                                | 1            | 87              |
| L2  | Urban            | Natural             | 01.27 - 02.01                     | 01.20 - 02.16                     | 1000–1400                | S-B, NG       | W, D            | -4                                 | 4            | 91              |
| L3  | Sub-urban        | Natural             | 08.26 – 08.30                     | 08.26 – 09.22                     | 16                       | W, T          | 0               | 16                                 | 0.2          | 92              |
| L4  | Sub-urban        | Natural             | 02.17 - 02.22                     | 02.17 - 03.16                     | < 400                    | HP            | W, DP           | -4                                 | 2            | 86              |
| L5  | Urban            | Natural             | 02.24 - 03.01                     | 02.17 - 03.16                     | 600–1000                 | S-B, W        | P, T            | 0                                  | 3            | 76              |
| L6  | Urban            | Natural             | 03.03 - 03.08                     | 02.17 - 03.16                     | > 1400                   | S-B, NG       | P, T            | -1                                 | 3            | 67              |

Examined buildings:

* Type of heating: S-B - stove-boiler, HP - heat pump, W - wood, WP - wood pellets, NG - natural gas.

** Type of windows: P - plastic, W - wooden, D - double pane glass, T - triplex pane glass; DP - double pane glass packs.
from the UV light. Aiming to estimate the influence of PAH photodegradation in the membranes indoors, naked membranes were co-located with protected membranes. The samplers were deployed at two meter height avoiding direct sunlight.

The active sampling was used to collect both particle and vapor-phase PAHs. PM$_{2.5}$ fraction aerosol particles were collected using PM$_{2.5}$ cyclone sampler (URG Corp., USA), at a flow rate of 16.7 l/min, on a glass fiber pre-baked filters (GF/A, Whatman International Ltd., UK). The gaseous phase PAHs were sampled using the XAD-2 sorbent tubes (Cat. No. 226–30–06, SKC Inc., USA), at an air flow rate of 2 l/min. Five daily (24 h) samples were taken at each location.

**Analytical Methods**

Further description of the analysis techniques are divided between the SPMD analysis (a) and the filter-sorbent analysis (b).

**Materials**

(a) N-hexane, 96% for gas chromatography (GC) residue analysis (Scharlau, Spain), n-heptane, Pestanal (Fluka, Switzerland). The mixtures of native 16 US EPA PAHs (Analytika, Czech Republic), $^{13}$C 16 US EPA PAH Cocktail (CIL, USA), and PAH/Dibenzothiophenes mixture (Chiron, Norway) were utilized.

(b) N-hexane, GC purity for pesticide residue analysis (34484, Fluka, Switzerland) and dichloromethane, GC purity for pesticide residue analysis (34488, Fluka, Switzerland) were used for extraction purposes. The mixtures of native PAHs (QTM PAH Mix, 47930-U, Supelco, Sigma-Aldrich Co. USA) and deuterated PAHs (PAH Mix 9, Dr. Ehrenstorfer GmbH, Germany) were used for standardization of samples. Octachlorororonaphthalene (442725, Supelco, Sigma-Aldrich Co. USA) was used for determination of recoveries of internal standard compounds. Silica gel 6 chromatographic (70–230 mesh, Eurochemicals, Slovakia) and anhydrous sodium sulphate (Eurochemicals, Slovakia) were used for sample cleaning purposes.

**Sample Preparation**

(a) The exposed membranes were dialyzed with two 250 ml portions of hexane (more detailed procedure is presented in Alvarez et al. (22). After the evaporation to 2–3 ml, the final volume of each dialysate was adjusted with n-heptane to 5 ml. 100 µl aliquots were mixed with $^{13}$C internal standards (2.5 ng per sample) in micro inserts of chromatographic vials, shortly sonicated, and forwarded for the analysis.
(b) The filters from PM$_{2.5}$ aerodynamic sampler and sorbents were extracted in an ultrasonic bath for 10 min with 4 ml of dichloromethane. An internal standard (deuterated PAHs, 50 ng per sample) was added to the samples before the extraction. Samples were concentrated by the nitrogen flow concentrator to 0.5 ml. The samples were cleaned in a column with a silica gel and anhydrous sodium sulphate, utilizing dichloromethane and hexane mixture (50/50%w) as an eluent to 4 ml of volume. After an additional concentration by nitrogen flow concentrator to 0.2 ml, the liquid was mixed with octachloronaphthalene (50 ng per sample) and transferred to a chromatographic vial with a micro insert.

