SOME INFERENCES ON THE MECHANISM OF ATMOSPHERIC GAS-PARTICLE PARTITIONING OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) AT ZARAGOZA (SPAIN)

M.S. Callén*, M.T. de la Cruz, J.M. López, R. Murillo, M.V. Navarro and A.M. Mastral
Instituto de Carboquímica (CSIC), Miguel Luesma Castán, 4, 50018 Zaragoza (Spain)

* Corresponding author. Phone number: +34 976 733977; Fax number: +34 976 733318
e-mail: marisol@icb.csic.es

Abstract

Gas-particle partitioning of pollutants is an important mechanism determining atmospheric processing and its impact to environmental and human health. In this paper, the gas-particle partitioning of polycyclic aromatic hydrocarbons (PAH) has been studied with the aim of determining the main mechanism of PAH partitioning in Zaragoza (Spain) aerosols. To reach this goal, the ambient concentrations of PAH (gas and particle phase) collected in this city for one year period (2003-2004) have been analyzed.

The partitioning between the particle and gas phases was studied according to three different models: the Junge adsorption model, the absorption into the organic matter model using the octanol-air (K_{OA}) partition coefficient and the absorption into the organic matter plus the adsorption onto the soot carbon model using the soot-air (K_{SA}) partition coefficients.

Experimental gas/particle partition coefficients (K_p) correlated well with the subcooled liquid vapour pressures (P_L^0) of PAH but with slopes higher than the expected value of -1. Experimental K_p values were well fit to the modelled ones when, in addition to absorption into organic matter, adsorption onto the soot carbon was considered. It could be concluded that the main partition mechanism in Zaragoza aerosols was explained by adsorption onto the soot carbon. However, K_p modelled values were affected by the different thermodynamic parameters related to soot types.

The influence of the organic matter and elemental carbon fractions on the K_p modelling was also studied. The different particle characteristics, local factors, the presence of non exchangeable fraction and non equilibrium were considered like main keys to explain deviations of the experimental K_p values from predictions according to models.

Keywords: PAH; Gas/particle partitioning; Atmospheric pollution; Soot-air; Octanol-air

1. Introduction

The widespread occurrence of Polycyclic Aromatic Hydrocarbons (PAH) in the environment and the adverse health effects makes that the identification and allocation of PAH in the urban aerosol be of importance for a better understanding of the origins, reactions and fate of these compounds in the atmosphere. Optimal strategies for the control of these air pollutants depend ultimately on such understanding.

Many PAH compounds have been shown to be mutagenic or carcinogenic and many others may act as co-carcinogens or tumour promoters (Luch, 2005). Exposure to these compounds can occur through multiple pathways, including contaminated surfaces, respirable particulate matter and, for the lower mass PAH, through the vapour phase. Precisely, the volatility properties of these compounds make them to be present both in vapour form and in association to particles facilitating their long-range transport (Grimalt et al., 1988). As it happens for other pollutants, once they are redistributed between gas and particle phases, PAH can be degraded by direct and/or indirect photolysis and deposited via wet and dry deposition mechanisms. When deposited, PAH may be revolatilized and transported over long distances and deposited again on soils and water surfaces far from their emissions.

In this way, the environmental fate of PAH depends, in part, on their distribution between the gas and particle phases. Some of the factors affecting to the shifting in the gas/particle distribution of PAH are ambient temperature variation, the nature of the aerosol and less intensive atmospheric reactions, during winter months, which could also lead subsequently to higher concentrations of PAH associated with atmospheric particles.

According to Wania et al. (1998), the distribution of semivolatile organic compounds between any sorbing surface materials (suspended aerosols or any earth surface, e.g.

soils, plants, bedrocks, water) and air depends mainly on temperature. At high temperatures, the air concentrations increase showing that volatilization from the surfaces is an important factor in the movement of these pollutants.

The partitioning of the semi-volatile organic compounds between the gas and particle phase has been studied thoroughly for the last years trying to predict atmospheric levels once the mechanism has been parameterised.

Initially, the partitioning was based on the Langmuir adsorption theory (Junge, 1977; Yamasaki et al., 1982) taking into account a mechanism of physical adsorption of the organic molecules on the particle surface. Afterwards, a mechanism based on the absorption of the semi-volatile organic compounds in the organic phase of the particle matter showed to be more relevant (Pankow, 1994a, 1994b).

Finizio et al. (1997) described the partitioning of persistent organic pollutants between air and organic films on aerosols employing the octanol-air partition coefficient (K_{OA}).

Recently, a new theory was developed by taking into account the PAH absorption in the organic matter as well as the adsorption on the particle matter soot (Dachs and Eisenreich, 2000, Fernández, 2002). The relative importance of both mechanisms in atmospheric aerosols has been evaluated through the comparison of the partition coefficients octanol-air (K_{OA}) and soot-air (K_{SA}) in different urban atmospheres.

In this work, the main goal was a better understanding of the atmospheric partitioning of PAH necessary to determine the environmental fate of, and human exposure to these pollutants. To reach this, the partial objectives of this investigation were to characterize gas-particle partitioning of PAH in an urban aerosol of Spain by studying the temperature dependence of PAH and by establishing the PAH retention mechanism in the particle matter, according to available models, by studying the influence of the variables affecting the modelling.

2. Material and methods

2.1 Sampling program

The study was performed in the city of Zaragoza (located in the North-East of Spain (41°39'49.38"N; 0°53'16.68"W) using a GUV-15H Graseby Andersen High-Volume sampler with volumetric flow controlled system provided with a PM₁₀ cut off inlet at 10 µm but modified to capture PAH in the particle phase (PTFE-coated, glass-fibre filters, 0.6 µm pore size) and in the gas phase (polyurethane foam; PUF) (López et al., 2005). Sampling efficiency was evaluated after the addition of a solution of deuterated p-terphenyl added to the PUF prior to sampling as a sampling evaluation standard (SES). Samples were collected every wk from April 7th, 2003 to July 5th, 2004 collecting a total of 50 samples.

Sampling time was 24 h, yielding sample volumes among 1600 and 1700 m³. Previous to sampling, filters and PUF were separately Soxhlet extracted for 24 h with dichloromethane (DCM) and kept in desiccators before and after sampling. Filters were also weighted before and after the sampling using an analytical balance (precision of 0.01 mg) to obtain the particle mass (Table 1 Supplementary material). After sampling, filters were wrapped in aluminium foil previously rinsed with hexane and stored in a freezer at -20 °C until analysis.

2.2. Extraction and analyses

The analytical protocol for PAH determination contained in the filters and PUF was carried out as previously published (Callén et al., 2007; Callén et al., 2008). The PUF and particle matter contained in the filters were separately extracted by Soxhlet during 18 h with DCM after the addition of deuterated-PAH surrogate standards containing the following PAH: acenaphthene-d₁₀ (Ace-d₁₀), anthracene-d₁₀ (An-d₁₀), benzo(a)pyrene-d₁₂ (BaP-d₁₂) and benzo(ghi)perylene-d₁₂ (BghiP-d₁₂). PAH quantification was

performed using the internal standard method relative to the closest eluting PAH surrogate.

The compounds quantified during sampling by GC-MS-MS, according to their elution orders, were: naphthalene (Np, m/z 102), acenaphthylene (Acy, m/z 150), acenaphthene (Ace, m/z 151), fluorene (Fl, m/z 163), phenanthrene (Phe, m/z 152), anthracene (An, m/z 152), 2+2/4-methylphenanthrene (2+2/4MePhe, m/z 189), 9-methylphenanthrene (9MePhe, m/z 189), 1-methylphenanthrene (1MePhe, m/z 189), 2,5-/2,7-/4,5-dimethylphenanthrene (DiMePhe, m/z 191), fluoranthene (Fth, m/z 200), pyrene (Py, m/z 200), benz(a)anthracene (BaA, m/z 226), chrysene (Chry, m/z 226), benzo(b)fluoranthene (BbF, m/z 250), benzo(k)fluoranthene (BkF, m/z 250), benzo(e)pyrene (BeP, m/z 250), benzo(a)pyrene (BaP, m/z 250), indeno(1,2,3-cd)pyrene (IcdP, m/z 274), dibenzo(a,h)anthracene (DahA, m/z 276), benzo(ghi)perylene (BghiP, m/z 274) and coronene (Co, m/z 298).

