Atmospheric Environment 44 (2010) 5022–5027

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Polycyclic aromatic hydrocarbons in air on small spatial and temporal scales – II. Mass size distributions and gas-particle partitioning

Gerhard Lammel[a,b,*], Jana Klánová[a], Predrag Ilić[c], Jiří Kohoutek[a], Bojan Gasić[d], Igor Kovacić[e], Lenka Škrdlíková[a]

[a] Masaryk University, Research Centre for Toxic Compounds in the Environment, Kamenice 3, 62500 Brno, Czech Republic
[b] Max Planck Institute for Chemistry, J.-J.-Becher-Weg 27, 55128 Mainz, Germany
[c] Institute for Protection, Ecology and Informatics, Vidovdanská 43, 78000 Banja Luka, Republic of Srpska, Bosnia and Hercegovina
[d] Institute for Chemical and Bioengineering, ETH Zürich, Hönggerberg, 8093 Zürich, Switzerland
[e] Republic Hydrometeorological Institute, Put Banjalučkog odreda b.b., 78000 Banja Luka, Republic of Srpska, Bosnia and Hercegovina

ARTICLE INFO

Article history:
Received 19 January 2010
Received in revised form
15 July 2010
Accepted 17 July 2010

Keywords:
Polycyclic aromatic hydrocarbons
Gas-particle partitioning
Urban aerosol
Spatial variability

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) were measured together with inorganic air pollutants at two urban sites and one rural background site in the Banja Luka area, Bosnia and Hercegovina, during 72 h in July 2008 using a high time resolution (5 samples per day) with the aim to study gas-particle partitioning, aerosol mass size distributions and to explore the potential of a higher time resolution (4 h-sampling).

In the particulate phase the mass median diameters of the PAHs were found almost exclusively in the accumulation mode (0.1–1.0 μm of size). These were larger for semivolatile PAHs than for non-volatile PAHs. Gas-particle partitioning of semivolatile PAHs was strongly influenced by temperature. The results suggest that the Junge–Pankow model is inadequate to explain the inter-species variation and another process must be significant for phase partitioning which is less temperature sensitive than adsorption. Care should be taken when interpreting slopes m of plots of the type $\log K_p = m \log p_L^0 + b$ based on 24 h means, as these are found sensitive to the time averaging, i.e. tend to be higher than when based on 12 h-mean samples.

1. Introduction

For polycyclic aromatic hydrocarbons (PAHs) the gaseous state is predominant for the lighter molecular weight PAHs, while the substances with more than 4 rings are preferentially associated with the aerosol particles (Finlayson-Pitts and Pitts, 2000; ECPACWG, 2001). Gas-particle partitioning is expected for organics of saturation vapour pressures in ambient air in the range $p_{sat} = 10^{-6}–10^{-2}$ Pa (Franklin et al., 2000). The phase partitioning of a compound, i, in aerosols can be quantified by the gas-particle partitioning coefficient K_P ($m^3\ \mu g^{-1}$):

$$K_P = c_{ip}/(c_{ig}c_m) \tag{1}$$

with the concentrations in the gaseous and particulate phases, c_{ig} and c_{ip}, and particulate matter mass concentration c_m (ng m^{-3}). If adsorption is dominating the process, then for the particulate-phase mass fraction of semivolatile substances, $\theta = c_{ip}/(c_{ig} + c_{ip})$, it should hold (Junge, 1977; Pankow, 1987):

$$\theta = c_J S/\left[c_J S + p_L^0\right] \tag{2}$$

with constant c_J, aerosol surface concentration S ($cm^2\ cm^{-3}$), and saturation vapour pressure of the super-cooled liquid p_L^0. Then, K_P could be expressed as (Pankow, 1987):

$$K_P = N_s A_m T e^{(Q_l - Q_v)/RT}/\left(16 p_L^0\right) \tag{3}$$

with surface concentration of sorption sites N_s, specific surface area of particulate matter $A_m = 10^6 S/c_m$ ($cm^2\ \mu g^{-1}$), the enthalpy of desorption from the surface Q_l and the enthalpy of vapourisation of the super-cooled liquid Q_v. For equilibrium partitioning the slope, m, of plots of the form

$$\log K_P = m \log p_L^0 + b \tag{4}$$

should be equal to −1 according to the Junge–Pankow model and the intercept, b, for constant temperature should be determined