**Instrumentation**

The measurements were carried out using two GC/MS systems:

(a) The dx-TOF (ALMSCO, UK), coupled with the GC (Trace GC Ultra, Thermo Fisher Science, USA), equipped with autosampler (Combi-xt PAL, CTC Analytics AG, Switzerland), and the column (Rxi-5ms, Restek Inc., USA). The injection volume was 1 µl, splitless mode, temperature of injector 300°C, carrier gas (helium) flow 1.4 ml/min. The temperature program was set to from 70°C (2 min), flowed by 18°C/min to 270°C, and 5°C/min to 316°C (2 min). The data acquisition was set from 100–300 m/z at 1 Hz, the temperatures of ion source and transfer line were 300°C and 320°C, respectively, the electron energy was 70 eV.

(b) The GC/MS system (GCMS-QP2010 Ultra, Shimadzu Corp., Japan) with a capillary column Rxi-5ms (Restek Inc., USA) operating according to a single ion monitoring method was used for the quantitative analysis of the extracted PAHs. The injection volume was 2 µl, splitless mode, temperature of injector - 250°C, carrier gas (helium) flow - 0.58 ml/min. The temperature program started at 50°C (3 min), followed by 10°C/min to 300°C (10 min). The MS scanning was performed from 30–450 m/z.

**Analysis**

(a) 16 US EPA PAHs (ATSDR, 2005) and methyl PAHs (1-methylnaphtalene, 2-methylnaphthalene, 1,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, 2-methylphenanthrene, 2,4-dimethylphenanthrene, 1,2,6-trimethylphenanthrene, 1,2,8-trimethylphenanthrene, dibenzothiophene, 2-methylbenzothiophene, 2,8-dimethyldibenzothiophene, 2,4,7-trimethyldibenzothiophene, 1-methylfluoranthene, 1-methylchrysene, 6-ethylchrysene) were quantified. Five performance reference compounds (Acenaphtene D10, Fluorene D10, Phenanthrene D10, Chrysene D12, Benzo(e)pyrene D12) were quantified.

(b) 16 US EPA PAHs were quantified. Due to analytical problems naphthalene was excluded. Benzo(b)fluoranthene was not detected.
Quality Control

Passive sampling. The sampling, sample preparation, and analysis were performed according to the good laboratory management practice. The membranes were shipped packed separately in air-tight containers to avoid contamination before and after the exposure. Prior to analysis containers were stored frozen at $-25^\circ$C. Membranes in duplicates (on two sampling sites) and two transport blanks were deployed in each sampling campaign, making it 10% of total number of samples taken. The analysis of blank samples has not shown any contamination.

Active sampling. Gas analyzer was calibrated by the manufacturer and checked by the metrological centre. One field blank sample and one laboratory blank sample were analyzed for every 10 samples. In the analyzed blank samples the amount of any given compound has not exceeded the lowest point of the calibration curve. Laboratory blanks, field blanks and solvent samples have not shown contamination of target compounds. The detection limits of each target compound were estimated as three standard deviations of base (noise) line. The testing of the breakthrough of compounds through the adsorbent was performed during sampling in field conditions. None of target compound was detected in the second- or third-stage-tube of adsorbent. 10% of duplicate samples were taken for quality control. The difference of concentration was up to 18% and was found to be not statistically significant.

Data Analysis

Results of analyses were statistically processed using SPSS 12 (IBM Corp., USA) and Origin 9 (OriginLab Corp., USA) software. Descriptive statistics were used for the representation of average PM, PAH, gaseous pollutant levels (median, 25th and 75th percentiles, minimum and maximum values). Spearman ranking correlation was used for the determination of a relationship between two parameters. The seasonal variation as well as differences between sampling methods were assessed using the nonparametric Mann-Whitney test, at a significance level of 0.05.

The levels of PAHs determined by the passive method have been calculated to the accumulated mass per day of sampling (ng/day). For a while, the calibration data of SPMDs in air were limited to the field-calibrated $R_S$ of polychlorinated biphenyls (PCBs) (23,24). Cranor et al. (25) significantly expanded kinetic data for SPMD air data by estimating uptake rate constants ($k_{uA}$) and SPMD-air partition coefficients ($K_{SA}$) for several classes of organic pollutants including 16 US EPA priority PAHs (25). This allows calculation of PAH concentrations in the air based on the concentration in SPMDs. However, the $K_{SA}$ is temperature dependent and should only be considered as valid within a very
narrow temperature range, 20–25°C (25). For this reason in this study SPMD data were interpreted as the amounts sequestered by the SPMD/day.