The meteorological parameters of the sampling place, temperature, relative humidity, rainfall, irradiation, wind direction and speed were provided by the Spanish National Institute of Meteorology (Table 1 in Supplementary material).

2.3. Quality control and quality assurance

Recoveries of the deuterated p-terphenyl sampling evaluation standard added to the PUF prior to sampling were satisfactory (recoveries lower than 50% or higher than 150% were not considered) (UNE 77250, 2001).

PAH losses during the analytical procedure were evaluated by adding a known amount of the above mentioned deuterated PAH surrogate standards previous to the Soxhlet extraction. The concentrations regarding the very volatile PAH, Np, Acy, Ace and Fl could not be accurately identified by using this method according to the obtained results, due to the low recovery, poor reproducibility of their results and for staying

below the limit of quantification. Therefore, these four PAH were not considered in the interpretation of results. IcdP and DahA were quantified together due to the problem of discerning both peaks in some samples with the majority contribution of IcdP. Regarding the rest of PAH, no corrections were applied.

The limit of detection (LOD) and quantification (LOQ) for individual compounds were obtained multiplying by three and ten the standard deviation of the blank filters, respectively, with the lowest detection limit for BkF: 0.001 ng m^{-3} and the highest one for Phe: 0.55 ng m^{-3} .

Analyses of four samples of an appropriate standard reference material (SRM 1649a, urban dust) provided by the National Institute of Standards and Technology (NIST) were carried out in order to check the analytical accuracy and precision. Measured values were comparable to certified values with relative error lower than 16% for all compounds (Phe, An, 1MePhe, Fth, Py, BaA, Chry, BbF, BkF, BaP and BghiP) except BeP (22.6%).

3. Results and discussion

3.1. Gas and particle PAH concentration

The average concentrations, the standard deviation and the minimum and maximum PAH concentrations in particle and gas phases and also in both phases for the performed sampling are shown in Table 1.

A great variation in PAH concentration in particle and gas phases was observed. The total PAH concentration in the particle phase varied between $1.5\text{-}29 \text{ ng m}^{-3}$ and in the gas phase between $1.6\text{-}27 \text{ ng m}^{-3}$. The lower molecular weight PAH species were mainly present in gas phase while higher molecular weight species were physically adsorbed on particulate surfaces (Pupp et al., 1976). IcdP+DahA, BghiP and Co were the majority compounds contributing to the total PAH supported in particle phase and

Phe, Fth, Py and the alkylated Phe to the gas phase (Table 1).

Phe (17%) and Co (11%) were the major PAH by considering both phases. The major contribution of Phe to the total PAH concentration was also found by Cincinelli et al. (2007) in air samples from Prato, Italy.

A positive correlation at 99% level of confidence between the gas and particle phases was found for all PAH from Phe till Chry and for the total PAH showing some grade of solid-gas equilibrium. No correlation between both phases was found for the heavier PAH. This lack of correlation was probably due to the concentrations of these compounds were above the detection limit in gas phase for only few sampling dates.

3.2. Gas/particle partitioning

The partition constant normalized with the total suspended particle concentration (K_p , $\text{m}^3 \mu\text{g}^{-1}$) is defined by the equation: (Pankow, 1987):

$$K_p = \frac{C_p / \text{TSP}}{C_g} \quad (1)$$

Where C_p and C_g are the concentrations of the organic semi-volatile PAH, in the particle and gas phases respectively (ng m^{-3}) and TSP is the total suspended particle ($\mu\text{g m}^{-3}$). In this work, it was introduced the PM_{10} concentration ($\mu\text{g m}^{-3}$) instead of the TSP. The higher the K_p value for a determined compound, the higher trend to the particle phase.

The average, the minimum and maximum values of $\log K_p$ for each PAH measured in the Zaragoza atmosphere are shown in Table 2. The difference in the $\log K_p$ values among the compounds was indicative of the different behaviour regarding their partitioning between the gas and particle phases. The average value for total PAH was -1.6 indicating the weak trend to adhere to the particle phase. Phe was much more

enriched in gas phase than in the particle phase and showed an average $\log K_p = -3.1$ while Co was enriched in the particle phase and its average $\log K_p$ was 0.7.

Higher values of K_p could be expected during cold season due to the low temperatures and the increase of organic semi-volatile compounds concentration in particle phase. The average values of the partition constant for the warm and cold season are shown in Table 2, with statistical significance at higher level than 95% in the case of 2+2/4MePhe, 9MePhe, Fth, Py and BbF. This trend was observed for most of the compounds, with the exception of Phe, Fth, IcdP+DahA and BghiP.

3.3. Temperature dependence of partition constant

One of the main variables affecting the partitioning is the temperature. Particle-gas distributions are inversely related to temperature, as first demonstrated by Yamasaki et al (1982):

$$\log K_p = m (1/T) + b \quad (2)$$

where m , slope and b , intercept of the regression lines, are empirical constants related to heat of phase change of the PAH and the properties of the individual compound together with the properties of the particulate matter.

In this work, values of $\log K_p$ were linearly regressed against $1/T$. The regression results, for species with statistically significant correlation parameters (99%) are presented in Table 3. Regression coefficients (r^2) fall in the range 0.41 (2+2/4MePhe)-0.85 (BkF), therefore 41-85% of the variance was explained by inverse temperature for most of PAH.

Absence of temperature-dependence of Phe and An partition constants was also reported by Sitaras et al. (2004) for Phe and Acy. It was attributed, together to low absolute values of m , to the presence of non-exchangeable fraction and to the reaction of PAH with OH.

In general, the shallowness of the slopes in this work seems to match with the typical slopes reported for other urban sites (Galarneau et al., 2006).

Two different mechanisms have been used to explain the gas-particle PAH partitioning: physical adsorption onto the aerosol surface and absorption into the aerosol organic matter. Independently of the mechanism type retaining PAH on the particle matter, the Equation 3 relates the K_P partition constant with the subcooled liquid vapour pressure of the pure compound, P_L^0 (Pa) according to Pankow (1994a):

$$\log K_P = m_r \log P_L^0 + b_r \quad (3)$$

Where m_r and b_r are empirical constants.

The P_L^0 values were calculated for each sampling date by taking into account the average temperature. The $\log$ of P_L^0 depends on the temperature and follows a linear relationship with it according to the equation:

$$\log P_L^0 = \frac{b}{T} + a \quad (4)$$

where b and a are constants depending on each specific pollutant. The vapour pressures were calculated according to Offenberg and Baker (1999), Paasivirta et al., (1999) and Lei et al. (2002) under the hypothesis that the selection of vapour pressures affected the results.

The linear correlation of $\log K_P$ constant versus the subcooled liquid vapour pressure P_L^0 for each sampling date during 2003-2004, according to the vapour pressures of the different authors above mentioned, was performed for the whole number of sampling events. Very similar results were found for the three references with good linear

correlations between $\log K_p$ and $\log P_L^0$. The correlation coefficients r^2 for these dates varied between 0.74 and 1.0 with an average value of 0.95 (Offenberg and Baker, 1999) (Table 4); 0.65 and 1.00 with an average value of 0.90 (Lei et al., 2002) and 0.67 and 0.97 with an average value of 0.87 (Paasivirta et al., 1999) (Table 2 in Supplementary material). The correlations were statistically significant at 99% level of confidence for 48 of the total studied samples. Slopes, under certain conditions, could be indicative of the dominant mechanism: adsorption or absorption determining the gas/particle partitioning.

Ideally, under equilibrium conditions, the slope m_r should be equal to -1 for either adsorption or absorption mechanisms, explaining the gas-particle PAH partitioning (Pankow, 1994a, 1994b). It is remarkable that for adsorption, the differences between the enthalpies of desorption and volatilization and the number of available adsorption sites must remain constant over a compound class. For absorption, the activity coefficients must remain constant over a compound class (Pankow, 1987; Pankow and Bidleman, 1992). Nevertheless, Goss and Schwarzenbach (1998) showed that deviations of $m_r = -1$ are not always indicative of lack of equilibrium. This deviation can be produced even if equilibrium sorption processes occur and sampling artefacts are negligible.