---

[*] Corresponding author. Masaryk University, Research Centre for Toxic Compounds in the Environment, Kamenice 3, 62500 Brno, Czech Republic. Tel.: +420 54949 2860; fax: +420 54949 2840.
E-mail address: lammel@recetox.muni.cz (G. Lammel).

1352-2310/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2010.08.001

by N_s and A_m. Deviation of m from −1, however, is inconclusive, as various possible reasons exist which usually cannot be addressed, such as non-equilibrium, temperature change during sampling, and absorption into OM (Pankow and Bidleman, 1992; Goss and Schwarzenbach, 1998). Non-equilibrium can be caused by kinetic constraints (introduction of fresh particles or clean air) or by the presence of nonexchangeable compounds on or in the particles.

As $\log p_L^0 \sim 1/T$ (Clausius–Clapeyron equation) eq. (4) is physically equivalent to plots of the form

$$\log K_P = A/T + B \tag{5}$$

which was derived from Langmuir adsorption theory (Yamasaki et al., 1982). For PAH absorption in primary or secondary organic particulate matter K_p would be given as (Pankow et al., 1994):

$$K_p = K_{OA} f_{OM} MW_{OCT} \zeta_{OCT} / \left(\rho_{OCT} MW_{OM} \zeta_{OM} 10^{12}\right) \tag{6}$$

with f_{OM} being the mass fraction of organic matter (OM) in particulate matter, MW_{OCT}, and MW_{OM} the mean molecular weights of octanol and the OM phase (g mol^{-1}), respectively, ρ_{OCT} the density of octanol (0.820 kg L^{-1}), ζ_{OCT} the activity coefficient of the absorbing compound in octanol, ζ_{OM} the activity coefficient of the compound in the OM phase. With the assumptions that $\zeta_{OCT} = \zeta_{OM}$ and $MW_{OCT}/MW_{OM} = 1$, eq. (6) can be simplified as:

$$\log K_p = m' \log K_{oa} + b' \tag{7}$$

with the octanol–air partitioning coefficient K_{oa}. Then, and when phase equilibrium is established the slope, m′, of plots of eq. (7) should be equal to +1 and the intercept, b′, equals $\log f_{OM}$-11.91.

$\log K_p$ of PAHs based on differentiating sampling of the gaseous and particulate fractions was found to be correlated with 1/T (or $\log p_L^0$) in a number of studies (Pankow and Bidleman, 1992; Subramanyam et al., 1994; Gustafson and Dickhut, 1997; Galarneau et al., 2006). This is in accordance with both adsorptive and absorptive mechanisms (Pankow et al., 1994). However, K_{oa} was suggested as a very good descriptor for PAH gas-particle partitioning (Finizio et al., 1997). Measurement of f_{OM} was not included, however. Over-prediction of θ by the adsorption model had been suggested by other studies at source and receptor sites (e.g. Balasubramanian and He, in press), including in Bosnia and Hercegovina (Radonić et al., 2009). In these studies, however, S had been estimated assumed to be constant rather than measured. Gas-particle partitioning of PAHs is presently understood as having adsorptive and absorptive contributions. In particular, a combination of absorption into OM and adsorption to soot seems to have a high potential to explain the observations (Lohmann and Lammel, 2004). While f_{OM}, likely to influence absorption, and soot, likely to influence adsorption had been covered in experimental studies (Mader and Pankow, 2002; Schauer et al., 2003), the aerosol surface concentration, S, has not been covered so far. Models which are based on more than 2 parameters, so-called poly-parameter linear free energy relationships, should be superior (Goss and Schwarzenbach, 2001). These can be used once the parameters for major aerosol components, e.g. ammonium salts, are becoming available.