Performance reference compounds (PRCs) were analyzed in this study but the re-calculation of SPMD data was not done due to the lack of data to support application of such recalculation for air samples. In water sampling, native naphthalene certainly reaches equilibrium after 28 days, but for air sampling there is no evidence that the same happens. In this study we compared sites and used similar sampling time for all sites in order to assess spatial variability. For this comparison, the compounds reaching curve linear phase of uptake is still possible. In addition, most previous studies have not used PRCs for calculating air concentrations. It made the comparison simpler as well as more extensive. In future, in order to use PRC concept for air sampling, more data on the PRC behavior in sub-zero Celsius air temperatures is needed to be more convinced about the re-calculations.

RESULTS AND DISCUSSION

Vapor PAH Levels as Determined by a Passive Sampling

The total amount of 16 PAHs investigated in SPMDs ranged from 10 to 138 ng/day outdoors, from 5–59 ng/day indoors in protected SPMDs and from 4–44 ng/day indoors in naked SPMDs during winter sampling campaign (Figure 1). In summer the levels were generally lower and constituted from 11–19 ng/day outdoors and from 19–27 ng/day indoors protected in sampler, and from 14–19 ng/day in indoor naked SPMDs.

Seasonal differences as well as the influence of the fuel burning for domestic heating purposes on the concentration of PAHs are well reflected. PAH concentrations in SPMDs deployed outdoors in winter were from 1.7–7.6 times higher than the respective concentration in summer, the difference being statistically significant at $p < 0.05$. The highest difference in winter was found at L3 where burning of wood and other solid fuels prevailed in the surroundings. In winter the ratio of the highest and the lowest concentration of PAHs in SPMDs deployed outdoors were 13.8 while in summer this ratio was only 1.7. The difference between amounts of PAHs indoors in winter and summer did not appear to be statistically significant ($p>0.05$). However, at all summer locations levels of PAHs were higher indoors than outdoors. This indicates domestic fuel burning, cooking and other activities as a source of PAHs indoors, in addition to the penetration of PAHs from the outdoor air.

Climatic factors have to be taken into consideration for the adequate interpretation of gaseous PAH sampling by SPMDs. Temperature ranges exhibited by environmental systems of northern latitudes can affect the vapor pressure and Henry’s law constants (H, Pa·m$^3$/mol) of individual compounds by as
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Figure 1: Total vapor-phase PAH concentrations indoors and outdoors in winter (left) and in summer (right) as sampled by passive samplers. The box-and-whisker plots represent averaged data across all sampling locations.

much as an order of magnitude. As a result, the temperature has a significant influence on partition coefficients that delineate the distribution of chemicals among the gas phase and airborne particulates. The uptake rate to the semipermeable membrane is also temperature dependent. Ockenden et al. estimated that sampling rates for PCBs were approximately four times higher in winter than in summer in the UK (23). Cicenaite et al. estimated equilibrium coefficients between air and SPMDs for naphthalene (Naph), o-chlorophenol (o-CPh) and p-ichlorobenzene (p-DCB) over a range of temperatures (-16, -4, 22, and 40°C) (26). The duration until the equilibrium in SPMDs was inversely proportional to the temperature. Seasonal differences in the wind speed during the SPMD exposures may also affect the SPMD air sampling rate. Higher wind speeds in winter may mean that the SPMDs experienced a larger volume of air (23). For indoor environments, variation in temperature and air flow may be considered insignificant.