The value of the slopes of those samples statistically significant in this work varied between -0.17 and -1.20 with an average value of -0.62 (± 0.25) (Table 4), shallower than the expected one according to equilibrium conditions (-1). Shallower slopes than -0.6 are, in general, interpreted to be due to absorption into the organic matter and values significantly steeper than -1 to adsorption process (Goss and Schwarzenbach, 1998). The slope value of -0.62 obtained in this work corresponds to the borderline value of -0.6 previously mentioned. In this way, it is not possible to surely identify the main gas

particle partitioning mechanism in the Zaragoza atmosphere and K_p were compared according to two models in the next section. However, the m_r values obtained in this work, corroborated other studies performed in other urban and rural areas for which m_r varied between -0.43 and -1.04 (Stracquadanio and Trombini, 2006; Tasdemir and Esen, 2007), -0.32 and .1.04 (Terzi and Samara, 2004), -0.30 and -1.14 (Galarneau et al., 2006).

Seasonal difference was found in the regression slope, tending to increase with increasing temperature (m_r warm season= -0.57; m_r cold season= -0.71). No explanation was found for this fact although in the bibliography this trend was also described by authors like Terzi and Samara (2004) for samples taken in the Western Greece. However, opposite trends were reported by Galarneau et al., (2006) for samples taken in the Great Lakes.

One of the experimental reasons which can produce a desviation of $m_r=-1$ is the chance of the sampling system has fault collecting representative samples of the gas and particle phases due to the PUF saturation and sorption of gas phase PAH to filters, sampling artefacts. The PUF saturation for high temperature dates and for long sampling periods could originate the saturation and the incorrect estimation of K_p to higher values than the real ones. In this work, all samples were taken during 24 h. PAH sampling was performed according to European normative (UNE 77250, 2001) to determine PAH in gas and particle phases and the used sampler was US-EPA designated as an approved method for the determination of PM10 concentration.

Regarding the adsorption of gas phase PAH to filters, no studies were performed by using backup filters and no correction were applied to these data sets. Taking into account bibliography, several studies showed that there were not significant differences when comparing results obtained with Hi-volume samplers, diffusion separator,

denuders and impactors (Knaup and Umlauf, 1992; Krieger and Hites, 1994). Therefore, it was assumed that the present data set was suitable for examination of gas particle PAH partitioning.

Finally, those samples in which the compound concentration is close to the detection limit showed an increase in the uncertainty for the K_p determination. In this work, only those dates in which, the PAH concentration in both phases were over the detection limit, were considered.

Other reasons associated with the lack of thermodynamic equilibrium that might contribute to shallow slopes can be caused by different factors: fast changes of temperature during sampling, chemical reactions in the atmosphere and local emissions producing compounds with no time enough to cold down and pass to the particle phase. In fact, pollution sources close to the sampling point, for example the proximity of the highway, could affect the gas/particle equilibrium. Regarding the temperature fluctuations during the sampling date, no clear evidence that temperature variations were responsible for shallow slopes was found. A more detailed study for each sample revealed that there were samples for which the temperature changes were higher than 10 °C and still showed steeper slopes. On the contrary, samples for which the temperature changes were lower than 6 °C still had shallow slopes.

The presence of non-exchangeable material could also affect the deviations of m_r . In fact, PAH are strongly associated onto the particle matter, adsorbed on the activated sites or trapped in the soot matrix and they are not able to participate in the gas-particle exchange. Nevertheless, they are extracted in the analysis step by using organic solvents (Bidleman, 1988). In this way, the K_p values obtained experimentally are higher than the ones predicted by theory according to the saturation vapour pressures in liquid phase. Moreover, at low levels de PM10 (average value= 32.2 $\mu\text{g m}^{-3}$), even a small

fraction of non exchangeable compound could cause notable deviations to the slopes (Pankow and Bidleman, 1992).

Simcik et al. (1998) also suggested that energy terms (activity coefficients, adsorption sites, enthalpies) are the major factors contributing to the shallower slopes independently of the adsorption or absorption dominates the sorption process. Differences in the chemical composition of atmospheric particles would affect these energy terms (Goss and Schwarzenbach, 1998). As the intercept b_r is mainly depending on properties associated with the aerosol and is related to these energy terms, a more detailed study of the variations in the b_r was carried out.

Variations of m_r produce variations in b_r in such a way that, in some cases, it is possible to explain this variation according to:

$$b_r = m_s m_r + b_s \quad (5)$$

Pankow and Bidleman (1992) showed that when there is a linear correlation between b_r and m_r , all the regressions of $\log K_P$ versus $\log P_L^0$ show a general trend to intersect on a point ($\log P_L^0$, $\log K_P$) defined by $(-m_r, b_r)$. 48 of the samples taken in Zaragoza in the 2003-2004 period for which there was an statistically significant correlation, showed the trend to intersect in the point $(-2.60, -2.05)$ with $r^2=0.833$. Similar values were reported in the literature for different locations in Greece (Terzi and Samara, 2004).

The chance of defining this intersection point allows carrying out the estimation of the partitioning constant of a compound between the particle and gas phases, K_P for a given value of $\log P_L^0$, it is to say for a specific temperature (equation 4). This can be useful in order to build a model to predict concentrations.

Therefore, assuming that sampling artefacts were minima, the most important reasons to have higher values of m_r than the expected ones, could be the presence of a PAH fraction non exchangeable, varying energy terms and differences in chemical

composition.

3.4. Comparisons between the partition constant K_P according to different models

Due to the lack of conclusive results obtained in the previous section regarding the predominant mechanism in Zaragoza aerosols, the absorption of PAH into the organic matter, in which the octanol-air partitioning coefficient, K_{OA} is used as an alternative to vapour pressure, and the adsorption onto the soot forming the PM_{10} , were also investigated.

When the partition mechanism consists of the absorption of the organic semi-volatile compounds into the organic matter, the partition constant is given by the equation

$$K_p(Oct.) = \frac{C_p / TSP}{C_g} = f_{OM} \frac{\zeta_{OCT}}{\zeta_{OM}} \frac{MW_{OCT}}{MW_{OM} \rho_{OCT} 10^{12}} K_{OA} \quad (6)$$

according to Finizio et al. (1997).

Where f_{OM} is the fraction of organic matter in the PM_{10} , ζ_{OCT} is the activity coefficient of the absorbing compound in octanol, MW_{OCT} is the molecular mass of octanol ($g\ mol^{-1}$) and ρ_{OCT} is the octanol density ($0.82\ Kg\ L^{-1}$). ζ_{OM} is the activity coefficient of the compound in the organic matter phase and MW_{OM} is the average molecular mass of that organic matter ($g\ mol^{-1}$). K_{OA} is the octanol-air partition coefficient ($L\ Kg^{-1}$).

Assuming that octanol models all the organic matter, $MW_{OCT}/MW_{OM}=1$ and $\zeta_{OCT}/\zeta_{OM}=1$, equation 6 can be transformed in:

$$\log K_p(Oct.) = \log K_{OA} + \log f_{OM} - 11.91 \quad (7)$$

Bibliography regarding studies in sediments prove the strong association between PAH and soot in aquatic systems. Because its presence in aquatic systems is consequence of

deposition processes from the atmosphere, it is expected that in the atmospheric particulate matter this association also exists (Crutzen and Andreae, 1990). Therefore, besides absorption, adsorption partitioning could also be an important sorption mechanism in the atmosphere.

The equation modelling the gas-particle partitioning, considering both mechanisms absorption and adsorption in the soot, is given by the equation:

$$K_p(oct + soot) = \frac{C_p / TSP}{C_g} = f_{OM} \frac{\zeta_{OCT}}{\zeta_{OM}} \frac{MW_{OCT}}{MW_{OM} \rho_{OCT} 10^{12}} K_{OA} + f_{EC} \frac{a_{EC}}{a_{AC} 10^{12}} K_{SA} \quad (8)$$

Where f_{EC} is the fraction of elemental carbon in the aerosol, a_{EC} and a_{AC} are specific surface area of the elemental carbon and activated carbon, respectively and K_{SA} is the soot-air partition coefficient ($L \text{ Kg}^{-1}$).