In field studies a time resolution of PAH measurement higher than 1/24 h was only rarely achieved. It was the aim of this study to characterize the phase behaviour of PAH and to test an adsorption model of gas-particle partitioning based on measured aerosol surface. PAH abundances and spatial and temporal variabilities during this campaign were presented in a companion paper (Lammel et al., 2010).

2. Methodology

2.1. Sites

Banja Luka is a major city in Bosnia and Hercegovina (200 000 inhabitants) and located 160 km inland from the Adriatic coast. Samples have been taken at 2 urban sites (town site and factory site) and 1 rural background site distance between 2.7 and 5.6 km from each other. Details are given in a companion paper (Lammel et al., 2010).

2.2. Sampling and analysis methods

PAHs were collected in the gaseous and particulate phases using high-volume samplers ($F \approx 12$ m^3 h^{-1}) equipped with one quartz filter and one polyurethane foam (PUF) plug or with 6 impactor stages and one PUF. During the day 3 high-volume and 1 impactor samples, and during the night 2 high-volume and 1 impactor samples have been taken at each site. On-site variability was addressed by deploying 3 high-volume samplers side by side at one of the sites, the factory site. More details of the sampling methods are given in the companion paper (Lammel et al., 2010).

Size-resolved particulate mass concentration was determined by gravimetry (pre-weighed glass-fibre filter membranes). Aerosol number concentration, N (cm^{-3}), was determined at the factory site using an optical particle counter (model 107, Grimm, Ainring, Germany; 31 channels between 0.25 and 32 μm of aerodynamic particle diameter, D), hence $N_{>0.25}$, and a condensation nucleus counter (model 3022A, TSI, Shoreview, USA; counting particles in the 0.007–1.0 μm size range), hence $N_{0.007-1.0}$. One channel of the OPC failed. The CNC was operated discontinuously and used for detection of eventual direct influence from sources (see Table S1 in the Supplementary material). Aerosol surface concentration, S (cm^{-1}), was derived as $S = \pi \Sigma_i N_i D_i^2$ assuming sphericity. Hereby, true S will be underestimated, in particular if particles of irregular form were abundant (e.g. Jaenicke, 1988). Comparisons with absolute methods (e.g. Pandis et al., 1991) suggest that the discrepancy may reach up to a factor of 2–3. The mass median diameter of PAH and of particulate matter mass, D_m (μm), was derived as $D_m = \Sigma_i m_i D_i / \Sigma_i m_i$ with D_i being the arithmetic mean diameters collected in the cascade impactor. Size-resolved PAH and particulate matter mass data are not available from the hill site, due to sample losses.

Meteorological parameters (air temperature, humidity, wind direction and velocity) were determined at all sites. Part of this data from the factory site was lost due to electronic failure.

28 3–6-ring PAHs, i.e. naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), indeno(123cd)pyrene (IPY), dibenz(ah)anthracene (DBA), benzo(ghi)perylene (BPE), retene (RET), benzo(b)fluorene (BBN), benzo(b)naphtho(21d)thiophene (BNT), benzo(ghi)fluoranthene (BGF), cyclopenta(cd)pyrene (CPP), triphenylene (TPH), benzo(j)fluoranthene (BJF), benzo(e)pyrene (BEP), perylene (PER), dibenzo(ac)anthracene (DCA), anthranthrene (AAN) and coronene (COR) were analysed by GC–MS. Field blank values of most analytes were below instrument limit of quantification (LOQ) in the impactor samples. The methodological uncertainty of PAH concentrations is quantified based on the variability among the 3 side-by-side samples taken at one of the sites (the factory site): This is justified as no systematic differences due to sampling height occurred. I.e., the difference between concentrations of samples from same height was not smaller than for different height. More details on the analysis method and