Outdoor PAH levels estimated in this study are similar to those found in SPMDs deployed outdoors in Sweden and Poland in 2000 (4), as well as to Bangkok (Thailand) as reported by Söderström et al. (18). In Bangkok, the total PAHs in SPMDs (131–134 ng/day) were reported at sites with high traffic intensity, while at a rural area the amount averaged to 17 ng/day, which is close to the lowest PAH concentration in Kaunas of 10 ng/day. Strandberg et al. reported results from SPMDs deployed indoors inside of 15 single-family
Swedish houses located in an area where domestic wood burning is widespread (5). They reported the total PAH amounts in SPMDs 30–350 ng/day in wood burning houses and 30–60 ng/day in non wood burning houses. Interestingly, in our study these amounts were lower – 4–44 ng/day. Amounts of methylated PAHs in this study were also generally lower than in Sweden (5). This may be due to the fact that our sampling campaign extended to the warmer period of the cold season, while in the areas of lower ambient temperatures a more intensive combustion of fuels may cause higher concentrations of combustion PAHs in the ambient air.

The effect of SPMD sampling techniques. There are several factors to consider when using SPMDs as outdoor and indoor air samplers. Sampling conditions in outdoor air measurements may differ significantly leading to a bias in data. A high wind speed affects the membrane and might reduce the thickness of a boundary layer and hence increase the uptake. In case of outdoor deployment it is important to provide sheltering from the wind, but the air circulation around the sampler must be sufficient to ensure that uptake rates are not reduced (17). In indoor air studies, however, a slow air movement around the membrane may cause the increase in the thickness of a boundary layer, especially if the SPMD is located in a protective sampler. At the same time, if SPMDs are exposed naked (not protected by any sampler), a concern related to the photo-degradation appears. The latter may not be of a major concern if SPMDs are deployed in places not affected by the direct sunlight (5).

The average ratios of PAHs in naked SPMDs and SPMDs deployed in a sampler for unsubstituted PAHs varied from 0.7–0.9 in winter and where equal 0.7 at all 4 locations investigated in summer. Lower levels of PAHs were generally found in naked SPMDs, most likely due to the photodegradation of susceptible species. A more intensive sunlight might have caused a more intensive photodegradation and consequently, a lower ratio during the summer campaign. However, a statistically significant difference (p < 0.05) observed for unsubstituted PAHs in winter and summer only. The averaged difference for methylated PAHs in winter and summer was not statistically significant most likely due to the higher photostability of methylated species. Information about photochemical properties of methylated PAHs is limited. Cvrckova et al. investigated the kinetics of photodegradation of two parent PAHs (anthracene and chrysene) and their methyl-derivatives during exposition to the UV irradiation in isooctane solutions (27). The authors concluded that the stability of methyl-derivatives was slightly better in comparison with parent PAHs.
Vapor- and Particle-Phase PAH Levels as Determined by an Active Sampling

The highest PAH concentration (sum of vapor and particle phase) value of 287 ng/m³ was registered at L1 in winter, while the lowest summer time value was reached in L5 (18.2 ng/m³; see Figure 2). Atmospheric mixing conditions at L1 were unfavourable for pollutant dispersion with very low wind speed, complemented by the lowest weekly temperature. Presumably, domestic fuel burning was more intensive which is reflected by the elevated PAH levels. However, the variation among PAH concentrations at the other five locations was low, including L4, which was the least densely populated with dominating gas boilers in the surroundings. The concentrations of individual PAHs from active sampling in indoor and outdoor air at the six sampling locations are presented in supplemented material (Table SM1, see Supplemental Data).

The vapor-phase PAH concentrations exceeded particle-phase concentrations on average by 3–4 times, both in winter and in summer. Low molecular weight compounds dominated, with the highest values observed for fluorine and phenanthrene. The distribution pattern of individual PAH compounds at L3 is demonstrated in Figure 3 and is very similar to observation by other authors (10,13,15).

Generally, the distribution of total concentrations of vapor and particle-phase PAHs at six locations obtained by active sampling differed from the data obtained by the passive sampling (Figure 2 vs. Figure 1). Air pollution data obtained by the passive sampling was more representative of the presumed pollution, based the housing density and types of fuels used in the area. This may mainly be attributed to the sampling duration, which was different for both techniques also to the absence of naphthalene in active sampling data The SPMD data represented the average for 28 days, while the data of filter based sampling represented weekly (5 days of 24-h samples) variation. Weekly
measurement campaigns do provide higher time resolution, but suffer from a quite episodic approach to the characterization of the air pollution in a particular area, while longer active measurement campaigns in many cases might be too costly. In addition, active measurements indoors are complicated due to noise generated by vacuum pumps, causing complaints from the residents.