Since both PAH and soot material are generated in combustion sources, they are present concurrently in the atmosphere. Soot is a subproduct of incomplete combustion. They consist of a nucleus of elemental carbon (EC), amorphous at macromolecular scale but with similar disposition to graphite at micro scale, surrounded by an organic carbon layer (OC). PAH are also formed in the incomplete combustion reactions and are precursors of this material through a radical mechanism (Mastral et al., 2000).

In this study, it was assumed that elemental carbon accounted for most of soot carbon and there was not difference between soot and elemental carbon, so $a_{EC}/a_{AC} = 1$ (Dachs and Eisenreich, 2000). In this way, it was calculated the K_p values following the equations 7 and 8 for Phe, Fth and Py.

Both partition coefficients, K_{OA} and K_{SA} are affected by the temperature. According to Dachs and Eisenreich (2000), K_{OA} can be obtained through the equation 9:

$$\log K_{OA} = A + \frac{B}{T} \quad (9)$$

Where A and B are experimental parameters.

K_{SA} can be obtained through the equation 10:

$$K_{SA} = \frac{K_{SW}}{H'} \quad (10)$$

Where K_{SW} is the soot-water partition coefficient and H' is the Henry's law constant which gives the relationship between the concentrations of a compound in gas phase and dissolution when both are in equilibrium at a temperature T. H' is dimensionless and can be estimated by using the volatilization heat (ΔH , kJ mol⁻¹) and entropy (ΔS , kJ mol⁻¹ K⁻¹) (equation 11). The values of K_{SW} were obtained from adsorption experiments on activated carbons according to Walters and Luthy (1984).

$$\ln H' = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

K_{SW} values can vary by over two orders of magnitude depending on the type of soot considered (Galarneau et al., 2006), modifying as well K_{SA} . In order to compare this effect on the modelled K_p , the values reported by Walters and Luthy (1984) for activated carbons and by Jonker and Koelmans (2002) for traffic, oil, wood, coal and diesel (SRM1650) soot were obtained. A log K_{SA} versus log P_L^0 (Offenberg and Baker, 1999) at 25°C was represented for Phe, Fth and Py for the different types of sorbents (Fig. 1). An excellent fit was obtained for the three PAH for activated carbons calculated according to Walters and Luthy (1984). When K_{SA} was calculated according to Jonker and Koelmans (2002), this fit was only better when wood soot was considered in the K_{SW} calculations. It is remarkable to say that the influence of the soot type will be

determinant over the particle/gas partitioning. Although one sample could be very well represented by a soot type, it could not happen with another and deeper characterization of the soot fraction in the aerosol for each sample would be necessary in order to better understand the PAH partitioning.

Regarding organic and elemental carbon, f_{OM} and f_{EC} values of 0.15 and 0.05 were used respectively in the estimation of K_p in eq 8. Similar values were reported for urban areas such as Chicago (Vardar et al., 2004), Bursa (Turkey, Cindorouk et al., 2007) and Barcelona (Viana et al., 2006).

Results based on the models, absorption and absorption+adsorption were compared against partition constants measured experimentally (Fig. 2) for each sampling date for Phe, Fth and Py. The model based on the PAH absorption into the organic matter predicted systematically partition constants lower for all PAH with ratios between the experimental and modelled K_p which ranged from 0.40 (Py) to 0.60 (Fth) (Table 5). Results were better when the model considered the adsorption onto the soot. Very good concordance with the experimental data were obtained with Walters and Luthy's $\log K_{SW}$ values, with ratios between the experimental and predicted K_p varying between 0.87 (Py) and 2.74 (Chry). The use of Jonker and Koelmans $\log K_{sw}$ dataset yielded to lower ratios and results were worse.

K_{SA} for the studied PAH was three orders of magnitude higher than K_{OA} when $\log K_{SW}$ dataset reported for Walters and Luthy were used in the calculations (Phe, $\log K_{OA}=8.03$, $\log K_{SA}=9.85$; Fth, $\log K_{OA}=9.24$, $\log K_{SA}=10.93$; Py, $\log K_{OA}= 7.86$, $\log K_{SA}=10.83$).

The important role of soot carbon in PAH partitioning was also corroborated by other authors (Dachs and Eisenreich, 2000; Vardar et al., 2004). Nevertheless, other authors like Galarneau et al. (2006) could not explain the deviations from other PAH like retene

and BaA based on soot types and attributed these changes to seasonal variability relationships.

(PARAGRAPH REGARDING CHRY REMOVED)

Other variables affecting K_p values are related to organic and elemental carbon contents in the aerosol because they depend on local factors and particle characteristics. In order to explore the sensitivity of the carbon fractions in the study of the gas/particle partitioning of PAH, the values of f_{OM} and f_{EC} were varied $\pm 25\%$ from their estimated values (Vardar et al., 2004). Ratios between experimental and modelled $\log K_p$ are shown in Table 5. Comparing with results obtained with $f_{OM}=0.15$ and $f_{EC}=0.05$, better fit was reached when PAH adsorption onto soot was considered besides absorption into organic matter regardless the carbon content. Furthermore, for all types of soot, ratios were closer to the unity when carbon fractions were 25% increased. In this case, $\log K_p$ modelled according to Walters and Luthy (1984) still fit better to the experimental data reported in this work.

Therefore, these results suggested that PAH adsorption onto the soot was significant and should be taken into account in the PAH partitioning between gas and particle phases. Although the elemental carbon concentration is normally lower than the organic carbon in the atmospheric particle matter (Dachs and Eisenreich, 2000), these results showed that less than 10% of the studied PAH were absorbed into organic matter versus more than 90% which were adsorbed onto the elemental carbon structure, being this last one the main partitioning mechanism in Zaragoza aerosols.

In general, only when the organic matter content is more than 100 times the elemental carbon, the absorption can be considered like the main mechanism to retain PAH in the particle phase, secondary aerosols (Dachs and Eisenreich, 2000). However, a deep characterization of the aerosol nature including the soot type, dependence with the

temperature of soot-air partitioning, non exchangeable fraction of aerosols, should be necessary in order to better understand the PAH partitioning and the fate.

4. Conclusions

This work provided relevant information regarding the gas/particle partitioning of PAH in the Zaragoza aerosols.

One of the influencing variables explaining the gas/particle partitioning, independently of the partitioning mechanism, is the temperature. It is observed that temperature is able to explain until 85% of the partitioning for PAH like BkF, showing seasonal behaviour for some of the studied PAH.

Three different models have been applied to study the partitioning between the particle and gas phases: the Junge adsorption model, the absorption into organic matter and the absorption into organic matter plus the adsorption onto the soot carbon. Experimental gas/particle partition coefficients are well correlated with the subcooled liquid vapour pressures of PAH, independently of the selected vapour pressures ($r^2=0.95$, $p<0.01$) but with slopes (-0.62) higher than the expected value of -1. It can be deduced that the exchangeable fraction of each PAH on aerosols, the chemical properties of the atmospheric particles and differences in energy terms could explain the variability between the experimental and modelled partition coefficients.

It is observed that experimental K_p values compared to the modelled ones were better fit when both, absorption into organic matter and adsorption onto the soot carbon are considered. This fit depends on the different types of soot obtaining better results when adsorption onto activated carbon is considered.

With regard to the influence of the organic matter and elemental carbon values, in all cases, better model fit is obtained when both values are increased 25%. However, the temporal variations in the partition coefficient in Zaragoza aerosols could be better

explained by considering the different properties of the aerosol particles (soot type), local factors, exchangeable fraction of each PAH on aerosols and the temperature dependence of soot-air partitioning.

Acknowledgements

Authors would like to thank the Government of Aragón (DGA) for the grant to M.T.C and the Spanish Government for the JAE doctoral contract to J.M.L and for the Juan de la Cierva contract to M.V.N.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at

References

- Bidleman, T.F., Billings, W.N., Foreman, W.T., 1986. Bidleman, T.F., 1986. Vapour particle partitioning of semivolatile organic compounds. Estimates from field collection. *Environ. Sci. Technol.* 20, 1038-1043.
- Bidleman, T.F., 1988. Atmospheric Processes: wet and dry deposition of organic compounds are controlled by their vapour particle partitioning. *Environ. Sci. Technol.* 22, 361-367.
- Callén, M.S., de la Cruz, M.T., Marinov, S., Mastral, A.M., Murillo, R., Stefanova, M., 2007. Hot gas cleaning in power stations by using electron beam technology. Influence on PAH emissions. *Fuel Proc. Technol.* 88, 273-280.
- Callén, M.S., de la Cruz, M.T., López, J.M., Murillo, R., Navarro, M.V., Mastral, A.M., Long-range atmospheric transport and local pollution sources on PAH concentrations in a South European urban area. Fulfilling of the European Directive. *Water Air Soil Poll. Water Air Soil Poll.* 190, 271-285.
- Cincinelli, A., Del Bubba, M., Martellini, T., Gambaro, A., Lepri, L., 2007. Gas-particle concentration and distribution of n-alkanes and PAH in the atmosphere of Prato

- (Italy). *Chemosphere*, 68, 472-478.
- Cindoruk, S.S., Esen, F., Tasdemir, Y., 2007. Concentration and gas/particle partitioning of polychlorinated biphenyls (PCBs) at an industrial site at Bursa, Turkey. *Atmos. Res.* 85, 338-350.
- Crutzen, P.J., Andreae, M.O., 1990. Biomass burning in the tropics. Impact on atmospheric chemistry and biogeochemical cycles. *Science* 250, 1669-1678.
- Dachs, J., Eisenreich, S.J., 2000. Adsorption onto aerosol soot carbon dominates gas–particle partitioning of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 34, 3690–3697.
- Finizio, A., Mackay, D., Bidleman, T., Harner, T., 1997. Octanol-air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols. *Atmos. Environ.* 31, 2289-2296.
- Galarneau, E., Bidleman, T. F., Blanchard, P., 2006. Seasonality and interspecies differences in particle/gas partitioning of PAH observed by the Integrated Atmospheric Deposition Network (IADN). *Atmos. Environ.* 40, 182-197.
- Goss, J-U., Schwarzenbach, R.R., 1998. Gas/solid and gas/liquid partitioning of organic compounds: Critical evaluation of the interpretation of equilibrium constants. *Environ. Sci. Technol.* 32, 2025-2032.
- Jonker, M.T.O., Koelmans, A.A., 2002. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations. *Environ. Sci. Technol.* 36, 3725–3734.
- Junge, C.E., 1977. Basic consideration in the atmosphere as related to the fate of global pollutants in the air and water environments. Wiley, New York.
- Knaup, H., Umlauf, G., 1992. Atmospheric gas-particle partitioning of organic compounds: comparison of sampling methods. *Atmos. Environ.* 26, 2259-2267.

- Krieger, M. S., Hites, R. A., 1994. Measurements of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in air with a diffusion denuder. *Environ. Sci. Technol.* 28, 1129-1133.
- Lei, Y.D., Chankalal, R., Chan, A., Wania, F., 2002. Supercooled liquid vapour pressures of the polycyclic aromatic hydrocarbons. *J. Chem. Eng. Data* 47, 449-455.
- López, J.M., Callén, M.S., Murillo, R.M., García, T., Navarro, M.V., de la Cruz, M.T., Mastral, A.M., 2005. Levels of selected metals in ambient air PM 10 in an urban site of Zaragoza (Spain). *Environ. Res.* 99, 58-67.
- Luch, A., 2005. *The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons*. Imperial College Press, ISBN 1-86094-417-5, London.
- Mastral, A.M., Callén, M.S., García, T., 2000. Fluidized bed combustion of fossil and non fossil fuels. A comparative study. *Energ. Fuel* 14, 275-281.
- Offenberg, J.H., Baker, J.E., 1999. Aerosol size distributions of polycyclic aromatic hydrocarbons in urban and over-water atmospheres. *Environ. Sci. Technol.* 33, 3324-3331.
- Paasivirta, J., Sinkkonen, S., Mikkelsen, P., Rantio, T., Wania, F., 1999. Estimation of vapor pressures, solubilities and Henry's law constants of selected persistent organic pollutants as functions of temperature. *Chemosphere*, 39, 811-832.
- Pankow, J.F., 1987. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.* 21, 2275-2290.
- Pankow, J.F., Bidleman, T.F., 1992. Interdependence of the slopes and intercepts from log log correlations of measured gas particle partitioning and vapor-pressure .1. Theory and analysis of available data. *Atmos. Environ.* 26, 1071-1080.
- Pankow, J.F., 1994a. An absorption-model of gas-particle partitioning of organic-

- compounds in the atmosphere. *Atmos. Environ.* 28, 185-188.
- Pankow, J.F., 1994b. An absorption-model of gas-aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.* 28, 189-193.
- Pupp, C., Lag, R.C., Murray, J.J., Pottier, R.F., 1976. Equilibrium vapour concentrations of some polycyclic aromatic hydrocarbons and the collection efficiencies of these air pollutants. *Atmos. Environ.* 8, 915-925.
- Simcik, M.F., Franz, T.P., Zhang, H., Eisenreich, S.J., 1998. Gas-particle partitioning of PCBs and PAH in the Chicago urban and adjacent coastal atmosphere: states of equilibrium. *Environ. Sci. Technol.* 32, 251 –257.
- Sitaras, L.E., Bakeas, E.B., Siskos, P.A., 2004. Gas/particle partitioning of seven volatile polycyclic aromatic hydrocarbons in a heavy traffic urban area. *Sci. Total Environ.* 327, 249-264.
- Terzi, E., Samara, C., 2004. Gas-particle partitioning of polycyclic aromatic hydrocarbons in urban, adjacent coastal and continental background sites of Western Greece. *Environ. Sci. Technol.* 38, 4973-4978.
- UNE 77250, 2001. Ambient air. Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons. Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analyses.
- Vardar, N., Tasdemir, Y., Odabasi, M., Noll, K.E., 2004. Characterization of atmospheric concentrations and partitioning of PAH in the Chicago atmosphere. *Sci. Total Environ.* 327, 163-174.
- Viana, M., Chi, X., Maenhaut, W., Querol, X., Alastuey, A., Mikus' kac, P., Vec' er' a, Z., 2006. Organic and elemental carbon concentrations in carbonaceous aerosols during summer and winter sampling campaigns in Barcelona, Spain. *Atmos. Environ.* 40, 2180-2193.

- Walters, R.W., Luthy, R.G., 1984. Equilibrium adsorption of polycyclic aromatic hydrocarbons from water onto activated carbon. *Environ. Sci. Technol.* 18, 395-403.
- Wania, F., Axelman, J., Broman, D., 1998. A review of processes involved in the exchange of persistent organic pollutants across the air-sea interface. *Environ. Pollut.* 102, 3-23.
- Yamasaki, H., Kuwata, K., Miyamoto, H., 1982. Effects of ambient temperature on aspects of airborne PAH. *Environ. Sci. Technol.* 16, 189-194.

Table 1. Average values, range of concentrations and standard deviation (SD) of the individual and total PAH concentrations (ngm⁻³) in the particle, gas and gas+ particle phases for the sampling performed in Zaragoza.