Table 2 presents the comparison of actively sampled vapor- and particle-phase concentrations of PAHs at various locations worldwide and also provides a comparison of PAH concentrations for a passive sampling. Concentrations of vapor-phase PAHs measured by active sampling ranged from 37.8–208.2 ng/m$^3$ in winter and 15.2–16.4 ng/m$^3$ in summer. Levels of particle-phase PAHs in winter were noticeably higher than in most places in Europe but were lower compared to locations in China.

**Diagnostic ratios of particulate- and vapor-phase PAHs.** The method of diagnostic ratios calculates binary ratios of two PAHs that are frequently found in emissions (30). Certain values of these ratios indicate particular sources of PAHs. Diagnostic ratios of the total concentration of two and three ring PAHs (low molecular weight, LMW) to four- to six-ring PAHs (high molecular weight, HMW) indicate whether the origin of PAHs is pyrogenic or petrogenic. In case of LMW/HMW > 1, a possible source of PAHs is petrogenic; otherwise the source may be considered as pyrogenic (31–33).

Most commonly used diagnostic ratios (29), as summarized in Table 3, show dominance of pyrogenic sources at most locations investigated. The data demonstrates the dominance of low molecular compounds over high molecular compounds both outdoors and indoors. It should be noted that efficiency of diagnostic ratios as a source identification tool has been questioned by
Table 2: Comparison of actively sampled concentration of vapor- and particle-phase total 16 US EPA PAHs at sampling locations, ng/m$^3$

| Location          | Kaunas | Birmingham, UK | Flanders, Belgium | Vicinity of Athens, Greece | Dalian, China | Xiaolongmen (background) | Gubeikou (rural) | Donghe (rural) | Beijing, (urban) | Beijing, China | Singapore, Singapore |
|-------------------|--------|----------------|-------------------|----------------------------|--------------|---------------------------|------------------|---------------|------------------|----------------|-------------------|
| Source            | this study | Alam et al. (16) | Ravindra et al. (10) | Vasilakos et al. (11) | Zhu et al. (15) | Wang et al. (14) | | | Ma et al. (13) | He et al. (12) |
| Sampling method   | XAD | XAD-4 winter | PUF high vol. all seasons | PUF high vol. winter | PUF high vol. all seasons | Active (PUF high vol.) all seasons | | | Active (PUF high vol.) |
| Vapor-phase       | winter summer | 38–210$^{a,b}$ | 16–110 | 24–26 | 41–155 | 19–85 | 88–356 | 291–1268 | 128–757 | 119 | 36 |
| concentration     | | PM$_{2.5}$ | PM$_{2.5}$ | PM$_{2.5}$ | TSP | TSP | PM$_{10}$ | TSP |
| Particle phase    | | 9–60$^b$ | 2–3$^b$ | 4–9 | 1–9 | 3 | 3–91 | 104 | 2–252 | 12.9–349 | 3.2–223 | 104 |
| concentration     | | PM$_{2.5}$ | PM$_{2.5}$ | TSP | TSP | TSP | PM$_{10}$ | TSP |

$^a$Due to analytical problems naphthalene was excluded.

$^b$Benzo(b)fluoranthene was not detected.
Table 3: Diagnostic ratios calculated from active sampling of vapor- and particle-phase total US EPA 16 PAHs concentrations during winter sampling campaign