	<u>Particle phase</u>			<u>Gas phase</u>			<u>Gas+particle phases</u>		
	<u>Average</u>	<u>SD</u>	<u>Range</u>	<u>Average</u>	<u>SD</u>	<u>Range</u>	<u>Average</u>	<u>SD</u>	<u>Range</u>
<u>Phe</u>	<u>0.129</u>	<u>0.20</u>	<u><0.11-1.3</u>	<u>2.2</u>	<u>1.9</u>	<u><1.8-9.9</u>	2.3	2.0	0.11-10
<u>An</u>	<u>n.d</u>	<u>0.021</u>	<u><0.068-0.097</u>	<u>0.45</u>	<u>0.38</u>	<u>0.060-2.3</u>	0.46	0.39	0.060-2.4
<u>2+2/4MePhe</u>	<u>0.013</u>	<u>0.021</u>	<u><0.041-0.096</u>	<u>0.66</u>	<u>0.49</u>	<u>0.046-2.2</u>	0.67	0.50	0.046--2.2
<u>9MePhe</u>	<u>0.047</u>	<u>0.049</u>	<u>0.01-0.30</u>	<u>0.82</u>	<u>0.66</u>	<u>0.070-3.2</u>	0.86	0.68	0.086-3.2
<u>1MePhe</u>	<u>0.019</u>	<u>0.028</u>	<u><0.035-0.15</u>	<u>0.69</u>	<u>0.57</u>	<u>0.026-2.7</u>	0.71	0.59	0.036-2.7
<u>DiMePhe</u>	<u>0.064</u>	<u>0.066</u>	<u><0.032-0.35</u>	<u>0.64</u>	<u>0.50</u>	<u>0.050-2.6</u>	0.70	0.51	0.081-2.6
<u>Fth</u>	<u>0.23</u>	<u>0.23</u>	<u>0.056-1.1</u>	<u>0.84</u>	<u>0.55</u>	<u><0.11-3.31</u>	1.1	0.71	0.18-4.4
<u>Pv</u>	<u>0.31</u>	<u>0.26</u>	<u>0.079-1.3</u>	<u>0.82</u>	<u>0.49</u>	<u>0.20-2.9</u>	1.1	0.68	0.43-4.2
<u>BaA</u>	<u>0.27</u>	<u>0.42</u>	<u>0.024-2.5</u>	<u>0.065</u>	<u>0.15</u>	<u><0.17-0.53</u>	0.33	0.50	<0.17-2.9
<u>Chrv</u>	<u>0.29</u>	<u>0.32</u>	<u>0.002-1.9</u>	<u>0.13</u>	<u>0.23</u>	<u><0.36-0.75</u>	0.41	0.45	<0.36-2.4
<u>BbF</u>	<u>0.46</u>	<u>0.48</u>	<u>0.10-3.1</u>	<u>0.018</u>	<u>0.06</u>	<u><0.11-0.38</u>	0.47	0.49	<0.11-3.1
<u>BkF</u>	<u>0.12</u>	<u>0.12</u>	<u>0.025-0.74</u>	<u>0.0054</u>	<u>0.017</u>	<u><0.065-0.11</u>	0.13	0.13	<0.065-0.74
<u>BeP</u>	<u>0.27</u>	<u>0.23</u>	<u>0.06-1.2</u>	<u>0.0069</u>	<u>0.020</u>	<u><0.044-0.13</u>	0.28	0.23	<0.044-1.2
<u>BaP</u>	<u>0.29</u>	<u>0.34</u>	<u>0.048-1.9</u>	<u>0.0042</u>	<u>0.013</u>	<u><0.06-0.083</u>	0.29	0.35	<0.06-1.9
<u>IcdP+DahA</u>	<u>1.1</u>	<u>1.2</u>	<u>0.084-7.4</u>	<u>0.0036</u>	<u>0.010</u>	<u><0.0295-0.071</u>	1.1	1.2	<0.0295-7.4
<u>BghiP</u>	<u>1.0</u>	<u>1.0</u>	<u>0.16-4.6</u>	<u>0.0021</u>	<u>0.0085</u>	<u><0.118</u>	1.0	1.0	<0.118-4.6
<u>Co</u>	<u>1.5</u>	<u>1.6</u>	<u>0.19-7.6</u>	<u>0.0057</u>	<u>0.012</u>	<u><0.01-0.058</u>	1.5	1.6	<0.01-7.6
<u>Total PAH</u>	<u>6.0</u>	<u>5.9</u>	<u>1.50-29</u>	<u>7.3</u>	<u>4.8</u>	<u>1.6-27</u>	13.3	9.6	3.8-54

Table 2. Average, minimum and maximum and seasonal average values of log Kp (m³ µg⁻¹) for the sampling performed in Zaragoza (n=50).

log Kp	Average	Range	Warm season	Cold season
Phe	-3.1	-1.7; -3.8	-2.8	-2.7
An	-2.8	-2.1; -3.2	-2.9	-2.7
2+2/4MePhe	-3.0	-2.5; -3.9	-3.3	-3.0
9MePhe	-2.7	-2.0; -3.4	-2.8	-2.6
1MePhe	-3.0	-2.5; -3.5	-3.1	-2.8
DiMePhe	-2.3	-1.2; -3.3	-2.4	-2.1
Fth	-2.1	-1.4; -2.9	-2.2	-1.9
Py	-1.9	-1.3; -2.7	-2.0	-1.8
BaA	-1.3	-0.8; -1.8	-1.5	-1.1
Chry	-1.4	-0.9; -2.0	-1.6	-1.2
BbF	-0.5	-0.1; -0.8	-0.6	-0.2
BkF	-0.6	-0.3; -1.1	-0.8	-0.5
BeP	-0.3	0.1; -0.7	-0.3	-0.2
BaP	-0.4	0.0; -1.1	-0.6	-0.2
IcdP+DahA	0.6	1.6; -0.3	0.6	0.6
BghiP	-0.1	0.1; -0.3	-0.1	-0.1
Co	0.7	1.7; -0.3	0.7	0.7
Total PAH	-1.6	-0.9; -2.5	-1.9	-1.7

Table 3. Linear regression results for $\log K_P = m(1/T) + b$ (m= slope, b= intercept, r^2 = coefficient of correlation, n= number of samples, %S= percentage of significance).

	T range (°C)	Slope	Intercept	r^2	n	%S
log Phe	2.3-29.3	1099	-6.6	0.045	47	15
log An	2.3-29.3	2225	-10.6	0.187	8	28
log 2+2/4MePhe	2.3-29.3	2595	-12.2	0.407	28	99
	15.1-29.3	4549	-19.1	0.478	14	99
log 9MePhe	2.3-29.3	2933	-12.9	0.482	49	99
	15.1-29.3	3532	-14.9	0.457	24	99
log 1MePhe	2.3-29.3	2732	-12.5	0.503	37	99
	15.1-29.3	2346	-11.2	0.257	18	95
log DiMePhe	2.3-29.3	4666	-18.5	0.556	40	99
	15.1-29.3	4315	-17.4	0.342	17	95
log Fth	2.3-29.3	2644	-11.2	0.544	48	99
	15.1-29.3	2598	-11.1	0.263	23	95
log Py	2.3-29.3	2845	-11.8	0.528	49	99
	15.1-29.3	3874	-15.3	0.615	33	99
log BaA	2.3-29.3	3030	-11.8	0.775	15	99
	15.1-29.3	2119	-8.1	0.778	6	95
log Chry	2.3-29.3	2895	-11.4	0.653	17	99
log BbjF	2.3-29.3	2615	-9.5	0.707	13	99
log BkF	2.3-29.3	2720	-10.1	0.847	9	99
log BeP	2.3-29.3	2338	-8.4	0.791	13	99
	15.1-29.3	1863	-6.8	0.689	6	95
log BaP	2.3-29.3	4014	-14.4	0.817	10	99

Table 4. Slope (m_r), intercept (b_r), correlation coefficient (r^2) and number of considered PAH (n) of the linear regression of $\log K_p$ relative to $\log P^0_L$ according to Offenberg and Baker (1999) for Zaragoza air samples.