| Diagnostic ratio                          | L1 W Out | L1 W In | L2 W Out | L2 W In | L3 W Out | L3 W In | L4 W Out | L4 W In | L5 W Out | L5 W In | L6 W Out | L6 W In | Petrogenic Katsayannis et al. (28) | Pyrogenic Rogge at al. (29) | Grass/coal/wood combust. | Non-traffic comb. | Traffic comb. |
|------------------------------------------|----------|---------|----------|---------|----------|---------|----------|---------|----------|---------|----------|---------|-----------------------------------|--------------------------|-------------------|----------------|----------------|
| Anthracene/ (Anthracene + Phenanthrene)  | 0.3      | 0.1     | 0.3      | 0.1     | 0.3      | 0.2     | 0.6      | 0.5     | 0.2      | 0.1     | 0.2      | 0.1     | < 0.1                            | > 0.1                    |                   |                |                |
| Fluoranthene/ (Fluoranthene + Pyrene)   | 0.5      | 0.7     | 0.6      | 0.2     | 0.6      | 0.7     | 0.5      | 0.7     | 0.5      | 0.5     | 0.6      | 0.5     | < 0.4                            | > 0.4                    | 0.4 - 0.5           | > 0.5           |                |
| Benz(a)anthracene/ (Benz(a)anthracene + Chrysene) | 0.6      | 0.5     | 0.5      | 0.9     | 0.3      | 0.4     | 0.4      | 0.7     | 0.6      | 0.6     | 0.6      | 0.8     | < 0.2                            | > 0.35                   |                   |                |                |
| Indeno(1,2,3-cd)pyrene/(Indeno(1,2,3-cd)pyrene + Benzo(ghi)perylene) | 0.6      | 0.3     | 0.4      | 0.9     | 0.4      | 0.7     | 0.6      | 0.8     | 0.2      | 0.2     | 0.5      | 0.5     | < 0.2                            | > 0.2                    | 0.2 - 0.5           | > 0.5           |                |
| SumLMW/SumHMW                           | 2.0      | 3.3     | 4.0      | 3.9     | 3.0      | 3.8     | 2.6      | 2.8     | 2.7      | 2.5     | 2.6      | 2.1     | > 0.51                           | ≤ 0.51                   |                   |                |                |
| SumCOMB/Total PAHs                      | 0.5      | 0.7     | 0.7      | 0.8     | 0.6      | 0.7     | 0.9      | 0.6     | 0.7      | 0.6     | 0.6      | 0.6     | > 0.51                           | ≤ 0.51                   |                   |                |                |

W Out and W In represents ratios of PAH concentrations in winter outdoors and indoors.
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Figure 4: Indoor to outdoor ratios of individual PAH concentrations in winter obtained with active and passive sampling.

various authors. Katsoyannis et al. demonstrated that transport of PAHs over a few kilometres can be enough to cause a change in the source identification interpretation, the most robust for air concentrations appeared to be ratio Benz[a]anthracene/(Benz[a]anthracene + Chrysene) (29). In our study the distance from emission sources to sampling locations was within tens of meters, thus the use of diagnostic ratios has certain relevance.

**Indoor/outdoor ratios of vapor-phase PAHs.** Indoor to outdoor ratios (I/O) of individual vapor-phase PAH amounts in winter obtained by passive and active sampling are presented in Figure 4. In most cases, the I/O was observed below unity, indicating outdoor air as the primary source of PAHs.
The I/O ratios were generally higher in the passively sampled data. Data from passive sampling also revealed more cases with I/O > 1, presumably due to the fact that during longer sampling time more PAH emission episodes indoors have been reflected. In Kaunas schools (3), however, the pattern of I/O ratio for individual PAHs was different presumably due to differences in indoor pollution sources.

CONCLUSIONS

The sampled amount of 16 PAHs investigated by passive sampling ranged from 10–138 ng/day outdoors, from 5–59 ng/day indoors during the winter sampling campaign. In summer the total concentration of PAHs varied from 11–19 ng/day outdoors and from 19–27 ng/day indoors. The total concentration of vapor- and particle-phase PAHs in winter in actively taken samples varied from 49–286 ng/m³ outdoors and from 28–83 ng/m³ indoors. Presumed contamination of air with PAHs outdoors based on type of fuel burned as well as density of houses at different sampling locations were well reflected in data obtained by SPMD methodology. Due to simplicity of SPMD methodology it can be used for screening campaigns outdoors, however due to differences in uptake rates the comparison between different seasons can be done with certain limitations.

In winter PAH levels were higher outdoors than indoors while in summer the situation was the opposite. Diagnostic ratio analysis revealed dominance of pyrogenic sources at most locations investigated. PAH levels in this study measured with SPMD methodology were similar to those found in urban locations in Poland, Belgium and some regions of China. However, levels of particle-phase PAHs in winter where noticeably higher than in all places in Europe and were lower if compared to locations in China.

SPMD methodology proved itself for measurements of PAHs indoors despite of quite low air velocities. In winter, the concentration of PAHs in the protected sampler and naked membranes did not differ significantly. For simplicity reasons, SPMDs might be used unprotected introducing a bias of around 20% but the bias is also depending of the photosensitivity difference between different PAHs. Protective sampler is needed for deployment of SPMDs both outdoors and indoors under conditions of more intensive sunlight.

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**SUPPLEMENTAL MATERIAL**

Supplemental data for this article can be accessed on the publisher’s website.

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