Date	m_r	b_r	r^2	n	PAH
07/04/2003	-0.6024	-3.3902	0.9821	4	Phe, Fth, Py, BeP
14/04/2003	-0.6667	-3.9137	0.9458	4	An, Fth, Py, BaA
21/04/2003	-0.6262	-3.3063	0.9136	4	Fl, An, Fth, BkF
28/04/2003	-0.8755	-4.6274	0.9985	3	Phe, Fth, Py
05/05/2003	-0.4717	-3.1905	0.9869	6	Fl, Phe, Fth, Py, BbF, BeP
12/05/2003	-0.1729	-2.4102	0.984	3	Fl, Phe, Py
19/05/2003	-0.5712	-3.3452	0.9767	3	Phe, Fth, Py
26/05/2003	-0.4086	-3.0552	0.9647	7	Phe, Fth, Py, BbF, BkF, BeP, BaP
02/06/2003	0.2135	-1.7638	0.9144	3	Phe, Fth, Py
09/06/2003	-0.6653	-3.7381	0.9023	4	Phe, An, Fth, Py
16/06/2003	-0.4559	-3.227	0.9953	4	Phe, Fth, Py, Chry
23/06/2003	-0.4969	-3.377	0.9914	3	Phe, Fth, Py
07/07/2003	-0.5417	-3.2822	0.8677	4	Phe, Fth, Py, BaP
14/07/2003	-0.6711	-3.8833	0.891	8	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP
22/07/2003	-0.5755	-3.6255	0.8971	4	Phe, Fth, Py, Chry
28/07/2003	-0.4167	-3.1547	0.9703	3	Phe, Fth, Py
18/08/2003	-0.8055	-4.5063	0.9893	7	Phe, Fth, Py, BaA, Chry, BbF, BeP
25/08/2003	-0.4486	-3.2879	0.8624	6	Phe, Fth, Py, BaA, Chry, BghiP
06/10/2003	-0.4298	-3.2591	0.8469	5	Fl, Fth, Py, BaA, Chry
20/10/2003	-0.48	-3.2496	0.7666	9	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP
24/11/2003	-0.6061	-3.7965	0.9004	9	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP
01/12/2003	-0.6874	-4.022	0.9119	10	Fl, Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP
09/12/2003	-0.8125	-4.9076	0.9641	9	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP
15/12/2003	-1.0204	-4.4286	0.9626	4	Phe, An, Fth, Py
12/01/2004	-0.761	-4.3785	0.997	6	Phe, An, Fth, Py, BaA, Chry
19/01/2004	-0.314	-2.506	0.9662	4	Phe, Fth, Py, BghiP
26/01/2004	-0.6839	-3.8359	0.9339	5	Phe, Fth, Py, BaA, Chry
09/02/2004	-0.6862	-3.9573	0.9993	4	Phe, An, Fth, Py
16/02/2004	-0.5356	-3.0537	0.7361	5	Fl, Phe, An, Fth, Py
23/02/2004	-1.0129	-4.8563	0.9974	3	Phe, Fth, Py
01/03/2004	-0.7653	-4.1806	0.9671	3	Phe, Fth, Py
08/03/2004	-1.1974	-5.2169	0.9939	3	Phe, Fth, Py
15/03/2004	-0.6732	-3.9074	0.937	6	Fl, Phe, An, Fth, Py, Chry

22/03/2004	-0.3361	-2.8178	0.872	9	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP
29/03/2004	-0.6104	-3.4755	0.9519	9	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP
05/04/2004	-0.6873	-3.6301	0.9931	3	Phe, Fth, Py
12/04/2004	-0.4915	-3.476	0.9846	6	Phe, Fth, Py, BaA, BbF, BeP
19/04/2004	-0.5099	-3.293	0.9987	3	Phe, Fth, Py
26/04/2004	-0.5735	-3.5065	0.9771	6	Fl, Phe, Fth, Py, BbF, BeP
03/05/2004	-0.6723	-3.4147	0.8622	3	Phe, Fth, Py
10/05/2004	-0.5252	-3.2333	0.9509	4	Phe, An, Fth, Py
17/05/2004	-1.055	-5.0411	0.9962	3	Phe, Fth, Py
24/05/2004	-0.7211	-4.5313	0.997	5	Phe, Fth, Py, BaA, Chry
31/05/2004	-0.496	-3.3049	0.986	3	Phe, Fth, Py
07/06/2004	-0.6804	-3.7923	0.9951	4	Phe, Fth, Py, BbF
14/06/2004	-1.055	-3.6604	0.9916	3	Phe, Fth, Py
21/06/2004	-1	-4.7695	0.9904	3	Phe, Fth, Py
05/07/2004	-0.3268	-3.176	0.9862	3	Phe, Fth, Py

Table 5. Experimental log Kp/predicted log Kp ratios for Phe, Fth and Py according to absorption model, absorption+adsorption onto activated carbon (Walters and Luthy, 1984) and absorption+adsorption onto different soot types (Jonker and Koelmans, 2002) models when a) $f_{OM}=0.15$, $f_{EC}=0.05$, b) f_{OM} and f_{EC} are increased 25% and c) f_{OM} and f_{EC} are decreased 25%.

Log $Kp_{exp}/\log Kp_{model}$	Phe			Fth			Py		
	a	b	c	a	b	c	a	b	c
ABS (Octanol)	0.59	0.60	0.58	0.60	0.61	0.58	0.40	0.40	0.39
ABS+ADS (Walters)	0.88	0.91	0.85	0.98	1.03	0.93	0.87	0.91	0.82
Oct+traffic soot	0.70	0.72	0.68	0.73	0.75	0.70	0.62	0.64	0.59
Oct+oil soot	0.61	0.63	0.60	0.63	0.65	0.61	0.49	0.51	0.48
Oct+wood soot	0.62	0.63	0.60	0.63	0.65	0.61	0.51	0.52	0.49
Oct+coal soot	0.63	0.64	0.61	0.61	0.63	0.59	0.47	0.48	0.45
Oct+diesel soot	0.64	0.65	0.62	0.66	0.68	0.63	0.54	0.56	0.52

Fig. 1. log K_{SA} versus log P_L^0 at 25 °C (Offenberg and Baker (1999)) for log K_{SW} values of (a) activated carbon (from Walters and Luthy (1984)), coal soot, coal and diesel soot (from Jonker and Koelmans (2002)) and (b) traffic, oil soot, wood soot and charcoal (from Jonker and Koelmans (2002)).

Fig. 2. Experimental and predicted log K_P values at the Zaragoza sampling site for Phe, Fth and Py using different models: the absorption (K_{OA}) and the absorption+adsorption models ($K_{OA}+K_{SA}$) with different sorbents.

Table 1. Data sheet relative to PM10 ($\mu\text{g m}^{-3}$), and meteorological conditions for each Zaragoza sample (2003-2004). (RH= Relative humidity; W speed= wind speed; W direction= Wind direction)

Date	PM10	Rainfall (mm)	T ($^{\circ}\text{C}$)	RH	Irradiation	W speed (m s^{-1})	W direction ($^{\circ}$)
07.04.03	35.42	0	13.1	51.9	284.5	2.6	296.0
14.04.03	30.54	0.4	13.6	66.4	93.4	4.0	113.7
21.04.03	21.77	0	13.7	70.7	304.7	1.4	43.7
28.04.03	34.92	0	19.4	62.1	270.8	2.4	112.1
05.05.03	23.83	18.0	15.2	79.0	106.3	2.4	287.1
12.05.03	34.30	0	18.5	64.6	322.7	1.6	266.0
19.05.03	35.00	0	20.6	61.7	318.4	3.2	338.6
26.05.03	28.04	0	15.6	50.1	351.7	7.8	309.9
02.06.03	32.92	0.2	21.6	66.3	269.9	1.7	99.2
09.06.03	48.18	0	25.1	61.1	279.7	1.9	166.6
16.06.03	40.01	0	26.3	51.0	284.2	2.6	263.0
23.06.03	74.85	0	28.3	37.2	329.4	2.7	177.5
30.06.03	36.12	0	25.4	48.3	285.1	4.1	280.5
07.07.03	44.02	0	25.8	54.8	326.1	1.6	228.4
14.07.03	61.06	0	27.4	40.6	323.5	2.6	153.4
21.07.03	47.70	0	26.0	56.1	327.0	2.3	237.2
28.07.03	34.10	0	24.8	46.1	324.8	3.3	289.1
18.08.03	39.46	0	24.1	59.5	277.8	1.2	90.9
25.08.03	33.54	0	26.1	51.9	278.9	2.6	273.6
06.10.03	28.14	0	11.3	63.0	185.3	2.0	280
20.10.03	16.86	0	15.1	72.9	129.2	2.6	300.6
24.11.03	19.58	0	9.9	74.4	94.5	2.0	292.6
01.12.03	20.03	0.2	8.6	73.3	71.8	2.0	268.9
09.12.03	36.26	0	7.4	83.3	39.5	2.2	89.3
15.12.03	23.29	0	9.3	61.9	102.7	5.5	295.0
12.01.04	46.31	0	8.8	84.8	54.5	1.5	11.6
19.01.04	12.62	0.2	5.7	48.6	120.5	9.7	315.4
26.01.04	18.10	0.6	9.9	83.4	88.9	2.5	357.5
02.02.04	21.88	0.2	6.9	97.1	37.38	1.3	326.9
09.02.04	45.55	0.2	2.7	86.3	118.3	1.1	12.9
16.02.04	32.99	0	9.0	56.4	156.7	7.1	313

23.02.04	18.84	0	6.8	71.0	148.8	3.8	322.2
01.03.04	27.31	0	2.3	61.2	200.2	5.0	308.3
08.03.04	22.63	0	7.6	56.6	213.2	5.8	291.7
15.03.04	46.08	0.2	10.1	76.4	208.5	1.4	341.5
22.03.04	14.41	0	8.6	59.1	188.5	6.0	325.2
29.03.04	7.94	25.6	7.3	92.6	20.5	1.3	220.3
05.04.04	25.48	0	13.9	67.9	258.2	3.1	280.9
12.04.04	34.33	0	10.7	50.0	297.1	7.4	316.7
19.04.04	17.30	0	10.2	62.8	272.2	3.4	283.6
26.04.04	39.49	0	15.8	67.2	316.1	1.1	18.8
03.05.04	13.45	5.6	12.5	79.7	75.9	4.3	315.7
10.05.04	21.04	9.0	14.1	77.6	193.2	1.5	309.3
17.05.04	45.29	0	19.7	56.0	341.2	2.4	174.6
24.05.04	34.73	0	18.6	61.5	310.4	2.5	137.9
31.05.04	32.54	0	21.3	51.0	319.2	2.6	293.8
07.06.04	39.27	0	23.5	51.5	271.9	2.5	146.9
14.06.04	40.08	0	29.3	43.6	347.5	5.0	300.1
21.06.04	39.40	0	20.3	54.9	318.9	1.5	134.3
05.07.04	34.84	0	24.6	56.3	317.8	2.2	212.5

1 **Table 2. Slope (m_r), intercept (b_r), correlation coefficient (r^2) and number of considered PAH (n) of the linear regression of log Kp relative to**
2 **log P_L according to Paasivirta et al. (1999) and Lei et al. (2002) for Zaragoza air samples.**

Date	m_r		b_r		r^2		n	PAH
	Paasi.	Lei	Paasi.	Lei	Paasi.	Lei		
07-04-03	-0.581		-3.169		0.945		4, 0	Phe, Fth, Py, BeP; -
14-04-03	-0.728	-0.566	-3.871	-3.905	0.804	0.891	4, 3	Phe, An, Fth, Py; Phe, An, Fth
21-04-03	-0.722		-3.794		0.91		4, 0	Phe, Fth, Py, BeP; -
28-04-03	-0.934		-4.528		0.879		3, 0	Phe, Fth, Py; -
05-05-03	-0.390	-0.596	-2.962	-3.691	0.926	0.973	5, 3	Phe, Fth, Py, BbF, BeP; Phe, Fth, BbF
19-05-03	-0.638		-3.335		0.942		3, 0	Phe, Fth, Py; -
26-05-03	-0.31	-0.540	-2.677	-3.533	0.797	0.993	7, 5	Phe, Fth, Py, BbF, BkF, BeP, BaP; Phe, Fth, BbF, BkF, BaP
02-06-03							0, 3, 0	-; Phe, Fth, Py; -
09-06-03		-0.576		-3.790		0.821	0, 3	-; Phe, An, Fth
16-06-03	-0.326	-0.375	-2.957	-3.222	0.924	0.992	4, 3	Phe, Fth, Py, Chry; Phe, Fth, Chry
23-06-03	-0.572	-0.599	-3.404	-3.721	0.967	0.998	4, 3, 3	Phe, Fth, Py, BaP; Phe, Fth, Py; Phe, Fth, BaP
07-07-03	-0.469	-0.557	-3.063	-3.383	0.758	0.676	7, 5	Phe, Fth, Py, BaA, Chry, BkF, BghiP; Phe, Fth, Chry, BkF, BghiP
14-07-03	-0.493	-0.651	-3.431	-3.956	0.801	0.793	8, 5	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP; Phe, Fth, Chry, BbF, BkF
22-07-03	-0.441	-0.481	-3.349	-3.590	0.959	0.942	4, 3	Phe, Fth, Py, Chry; Phe, Fth, Chry
28-07-03	-0.468		-3.159		0.949		4, 0	Phe, Fth, Py, BaP; -
18-08-03	-0.588	-0.793	-3.901	-4.755	0.853	0.899	7, 4	Phe, Fth, Py, BaA, Chry, BbF, BeP; Phe, Fth, Chry, BbF
25-08-03	-0.407	-0.484	-3.13	-3.442	0.713	0.702	6, 4	Phe, Fth, Py, BaA, Chry, BghiP; Phe, Fth, Chry, BghiP
20-10-03	-0.37	-0.498	-2.829	-3.315	0.667	0.649	9, 6	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP; Phe, Fth, Chry, BbF, BkF, BaP

								Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP; Phe, Fth, Chry, BbF, BkF, BaP
24-11-03	-0.462	-0.627	-3.184	-3.889	0.766	0.701	9, 6	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP; Phe, Fth, Chry, BbF, BkF, BaP
01-12-03	-0.633	-0.974	-3.373	-5.428	0.827	0.886	9, 6	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP; Phe, Fth, Chry, BbF, BkF, BaP
09-12-03	-0.621	-0.923	-4.054	-5.451	0.824	0.838	9, 6	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP; Phe, Fth, Chry, BbF, BkF, BaP
15-12-03	-1.174	-0.987	-4.459	-4.638	0.912	0.953	4, 3	Phe, An, Fth, Py; Phe, An, Fth
12-01-04	-0.627	-0.617	-3.870	-4.270	0.892	0.996	6, 4	Phe, An, Fth, Py, BaA, Chry; Phe, An, Fth, Chry
19-01-04	-0.325	-0.383	-2.418	-2.751	0.959	0.929	4, 3	Phe, Fth, Py, BghiP; Phe, Fth, BghiP
26-01-04	-0.554	-0.536	-3.327	-3.619	0.889	0.957	5, 3	Phe, Fth, Py, BaA, Chry; Phe, Fth, Chry
09-02-04	-0.775	-0.623	-3.925	-3.998	0.919	1.000	4, 3	Phe, An, Fth, Py; Phe, An, Fth
16-02-04		-0.176		-2.232		0.234	0, 3	-; Phe, An, Fth
23-02-04	-1.095		-4.691		0.897		3, 0	Phe, Fth, Py; -
01-03-04	-0.872		-4.146		0.965		3, 0	Phe, Fth, Py; -
15-03-04	-0.595	-0.661	-3.704	-4.243	0.896	0.982	5, 4	Phe, An, Fth, Py, Chry; Phe, An, Fth, Chry
22-03-04	-0.232	-0.427	-2.364	-3.267	0.809	0.849	9, 6	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP; Phe, Fth, Chry, BbF, BkF, BaP
29-03-04	-0.461	-0.725	-2.812	-4.103	0.797	0.948	9, 6	Phe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP; Phe, Fth, Chry, BbF, BkF, BaP
12-04-04	-0.369	-0.568	-2.991	-3.825	0.929	1.000	6, 6,	Phe, Fth, Py, BaA, BbF, BeP; same;
19-04-04	-0.531		-3.177		0.835		3, 0	Phe, Fth, Py; -
26-04-04	-0.467	-0.688	-3.203		0.872		5, 3	Phe, Fth, Py, BbF, BeP; Phe, Fth, BbF
10-05-04		-0.390		-3.125		0.956	0, 3	-; Phe, An, Fth

17-05-04	-1.243		-4.932		0.893		3, 0	Phe, Fth, Py; -
24-05-04	-0.556	-0.583	-4.023	-4.488	0.861	1.000	5, 3	Phe, Fth, Py, BaA, Chry; Phe, Fth, Chry
07-06-04	-0.632	-0.801	-3.298	-4.224	0.954	0.968	4, 4, 3	Phe, Fth, Py, BbF; same; Phe, Fth, BbF
21-06-04	-1.092		-4.707		0.914		3, 0	Phe, Fth, Py; , -
05-07-04	-0.324		-3.11		0.753		3, 0	Phe, Fth, Py; -

4

5

6